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ABSTRACTS OF PAPERS ON ORGANIC, PHYSIOLOGICAL, AND AGRICULTURAL CHEMISTRY.

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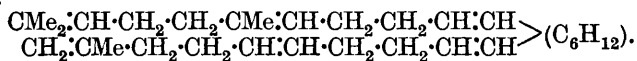
PART I.

Organic Chemistry.

Composition of Paraffin Wax. III. FRANCIS FRANCIS, CYRIL MERCER WATKINS, and REGINALD WILFRED WALLINGTON (T., 1922, **121**, 2804—2810).

Constitution of Squalene. RIKÔ MAKIMA and BENNOSUKÉ KUBOTA (*Sci. Papers Inst. Phys. Chem. Research*, 1922, **1**, 7—21).—Squalene, $C_{30}H_{50}$, is a highly unsaturated hydrocarbon isolated from shark's liver oil by Tsujimoto (*J. Chem. Ind. Japan*, 1906, **9**, 958; 1917, **20**, 953, 1069; A., 1916, **i**, 786; 1918, **i**, 89) and may be identical with Chapman's spinacene (T., 1917, **111**, 56). The material used was the oil from the liver of *Squalus Mitsukurii*, and had b. p. 284—285°/25 mm., d_4^{20} 0.8596, n_D^{20} 1.4959. When treated in chloroform solution with oxygen containing 5—7% of ozone, squalene hexaozonide, $C_{30}H_{50}(O_3)_6$, was obtained, which suffered decomposition when boiled with water; the products obtained from the ozonide prepared from 27 g. of squalene were as follows: carbon dioxide 1.82 g., formaldehyde undetermined, acetone 1.01 g., acetone peroxide 0.7 g., lævulinaldehyde 0.84 g., formic acid 0.68 g., succinic acid 8.35 g., lævulic acid 9.3 g., an unknown acid, $C_8H_{14}O_6$, m. p. 132—134°, 1.5 g., and another unknown acid, $C_6H_{10}O_5$, m. p. 191—192°, 0.5 g. From the products of the dry distillation of squalene under atmospheric pressure, isoprene and a colourless liquid, b. p. 62.5—65°/17 mm., d_4^{20} 0.8208,

n_D 1.4621 (probably *cyclodihydroxymyrcene*), were isolated. By heating with a mixture of glacial acetic acid and 2% of concentrated sulphuric acid at 65–68° during three hours, squalene was found to be converted into an isomeride containing at least two rings. Further, squalene does not contain conjugated double bonds, and is easily reduced to a dodecahydro-derivative by hydrogen in the presence of platinum black. From these facts, the authors regard squalene as a higher aliphatic terpene, probably a dihydro-triterpene, and suggest the following formula for it as probable, but the nature of the right-hand group, $\cdot\text{CH}\cdot(\text{C}_6\text{H}_{12})\cdot\text{CH}\cdot$, is still not clear:



K. K.

Action of Silver Sulphate in Sulphuric Acid Solution on Ethyl Bromide. E. A. SCHILOV (*Bull. Inst. Polyt. Ivanovo-Voznesensk.*, 1922, 6, 233).—Alcohol is now found (cf. A., 1922, i, 913) among the products of the action of a sulphuric acid solution of silver sulphate on ethyl bromide, so that the ethylsulphuric acid formed evidently undergoes considerable hydrolysis. The conclusion is drawn that the reaction proceeds quantitatively in accordance with the equation $\text{HAgSO}_4 + \text{EtBr} = \text{AgBr} + \text{EtHSO}_4$.

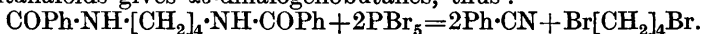
T. H. P.

The Preparation of $\alpha\delta$ -Dihalogen Derivatives of Butane. C. S. MARVEL and A. L. TANENBAUM (*J. Amer. Chem. Soc.*, 1922, 44, 2645–2650; cf. von Braun, A., 1907, i, 127).—A good yield of $\alpha\delta$ -dibromobutane may be obtained by the following series of reactions. $\alpha\gamma$ -Dibromopropane is converted into γ -phenoxypropyl bromide by the action of sodium phenoxide, and this in turn into phenoxypropyl cyanide by the action of sodium cyanide. This cyanide is hydrolysed by alcoholic sulphuric acid, and the resulting ethyl phenoxybutyrate when reduced by sodium and absolute alcohol in toluene is converted into phenoxybutyl alcohol, b. p. 162–164°/19 mm., n_D^{20} 1.520, giving a *p*-nitrobenzoate, m. p. 91°. The alcohol, when heated with hydrobromic acid containing a little sulphuric acid, yields a mixture of γ -phenoxybutyl bromide, m. p. 41°, and the required $\alpha\delta$ -dibromobutane, which may be separated by fractional distillation. In reducing ethyl phenoxybutyrate as described above (cf. Levene and Allen, A., 1917, i, 3), it is essential, if a high yield is to be obtained, to use alcohol that has been distilled first over calcium oxide and then over sodium, and to exclude all traces of moisture during the reduction. This method of reduction was also applied successfully to the reduction of esters of octoic, lauric, and myristic acids to the corresponding alcohols, and also to the reduction of certain cyanides to the corresponding primary amines.

W. G.

Synthesis of Halogenated Compounds of the Butane Series. JULIUS VON BRAUN and GEORG LEMKE (*Ber.*, 1922, 55, [B], 3526–3536).— $\alpha\delta$ -Dihalogenated butanes may be prepared conveniently

by oxidising *cyclohexanol* to adipic acid, conversion of the latter into the amide, and thence into the dibenzoyl derivative of $\alpha\delta$ -diaminobutane. Treatment of the latter compounds with phosphorus pentahaloids gives $\alpha\delta$ -dihalogenobutanes, thus :



The reaction in this case proceeds in exactly the same manner as with the dibenzoyl derivative of $\alpha\epsilon$ -pentamethylenediamine and its higher homologues.

The oxidation of *cyclohexanol* to adipic acid (cf. Mannich and Hâncu, A., 1908, i, 245) is conveniently effected by the gradual addition of finely-divided potassium permanganate to a well-stirred suspension of *cyclohexanol* in aqueous sodium carbonate solution at 15—30°, the yield of acid being 70% of that theoretically possible. The acid is transformed by thionyl chloride at the atmospheric temperature into the corresponding chloride, which is converted by ammonia into the amide (yield 90%). The latter is converted by bromine and sodium hydroxide into $\alpha\delta$ -diaminobutane, which, without being isolated, is further converted into the dibenzoyl derivative, m. p. 176—177°, the yield being 60%. Phosphorus pentabromide transforms the latter into $\alpha\delta$ -dibromobutane, b. p. 80—82°/14 mm., in 70% yield. The similar action of phosphorus pentachloride gives a mixture of $\alpha\delta$ -dichlorobutane and δ -chlorobutylbenzamide, $\text{Cl}[\text{CH}_2]_4\cdot\text{NHBz}$, m. p. 54—55°.

$\alpha\delta$ -Dibromobutane reacts energetically with bromine in the presence of iron, yielding mainly $\alpha\beta\gamma$ -tribromobutane, b. p. 102—103°/14 mm. The position of the bromine atoms is deduced from the observation that the compound reacts energetically with magnesium in the presence of ether, in accordance with the equations : $2\text{C}_4\text{H}_7\text{Br}_3 + 3\text{Mg} = 3\text{MgBr}_2 + \text{C}_8\text{H}_{14}$ and $\text{C}_4\text{H}_7\text{Br}_3 + 2\text{Mg} = \text{MgBr}_2 + \text{C}_4\text{H}_7\cdot\text{MgBr}$. The former reaction predominates very greatly. If the product is treated with carbon dioxide, a hydrocarbon (or mixture of hydrocarbons), C_8H_{14} , and an acid, $\text{C}_4\text{H}_7\cdot\text{CO}_2\text{H}$, are obtained. The latter substance is present in too small quantity to permit its isolation, but its oxidation to methylmalonic acid shows it to have the constitution $\text{CH}_3\cdot\text{CH}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$. The hydrocarbon is oxidised to succinic acid, but does not appear to yield adipic acid. The course of the reaction differs entirely from that observed by von Braun and Deutsch (A., 1912, i, 106), and can only be explained simply on the assumption that the product is $\alpha\beta\gamma$ -tribromobutane. Bromination of the $\alpha\delta$ -compound, as in the case of $\alpha\epsilon$ -dibromopentane (von Braun and Kirschbaum, A., 1920, i, 2), is accompanied by a displacement of a bromine atom. More vigorous bromination of $\alpha\delta$ -dibromobutane leads to the production of $\alpha\beta\gamma\delta$ -tetrabromobutane, m. p. 117°.

δ -Chlorobutylbenzamide, like the benzoyl derivative of ϵ -chloroamylamine, but unlike those of γ -chloropropylamine or β -chloroethylamine, reacts readily with aluminium chloride and benzene, yielding thereby *N*-benzoyl- δ -phenylbutylamine, m. p. 83° (cf. A., 1910, i, 819); the corresponding *hydrochloride* crystallises in leaflets, m. p. 159°.

N- δ -Chlorobutylbenzamide is transformed by diethylamine into

N- δ -diethylaminobutylbenzamide, $\text{NEt}_2 \cdot [\text{CH}_2]_4 \cdot \text{NHBz}$, a colourless, viscous liquid, b. p. 225—228°/13 mm., the salts of which exhibit little tendency to crystallise. It is hydrolysed by concentrated hydrochloric acid to δ -diethylaminobutylamine, a colourless, fairly mobile liquid, b. p. 78—79°/13 mm. (*picrate*, yellow needles, m. p. 157°; *chloroplatinate*, yellow crystals, m. p. 195°); it is remarkable that the base does not react with nitrous acid.

Sodium benzoisulphinide is converted by ethylene dibromide at 170—180° almost entirely into *N*- β -bromoethylbenzoisulphinide, $\text{C}_6\text{H}_4 \langle \text{SO}_2 \rangle \text{N} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{Br}$. Under precisely similar conditions, trimethylene bromide gives $\alpha\gamma$ -dibenzoisulphinidopropane, a crystalline powder, m. p. 196°, in 47% yield. Tetramethylene bromide behaves similarly to the trimethylene compound, giving $\alpha\delta$ -dibenzoisulphinidobutane, $\text{C}_6\text{H}_4 \langle \text{SO}_2 \rangle \text{N} \cdot [\text{CH}_2]_4 \cdot \text{N} \langle \text{SO}_2 \rangle \text{C}_6\text{H}_4$, m. p. 204—206°, in 40% yield. H. W.

Unsaturated Residues in Chemical and Pharmacological Relationship. III. JULIUS VON BRAUN and GEORG LEMKE (*Ber.*, 1922, 55, [B], 3536—3559; cf. von Braun and Köhler, A., 1918, i, 162; von Braun and Braunsdorf, A., 1921, i, 772).—A further examination of the possibility of an intimate connexion between the peculiar physiological activity of compounds containing the allyl group, the relatively weak union of allyl with oxygen, nitrogen, sulphur, and halogen, and the $\beta\gamma$ -position of the double bond. The latter appears to be important in its effect on the physiological activity of the substances, since *N*-cinnamyl-norcodeine is exactly analogous to *N*-allylnorcodeine in its antagonistic action towards morphine.

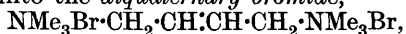
An extended study has been made of compounds containing the group $\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2\cdot$, since this may be regarded in a measure as a doubled allyl, and also because cases of *cis*- and *trans*-isomerism are to be expected. In the latter respect, the experiments are disappointing, since the initial material, *cis*-butadiene dibromide, is found to be unusually labile and to pass under the influence of a great variety of chemical reagents into the *trans*-modification of which it gives derivatives. The comparison of a series of compounds, $\text{CH}_2\text{X}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2\text{X}$, with a similar series of substances, $\text{CH}_2\text{X}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{X}$, shows in general that the butadiene closely resemble the allyl derivatives in respect of the feeble union of the unsaturated carbon chain with halogen, oxygen, nitrogen, and sulphur. As is to be expected, the unsaturated compounds show less tendency to form the thiophen ring than does the saturated butane derivative, but, on the other hand, its ability to yield a pyrroline derivative (although only in small yield) is somewhat surprising.

When compared with the simpler allyl compounds, the butenyl compounds are unusually inactive physiologically, so that the chemical analogy of the substances is not accompanied by pharmacological analogy. This result appears to be due either to the

great increase in the size of the molecule or to the spatial proximity of the physiologically active centres in the presence of the chain $\cdot\text{CH}_2\cdot\text{CH}:\text{CH}\cdot\text{CH}_2\cdot$, which is such as to cause mutual disturbance.

N-Cinnamylnorcodeine, $\text{OMe}\cdot\text{C}_{16}\text{H}_{14}\text{O}(\text{OH})\text{N}\cdot\text{CH}_2\cdot\text{CH}:\text{CHPh}$, a colourless substance, m. p. 78° after softening at 74° , is prepared by the treatment of a solution of norcodeine in chloroform with cinnamyl bromide at 100° ; the *sulphate*, *hydrochloride*, and *chloroplatinate*, a pale yellow powder, decomp. 208° , are described.

For the preparation of $\alpha\delta$ -dibromo- Δ^8 -butene, $\alpha\beta\gamma\delta$ -tetrabromobutane is debrominated with zinc dust and alcohol, the $\Delta^{\alpha\gamma}$ -butadiene which is evolved is dissolved in chloroform and treated with one molecular proportion of bromine. The mixture of stereoisomerides thus produced is separated by rapid distillation under diminished pressure into the previously described solid *trans*- $\alpha\delta$ -dibromo- Δ^8 -butene, b. p. about 78 – $80^\circ/13$ mm., m. p. 53° , and *cis*- $\alpha\delta$ -dibromo- Δ^8 -butene, b. p. $59^\circ/13$ mm., which does not solidify in a freezing mixture of ice and salt. The constitution of the latter substance is now elucidated by the observation that it is oxidised by permanganate to a liquid glycol and finally to bromoacetic acid, but it appears doubtful whether the compound as thus prepared is quite homogeneous. It passes into the solid *trans*-modification slowly at the atmospheric temperature, rapidly when heated. The change is catalytically accelerated in particular by halogen acids, and to a smaller extent by sulphuric acid. The addition of hydrogen bromide to $\alpha\delta$ -dibromo- Δ^8 -butene is effected by protracted heating of the substance with a fuming solution of hydrogen bromide in glacial acetic acid at 100° (it is immaterial which modification of the dibromo-compound is used), whereby $\alpha\beta\delta$ -tribromobutane, b. p. 108 – $112^\circ/14$ mm., is produced in 65% yield (cf. von Braun and Deutsch, A., 1912, i, 106). $\alpha\delta$ -Dibromo- Δ^8 -butene is hydrolysed much more rapidly than $\alpha\delta$ -dibromobutane by hot water. It is rapidly transformed by trimethylamine in the presence of benzene at 20° into the *diquaternary bromide*,

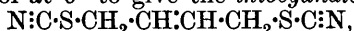


a very hygroscopic solid, m. p. about 295 – 300° (the corresponding *chloroplatinate* is a yellow powder, m. p. 246°); under similar conditions of time, temperature, and concentration, $\alpha\delta$ -dibromobutane remains unaffected, but when more drastically treated it becomes converted into the substance $\text{NMe}_3\text{Br}\cdot[\text{CH}_2]_4\cdot\text{NMe}_3\text{Br}$, m. p. 295° . $\alpha\delta$ -Dibromobutane does not react with an ethereal solution of magnesium phenyl bromide, even on protracted heating; under similar conditions, $\alpha\delta$ -dibromo- Δ^8 -butene is fairly readily transformed into γ -benzylallyl bromide, $\text{CH}_2\text{Ph}\cdot\text{CH}:\text{CH}\cdot\text{CH}_2\text{Br}$, b. p. 112 – $115^\circ/14$ mm. Treatment of $\alpha\delta$ -dibromo- Δ^8 -butene with a large proportion of the Grignard's reagent leads to the production of $\alpha\delta$ -diphenyl- Δ^8 -butene, which, however, could not be separated completely from diphenyl.

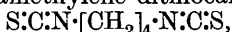
$\alpha\delta$ -Diphenoxy- Δ^8 -butene, $\text{OPh}\cdot\text{CH}_2\cdot\text{CH}:\text{CH}\cdot\text{CH}_2\cdot\text{OPh}$, m. p. 83 – 84° , is readily prepared by boiling $\alpha\delta$ -dibromo- Δ^8 -butene with an alcoholic solution of sodium phenoxide. In striking contrast to $\alpha\delta$ -diphenoxybutane, the unsaturated compound is extensively

decomposed at its boiling point, but it was not found possible to isolate the presumable product $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ of the change or any of its derivatives in the homogeneous condition.

$\alpha\delta$ -Dibromo- Δ^{β} -butene reacts readily with ammonium thiocyanate dissolved in alcohol at 0° to give the *thiocyanate*,



prisms, m. p. 82° ; the constitution of the compound follows from the observations that it is indifferent towards bases, gives an intense odour of mercaptan when treated with zinc and hydrochloric acid, and is converted by thiobenzoic acid into the *dithio-urethane*, $\text{NH}_2\cdot\text{CS}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CH}:\text{CH}\cdot\text{CH}_2\cdot\text{S}\cdot\text{CS}\cdot\text{NH}_2$, m. p. 165° (decomp.). The thiocyanate is relatively very stable towards rise in temperature, differing in this respect from allyl thiocyanate; at 150° , however, it rapidly undergoes a complex change which does not lead to well-defined products. *Tetramethylene dithiocyanate*, b. p. $193\text{--}195^{\circ}/14\text{ mm.}$, is readily prepared in the usual manner; it is converted by thiobenzoic acid into tetramethylene-bisdithiourethane, m. p. 154° (cf. von Braun, A., 1910, i, 13). For the preparation of tetramethylene dithiocarbimide,



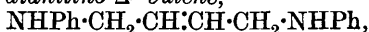
a solution of tetramethylenediamine in alcohol is treated with carbon disulphide (whereby *tetramethylene dithiocarbamate*, m. p. 150° , is slowly precipitated) and subsequently with iodine, a solution of sodium in alcohol, and again with iodine; the *dithiocarbimide* is thus obtained as a yellow liquid which could not be caused to solidify. It is very unstable, and decomposes slowly when preserved at the atmospheric temperature, rapidly and completely when warmed. With aniline, it yields *NN'*-*diphenyltetramethylenedithiocarbamide*, $\text{C}_4\text{H}_8(\text{NH}\cdot\text{CS}\cdot\text{NHPh})_2$, m. p. 169° ; with an alcoholic solution of methylamine it gives *NN'*-*dimethyltetramethylenedithiocarbamide*, a crystalline powder, m. p. 128° , whilst with ammonia dissolved in alcohol it yields *tetramethylenedithiocarbamide*, $\text{C}_4\text{H}_8(\text{NH}\cdot\text{CS}\cdot\text{NH}_2)_2$, m. p. 198° .

The action of cyanogen bromide on an ethereal solution of $\alpha\delta$ -tetramethyldiamino- Δ^{β} -butene leads to the production of *trans*- $\alpha\delta$ -dibromo- Δ^{β} -butene, dimethylcyanamide, and the quaternary compound, $\text{NMe}_2\text{Br} < \begin{array}{c} \text{CH}_2\cdot\text{CH}:\text{CH}\cdot\text{CH}_2 \\ \text{CH}_2\cdot\text{CH}:\text{CH}\cdot\text{CH}_2 \end{array} > \text{NMe}_2\text{Br}$, m. p. 242° (*chloroplatinate*, golden-yellow octahedra, m. p. 294°). Since the possibility existed that the latter substance might in reality be *N*-dimethylpyrrolinium bromide, $\begin{array}{c} \text{CH}\cdot\text{CH}_2 \\ | \\ \text{CH}\cdot\text{CH}_2 \end{array} > \text{NMe}_2\text{Br}$, the latter was

prepared by the action of two molecular proportions of dimethylamine on a solution of $\alpha\delta$ -dibromo- Δ^{β} -butene in benzene at 100° ; in contrast to the substance just described, it is a liquid which does not solidify even when strongly cooled (*chloroplatinate*, m. p. 242°). $\alpha\delta$ -Tetramethyldiaminobutane cannot be prepared directly from the corresponding bromide and dimethylamine, since the tendency towards ring formation is so great that *N*-dimethylpyrrolinium bromide is produced even when a large excess of the base is used. The ditertiary base, b. p. 169° , is, however, pre-

pared in very moderate yield by the decomposition of *NN'*-hexamethyltetramethylenediammonium hydroxide (cf. Willstätter and Heubner, A., 1907, i, 959); an unsaturated base, probably δ -dimethylamino- Δ^{α} -butene, $\text{NMe}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2$, b. p. 82—85°, is formed as by-product. The ditertiary base reacts energetically with cyanogen bromide, with elimination of methyl bromide from one or both ends of the molecule.

$\alpha\delta$ -Dibromobutane is converted quantitatively by aniline into 1-phenylpyrrolidine, $\begin{matrix} \text{CH}_2 \cdot \text{CH}_2 \\ | \quad | \\ \text{CH}_2 \cdot \text{CH}_2 \end{matrix} > \text{NPh}$, b. p. 124°/14 mm., a colourless liquid which rapidly becomes brown when exposed to air; it gives a *picrate*, m. p. 114°, and a *methiodide*, m. p. 150°. Under precisely similar conditions, $\alpha\delta$ -dibromo- Δ^{β} -butene gives minimal quantities of 1-phenyl- Δ^3 -pyrroline, $\begin{matrix} \text{CH} \cdot \text{CH}_2 \\ | \quad | \\ \text{CH} \cdot \text{CH}_2 \end{matrix} > \text{NPh}$, a mixture of compounds formed by the action of several dibromide and aniline molecules and $\alpha\delta$ -dianilino- Δ^{β} -butene,

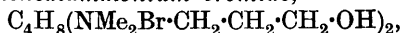


a viscous liquid, b. p. above 300°/14 mm., which is conveniently characterised as the *bis-nitrobenzoyl* derivative, slender needles, m. p. 210°.

When boiled with an aqueous alcoholic solution of potassium sulphide (under the conditions which lead to the production of tetrahydrothiophen from $\alpha\delta$ -dibromobutane), $\alpha\delta$ -dibromo- Δ^{β} -butene is converted into a complex, caoutchouc-like mass.

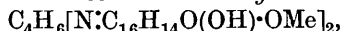
4-Pyrrolidinoantipyrine, m. p. 128°, is prepared by warming $\alpha\delta$ -dibromobutane with 4-aminoantipyrine on the water-bath or from its components in alcoholic solution; the corresponding *hydrochloride* and *methiodide* could not be caused to crystallise. 4-Aminoantipyrine and $\alpha\delta$ -dibromo- Δ^{β} -butene in the presence of acetone give complex products of high molecular weight and (in 40% yield), 4- Δ^3 -pyrrolinoantipyrine, m. p. 155°.

γ -Hydroxypropyldimethylamine reacts fairly readily with $\alpha\delta$ -dibromobutane at 100° to yield *NN'*-tetramethyl-*NN'*-di- γ -hydroxypropyltetramethylenediammonium bromide,



m. p. 194°, and with $\alpha\delta$ -dibromo- Δ^{β} -butene in benzene solution to give *NN'*-tetramethyl-*NN'*-di- γ -hydroxypropyl- Δ^{β} -butenylenediammonium bromide, a very hygroscopic solid, m. p. 188° (*chloroplatinate*, m. p. 213°).

$\alpha\delta$ -Dibromo- Δ^{β} -butene is converted by an excess of norcodeine dissolved in chloroform into $\alpha\delta$ -dinorcodeyl- Δ^{β} -butene,



m. p. 132° after softening at 125°; the corresponding *sulphate*, *hydrochloride*, *chloroplatinate*, and *picrate* are described. $\alpha\delta$ -Dibromobutane and norcodeine, on the other hand, give exclusively *norcodeiniumpyrrolidinium bromide*, $\text{C}_4\text{NH}_8\text{Br} : \text{C}_{16}\text{H}_{14}\text{O}(\text{OH}) \cdot \text{OMe}$.

$\alpha\delta$ -Dibromobutane, hydrocupreine, and alcoholic potassium hydroxide solution give $\alpha\delta$ -dihydrocupreylbutane, decomp. 232°, in 56% yield. In similar circumstances, $\alpha\delta$ -dibromo- Δ^{β} -butene

yields $\alpha\delta$ -dihydrocupreyl- Δ^{β} -butene, m. p. 215—218° after becoming black at 200°. H. W.

A Synthesis of β -Chloroallyl Chloride. ARTHUR J. HILL and EDWIN J. FISCHER (*J. Amer. Chem. Soc.*, 1922, **44**, 2582—2595).—Starting from glycerol, β -chloroallyl chloride may be prepared with good yields by the following procedure. The glycerol, previously dehydrated, is saturated with dry hydrogen chloride after the addition of glacial acetic acid to the extent of 6% of its weight as a catalyst. The $\alpha\gamma$ -dichlorohydrin mixed with a small amount of the $\alpha\beta$ -isomeride is converted into epichlorohydrin by pouring it into 30% aqueous sodium hydroxide at 12—15°. The epichlorohydrin is then reconverted into the $\alpha\gamma$ -dichlorohydrin by the action of concentrated hydrochloric acid. To 300 g. of the dichlorohydrin are added 240 g. of phosphoryl chloride and the mixture is heated on a water-bath for three hours and then for five hours at 180°, after which it is distilled under slightly diminished pressure. Between 225° and 230°, β -chloroallyl chloride distils over. Phosphoric oxide may be used instead of the oxychloride, but the yield is thereby considerably reduced. In either case, the dehydration of the dichlorohydrin is preceded by ester formation, and the higher temperature is necessary for the decomposition of these intermediate products. Other dehydrating agents tried were potassium hydrogen sulphate, sulphuric acid, oxalic acid, boric anhydride, thionyl chloride, and phosphorus trichloride, but in no case could the chloroallyl chloride be obtained.

β -Chloroallyl chloride may be used for the alkylation of malonic esters, and the following compounds have been prepared. *Diethyl chloroallylmalonate*, b. p. 161—163°/12 mm., *diethyl di(chloroallyl)malonate*, b. p. 190°/12 mm. or 300°/760 (decomp.), and *diethyl ethylchloroallylmalonate*, b. p. 157—160°/12 mm. W. G.

Purification of Methyl Alcohol by means of Sodium Hypochlorite. ROBERT CHARLES MENZIES (*T.*, 1922, **121**, 2787—2793).

Union of Hydrogen with Acetylene Derivatives. XIII. Mechanism of the Catalytic Hydrogenation of Dimethylhexinenediol. J. S. ZALKIND and (MLLE) M. S. PESCHERKOVA (*J. Russ. Phys. Chem. Soc.*, 1920, **52**, 186—190).—The values obtained by Zalkind and Pischtschikov (*A.*, 1915, ii, 435) for the velocity of hydrogenation of tetramethylbutinenediol in presence of colloidal palladium showed that, as the reaction proceeds, the value of k , calculated from the formula for unimolecular reactions, at first increases. Such increase was regarded as due to the gradual removal of the acetylenic glycol. Further experiments show that this is not the case. The velocity of the reaction is found to be greatly increased if the palladium is first saturated with hydrogen and then left for some time (sixty hours) in contact with the acetylenic glycol prior to commencement of the hydrogenation. The retardation of the hydrogenation in its early stages is evidently due to the formation, either chemically or by adsorption, of intermediate compounds. T. H. P.

Equilibrium in Systems Composed of Water and Alcohols : Methyl Alcohol, Pinacone, Glycerol, and Erythritol. NICOLAI ANTONOVICH PUSHIN and ALEXANDRA ALEXANDROVNA GLAGOLEVA (T., 1922, **121**, 2813—2822).

Catalytic Dehydration of Alcohols in the Wet Way. I. Olefines and Cyclenes. J. B. SENDERENS (*Ann. Chim.*, 1922, [ix], **18**, 117—145; cf. A., 1912, i, 406).—A review of the author's work on this subject (A., 1910, i, 649, 651; 1912, i, 331, 441), from which the conclusion is drawn that, of the available catalysts, aluminium sulphate and potassium hydrogen sulphate are of restricted application whilst concentrated sulphuric acid is effective in almost all cases. Theoretically, the dry method of catalysis is more efficient, but in practice the wet method is preferable, owing to its rapidity and the ease with which it may be carried out. H. J. E.

Catalytic Dehydration of Alcohols in the Wet Way. II. Ester-formation. J. B. SENDERENS and J. ABOULENC (*Ann. Chim.*, 1922, [ix], **18**, 145—188; cf. preceding abstract, also Berthelot, A., 1879, 866, and Fischer and Speier, A., 1896, i, 201).—A general review of the authors' work (A., 1911, i, 600, 637; 1912, i, 694; 1913, i, 41, 42; 1914, i, 379) shows that concentrated sulphuric acid is by far the most advantageous catalyst, operating efficiently in all the different variations of the general reaction.

H. J. E.

Vapour Pressures, Densities, and some Derived Quantities for Ethyl Ether at Low Temperatures. ROBERT S. TAYLOR and LEIGHTON B. SMITH (*J. Amer. Chem. Soc.*, 1922, **44**, 2450—2463).—The densities and vapour pressures of ethyl ether have been measured over the lower range of temperature. The following density values are recorded: -120° , 0.86195; -110° , 0.85192; -80° , 0.82141; -75° , 0.81640; -70° , 0.81114; -50° , 0.79032; -45° , 0.78510; -40° , 0.77970; -35° , 0.77425; 0° , 0.73629; 20° , 0.71349; 35° , 0.69576; 40° , 0.68979; 55° , 0.67116, and 60° , 0.66501. It is found that the density above 0° is represented by the equation $d = 73629 - 0.0011138t - 0.000001237t^2$, and that below 0° by $d = 73629 + 0.0011044t - 0.0000004772t^2$. From these equations, the density and specific volume have been calculated for every 5° from -120° to $+70^{\circ}$ and the values compared with the present results and those of other investigators. The recorded vapour pressure values are: -60.799° , 3.95 mm.; -55.748° , 5.93 mm.; -50.873° , 8.77 mm.; -45.998° , 12.62 mm.; -41.125° , 17.78 mm.; -36.231° , 24.77 mm.; -31.329° , 34.03 mm.; -26.421° , 45.81 mm.; -21.502° , 61.31 mm.; -16.578° , 80.67 mm.; -11.637° , 104.79 mm.; -6.698° , 134.76 mm.; $+0.009^{\circ}$, 186.13 mm.; 4.975° , 233.73 mm.; 9.937° , 290.62 mm.; 14.903° , 358.15 mm.; 19.871° , 437.70 mm. It is found that the vapour pressures between -60° and $+20^{\circ}$ are given by the equation $\log p = -(2168.599/T) + 13.882702 - 0.01814165T + 0.00001718195T^2$, and by means of this formula the values of the vapour pressure have been calculated for every five degrees over the range -65°

to $+25^{\circ}$ and the values compared with the present experimental values. From the above-mentioned data and an equation of condition, the latent heats of evaporation and the change in internal energy on evaporation have been calculated. A relationship connecting the specific volume of the liquid and the internal energy change on evaporation is given. From the latent heats there was obtained the difference in saturation specific heats of the vapour and liquid, and from these, when compared with Regnault's values for the liquid, some values of the specific heat of the vapour at constant pressure were deduced.

J. F. S.

The Oxidation of $\alpha\delta$ - and $\alpha\epsilon$ -Oxides. ADOLF FRANKE and FRITZ LIEBEN (*Monatsh.*, 1922, **43**, 225—236).—The oxidation with potassium permanganate of a number of anhydrides of $\alpha\delta$ - and $\alpha\epsilon$ -glycols was studied to determine whether it would be possible to deduce the constitution of such compounds from their oxidation products. $\alpha\epsilon$ -Oxidopentane was converted smoothly into glutaric acid whilst $\alpha\epsilon$ -oxidohexane gave principally succinic and acetic acids, rupture of the ring taking place between the δ and ϵ carbon atoms. The latter oxidation therefore follows the same lines as that of $\alpha\delta$ -oxidopentane, which gave principally acetic and oxalic acids (not the expected malonic acid), and only to a small extent formic and succinic acids. It is noteworthy that the $\alpha\epsilon$ -oxidohexane prepared from 1 : 5-hexandiol was identical with that previously prepared from 1 : 6-hexandiol (*Monatsh.*, 1914, **35**, 931). This follows, not only from their similar physical properties, but also from their identical oxidation products. When the oxide contains a tertiary carbon atom, oxidation goes only as far as the lactone; thus $\beta\zeta$ -oxido- β -methylhexane gives δ -methylhexolactone, $\text{CMe}[\text{CH}_2]_3\text{CO}$, and only very little acetone and succinic acid.

E. H. R.

Trichloroethyl Carbamate. R. WILLSTÄTTER, W. DUISBERG, and T. CALLSEN (U.S. Pat. 1427506).—*Trichloroethyl carbamate*, white needles, m. p. 64 — 65° , is obtained by interaction of carbamyl chloride and trichloroethyl alcohol in ethyl ether solution.

CHEMICAL ABSTRACTS.

Researches on Residual Affinity and Co-ordination. XIV. Interactions of Metallic Salts and Dimethyldithiolethylene. GILBERT T. MORGAN and WILFRID LEDBURY (*T.*, 1922, **121**, 2882—2894).

Synthesis of Alkylidenecyanoacetic Acids and of Substituted Succinic Acids. II. Preparation of Acids containing Saturated Aliphatic Residues and the Constitution of the Aliphatic Alkylidenecyanoacetic Esters. ARTHUR LAPWORTH and JOHN ALEXANDER McRAE (*T.*, 1922, **121**, 2741—2755).

Catalytic Hydrogenation and the Potential of the Hydrogen Electrode. JAMES B. CONANT and HAROLD B. CUTTER (*J. Amer. Chem. Soc.*, 1922, **44**, 2651—2654).— $\beta\beta$ -Dimethylacrylic acid

can be hydrogenated in 0.1*N*-hydrochloric acid solution by hydrogen in the presence of a catalyst, but is not reduced by chromous chloride in aqueous solution, although the reducing power of the latter reagent, as measured by its oxidation-reduction potential, is 0.3 volt greater than that of the former reagent. Maleic acid is reduced by chromous chloride, but not by sodium hyposulphite, whilst dibenzoyl ethylene is reduced by both reagents. As a result of these tests, the authors consider that the process of catalytic hydrogenation cannot be successfully formulated in terms of oxidation-reduction potentials. It is suggested that in one case there is a process of hydrogenation, that is, the simple adding on of hydrogen atoms, whilst in the other case there is reduction, that is, the process involves electron addition and is of an irreversible type.

W. G.

Unsaturated Fatty Acids of Brain Cephalins. P. A. LEVENE and IDA P. ROLF (*J. Biol. Chem.*, 1922, **54**, 91—98).—An investigation of the fatty acids of brain cephalin on the lines recently applied to lecithin (cf. A., 1922, i, 621) has shown that stearic, oleic, and arachidonic acids are present in cephalin. Other saturated and unsaturated acids are also present, but have not yet been isolated in a pure state. No evidence has been obtained of the presence of linolic acid.

E. S.

Unsaturated Fatty Acids of Brain Lecithins. P. A. LEVENE and IDA P. ROLF (*J. Biol. Chem.*, 1922, **54**, 99—100).—The fatty acids from brain lecithin contain oleic and arachidonic acids.

E. S.

Preparation and Properties of Tri-iodopyruvic Acid. M. GARINO and E. ZUNINI (*Gazzetta*, 1922, **52**, ii, 220—225).—Tri-iodopyruvic acid, $C_3H_3O_4I_3$, prepared by treating pyruvic acid with iodic and hydriodic acids, forms lemon-yellow crystals with a slightly pungent odour, m. p. about 97°. It is highly unstable, especially in contact with organic substances and under the influence of light; its aqueous solution is relatively stable if iodic acid is present.

T. H. P.

Glucinum Compounds. JULIUS MEYER and ERWIN MANTEL (*Z. anorg. Chem.*, 1922, **123**, 43—55).—Glucinum salts of organic acids are very difficult to obtain in the pure crystalline form; the composition, properties, and constitution of many of these salts have not been clearly proved. The authors attempted to prepare the malonate, but were unable to obtain the pure product. They were, however, able to prepare some double salts, to which they assign the constitution $[Gl(CH_2(CO_2)_2)_2]K_2$, $[Gl(CH_2(CO_2)_2)_2]Na_2 \cdot H_2O$, and $[Gl(CH_2(CO_2)_2)_2](NH_4)_2$ (cf. Wirth, A., 1914, i, 657). The authors discuss the constitution of basic glucinum acetate and they argue that Glasmann's structure (cf. A., 1908, i, 120) cannot be accepted. Biltz's suggestion, $[Gl(\overset{HO}{\underset{HO}{|}})]_3OAc$, is also shown to be untenable. The present authors suggest $[GlO(Gl(OAc)_2)_3]$. They were, however, unable to find much support for this structure.

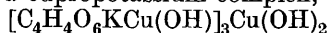
W. T.

Tervalent Manganese. III. JULIUS MEYER and WALTER SCHRAMM (*Z. anorg. Chem.*, 1922, **123**, 56—68).—Diaquo-dimalonatomanganic acid was prepared, $[\text{Mn}(\text{H}_2\text{O})_2(\text{CH}_2(\text{CO}_2)_2)_2]\text{H}$, as well as its lithium, sodium, potassium, rubidium, and ammonium salts. These compounds are olive-green, they dissolve in water, forming yellow solutions, and they are readily hydrolysed with the separation of manganic hydroxide. The potassium salt of trimalonatomanganic acid, $[\text{Mn}(\text{CH}_2(\text{CO}_2)_2)_3]\text{K}_3$, was prepared from the above potassium salt. This substance is red, but from a concentrated solution, especially in the presence of malonic acid, green crystals of the potassium diaquo-dimalonatomanganate separate. The tri-lithium, -sodium, and -ammonium salts could not be obtained in a pure state owing to their very high solubility. The tripotassium salt was found to be stable towards light (cf. the analogous oxalate). The colour and constitution of manganic salts are briefly discussed. W. T.

Formation of γ -Alkylidene Derivatives from Ethylidene-malonic Ester. LUCY HIGGINBOTHAM and ARTHUR LAPWORTH (*T.*, 1922, **121**, 2823—2830).

The Conditions Underlying the Formation of Unsaturated and Cyclic Compounds from Halogenated Open-chain Derivatives. V. Products Derived from α -Halogenated β -Methylglutaric Acids. CHRISTOPHER KELK INGOLD (*T.*, 1922, **121**, 2676—2695).

The Neutralisation of Tartaric Acid in Presence of Metallic Chlorides. Neutral and Buffer Zones. L. J. SIMON (*Compt. rend.*, 1922, **175**, 887—890; cf. Simon and Zivy, A., 1922, ii, 880).—A mixture of potassium tartrate and potassium hydrogen tartrate constitutes a buffer solution, and the author has studied the effect of adding to it copper, zinc, and ferric chlorides. In the case of copper, the buffer effect increases and the results obtained point to the existence of a cupropotassium complex,

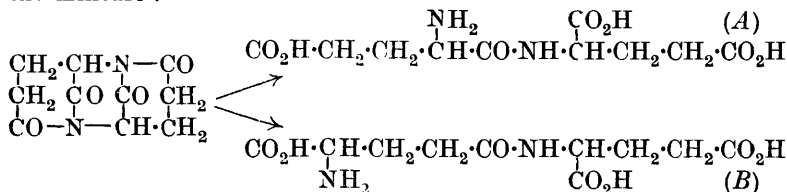


(cf. Masson and Steele, *T.*, 1899, **75**, 725). Although a complex, $\text{C}_4\text{H}_4\text{O}_6\text{KZn}\cdot\text{OH}$, may be formed on addition of zinc chloride, the buffer effect is unaltered, but the presence of ferric chloride leads to a marked decrease of the zone in which the effect is obtained.

H. J. E.

The Action of Glycerol on Glutamic Acid when Heated. Formation of *cyclo*Glutamylglutamic Acid (2:5-Diketopiperazine-3:6-dipropionic Acid) and of Glutamylglutamic Acid. A. BLANCHETIÈRE (*Bull. Soc. chim.*, 1922, [iv], **31**, 1045—1063).—The condensation of glutamic acid in presence of glycerol (cf. Abderhalden and Kautzsch, A., 1910, i, 230, 768) was effected on heating at 170° for eight hours, yielding a product which was separated as barium salt by addition of baryta water. The product is not a polyglutamic acid analogous to the polyaspartic acids (cf. Schaal, A., 1871, 129; also Schiff, A., 1898, i, 67; 1899, i, 195), but 2:5-diketopiperazine-3:6-dipropionic acid. By treat-

ment with aqueous sodium hydroxide, the substance was converted into glutamic acid, passing through the intermediate stage of glutamylglutamic acid. The latter was separated by Fischer's original method, and on evaporation from alcohol-water mixture yielded an amorphous mass, m. p. 167—168°. From a consideration of the constitution of the *cyclo*-acid, it is probable that cleavage of the molecule may occur in two ways (cf. Ravenna, A., 1922, i, 180) and that the acid thus obtained is a mixture of the two possible products. The reaction is shown structurally as follows, the formula *A* representing the substance which forms the bulk of the mixture :



H. J. E.

The Preparation of Ethanetetracarboxylic Acid. C. MANNICH and ERICH GANZ (*Ber.*, 1922, 55, [B], 3509—3510).—The preparation of ethanetetracarboxylic acid in moderate amount by the hydrolysis of the corresponding ester is greatly hampered by the difficulty of effecting the reaction by acid or alkali in a satisfactory manner (cf. Philippi and Hanusch, A., 1920, i, 594). It is therefore preferable to obtain the acid by the catalytic hydrogenation of ethylenetetracarboxylic acid dissolved in acetone in the presence of palladised charcoal. The elimination of carbon dioxide during the process cannot be completely avoided, but the pure acid, m. p. 167—169° (decomp.), can be isolated by repeated crystallisation of the crude product from acetone. H. W.

The Action of Hydrogen Peroxide on Formaldehyde. The Theory of Oxidative Processes. A. BACH and A. GENEROSOW (*Ber.*, 1922, 55, [B], 3560—3566).—Formaldehyde is oxidised by hydrogen peroxide to formic acid and hydrogen. The latter must be derived either from the water or the hydrogen peroxide, and since it is also obtained by the use of other hydrogen-free oxidising agents (potassium chromate, potassium permanganate, lead oxide) in alkaline solution, it appears valid to assume that it originates from the water. The hydrogen peroxide appears to be protected from reduction by the liberated hydrogen by the formation of a complex compound with formaldehyde, the reduction of which is a slower process than the union of the hydrogen atoms to molecules. The interpretation of the course of the reaction in accordance with Traube's theory of oxidation in the presence of water assumes that the formaldehyde molecule in consequence of the removal of a hydrogen atom by oxidation acquires the power of combining with a hydroxyl-ion with the production of formic acid and liberation of the equivalent quantity of hydrogen, whereas

Wieland's theory requires that the formaldehyde hydrate molecule should be able by partial dehydrogenation to decompose spontaneously into formic acid and hydrogen, thus: $\text{CH}_2\text{O} + \text{H}_2\text{O} = \text{CH}_2(\text{OH})_2$. $2\text{CH}_2(\text{OH})_2 + \text{H}_2\text{O}_2 = 2\text{CH}(\text{OH})_2 + 2\text{H}_2\text{O}$. $2\text{CH}(\text{OH})_2 = 2\text{CH}_2\text{O}_2 + \text{H}_2$. The observed facts are best interpreted by the former theory.

Wieland's application of the dihydrogenation theory to biological oxidative processes is criticised at length. The experimental foundation of Wieland's assumption of the identity of oxidising and reducing ferments rests on observations with tissues and their extracts, which are unsuitable for the purpose, since they show not only oxidising and reducing but also hydrolytic properties. In spite of many attempts, it has not been found possible to effect a reduction with purified peroxydase. H. W.

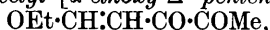
Preparation of α -Trioxymethylene and a New Polymeride of Formaldehyde. DALZIEL LLEWELLYN HAMMICK and ALFORD REGINALD BOEREE (T., 1922, 121, 2738—2740).

Preparation of Acetaldehyde. E. WERTHEIM (*J. Amer. Chem. Soc.*, 1922, 44, 2658—2659).—Certain modifications are suggested in the method of Adams and Williams (cf. A., 1922, i, 222) for the preparation of acetaldehyde by the oxidation of alcohol. The mechanical stirring is replaced by a steady stream of carbon dioxide. The oxidising agent recommended is a mixture of 115 g. of nitric acid (*d* 1.42), 60 g. of sodium dichromate, 20 g. of sulphuric acid (*d* 1.84), and 220 c.c. of water, these quantities sufficing to oxidise 25 g. of alcohol. The alcohol is heated to boiling and the oxidising mixture is run slowly into it, the time taken being about twenty minutes. W. G.

A New Extractive and Absorptive Medium for Scientific and Technical Purposes. GERHARD SCHMITT (*Petroleum Times*, 1922, 8, 249—250).—A solution of sulphur dioxide in acetone (equal parts) has great solvent power for unsaturated organic compounds and resinous substances, and possesses all the advantages of liquid sulphur dioxide whilst it is more convenient to manipulate. It is easily recovered by distillation, there being practically no chemical action on the extracted substance; moreover, extraction can be carried out at low temperatures in an open vessel. Its application to the extraction of soluble substances from coal, lignite, etc., is specially mentioned. CHEMICAL ABSTRACTS.

Ethoxymethylenediacyetyl [α -Ethoxy- Δ^4 -pentene- γ -dione] and α -Ethoxypentane- γ -dione. OTTO DIELS and JUSTUS PETERSEN (*Ber.*, 1922, 55, [B], 3449—3457).—The only representative of the simple $\alpha\beta$ -unsaturated 1:2-diketones which has been described previously is styryl methyl diketone, $\text{CHPh}:\text{CH}\cdot\text{CO}\cdot\text{CO}\cdot\text{Me}$ (Diels and Andersonn, A., 1911, i, 464; Diels and Sharkoff, A., 1913, i, 875). A second member of this class, ethoxymethylenediacyetyl, has now been prepared and examined.

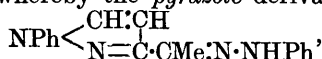
Ethoxymethylenediacyetyl [α -ethoxy- Δ^a -pentene- $\gamma\delta$ -dione],



is prepared in poor yield by the action of ethyl orthoformate on dimethyl diketone dissolved in boiling acetic anhydride. It is a dark yellow liquid, b. p. $85-86^\circ/10$ mm., $d_4^{14.3}$ 1.0532, $n_D^{14.3}$ 1.44950, $n_F^{14.3}$ 1.46601, which solidifies completely at -20° to a mass of yellow crystals which melts at -10° . Its vapours have a pronounced olive-green colour. It somewhat readily becomes viscous, and ultimately resinifies when preserved. It is rapidly decomposed by alkali hydroxides, ammonia, and concentrated acids, but the sensitiveness of the substance to these reagents is such that definite products of the change cannot be isolated. When treated with *o*-phenylenediamine in the presence of pyridine, it gives the *quinoxaline* deriv-

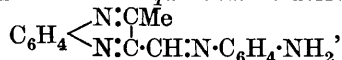
ative, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{N}=\text{CMe} \\ \text{N}=\text{C} \end{smallmatrix} \text{CH}:\text{CH}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$, leaflets, m. p. 183° .

With aniline in methyl-alcoholic solution, it gives the *anilanilide*, small, colourless needles, m. p. $187-188^\circ$, to which the constitution $\text{NHPh}\cdot\text{CH}:\text{CH}\cdot\text{CO}\cdot\text{CMe}:\text{NPh}$ is ascribed. When treated with phenylhydrazine under very mild conditions, the ethoxymethylene compound yields the *monophenylhydrazone*, $\text{OEtCH}:\text{CH}\cdot\text{CO}\cdot\text{CMe}:\text{N}\cdot\text{NHPh}$, yellowish-brown rodlets, m. p. 152° , the constitution of which is established by the observation that, under more energetic conditions, a second molecular proportion of phenylhydrazine enters into the reaction, whereby the *pyrazole* derivative,



pale yellow leaflets, m. p. 182° , is formed. The addition of piperidine to a solution of ethoxymethylenediacyetyl in light petroleum leads to the formation of the *piperilide*, $\text{C}_{10}\text{H}_{15}\text{O}_2\text{N}$, lemon-yellow needles, m. p. 81.5° .

Ozonisation of α -ethoxy- Δ^a -butene- $\gamma\delta$ -dione dissolved in chloroform and subsequent decomposition of the oily *ozonide* with water leads to the production of $\alpha\beta$ -diketobutaldehyde, $\text{CH}_3\cdot\text{CO}\cdot\text{CO}\cdot\text{CHO}$; the compound has not yet been isolated, but its existence is placed beyond doubt by the conversion of the crude material by means of *o*-phenylenediamine into the *quinoxaline* derivative,



leaflets, m. p. 166° .

α -Ethoxy- Δ^a -pentene- $\gamma\delta$ -dione is smoothly hydrogenated in methyl-alcoholic solution in the presence of colloidal palladium to α -ethoxypentane- $\gamma\delta$ -dione, $\text{OEt}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{COMe}$, b. p. $70-73^\circ/13$ mm., $d_4^{15.6}$ 1.0690, $n_D^{15.6}$ 1.43588, $n_F^{15.6}$ 1.44477, which is much more stable than the corresponding unsaturated compound; the *disemicarbazone*, m. p. 244° (decomp.) after previous darkening, is described.

Attempts have been made to replace dimethyl diketone in the condensation just described by the less expensive methyl ether of its oxime, $\text{CH}_3\cdot\text{CO}\cdot\text{CMe}:\text{N}\cdot\text{OMe}$. In this case, however, the use of ethyl orthoformate and acetic anhydride is unsuccessful. The

alternative method of condensation (action of sodium ethoxide and ethyl orthoformate) gives well-defined products in the formation of which the ester does not take a part. The isolation of a *substance*, $\text{OMe}\cdot\text{N}:\text{CMe}\cdot\text{CO}\cdot\text{CH}:\text{CMe}\cdot\text{CMe}\cdot\text{N}\cdot\text{OMe}$, long, lustrous needles, m. p. 50° (*phenylhydrazone*, $\text{C}_{16}\text{H}_{22}\text{O}_2\text{N}_4$, yellow leaflets, m. p. 110°), and of a *product*, $\text{C}_{10}\text{H}_{16}\text{O}_3\text{N}_2$, hexagonal leaflets, m. p. 138.5° , is described; the constitution of the latter has not been elucidated. H. W.

1 : 3 : 4 : 6-Tetramethyl Fructose. JAMES COLQUHOUN IRVINE and JOCELYN PATTERSON (T., 1922, **121**, 2696—2703).

Structure of Fucose. E. P. CLARK (*J. Biol. Chem.*, 1922, **54**, 65—73).—The method for the preparation of fucose has been improved. Using the methods employed by Hudson and Chernoff (A., 1918, i, 335) in the case of rhamnose, a *methyl tetronolactone*, m. p. 110° , $[\alpha]_D^{20} - 63.65^\circ$, and a *methyl tetronamide*, m. p. 112.5° , $[\alpha]_D^{20} + 18.48^\circ$, have been obtained from fucose. Fuconic acid, when saturated with ammonia in alcoholic solution, yields *fuconamide*, m. p. 180.5° , $[\alpha]_D^{20} - 31.13^\circ$. On the basis of the relationships which exist between the configuration and rotation of lactones and amides of sugar acids (Hudson, A., 1910, i, 220; 1918, i, 293), it is concluded from the above data that the configuration assigned to fucose by Mayer and Tollens (A., 1907, i, 588) is correct. E. S.

Oxidation of Carbohydrates with Nitric Acid. PAUL HAAS and BARBARA RUSSELL-WELLS (*Biochem. J.*, 1922, **16**, 572—573).—The carbohydrate constituents of *Chondrus crispus*, sucrose, lactose, dextrose, and lævulose, on oxidation with nitric acid, yield a substance similar to glycuronic acid which reduces Fehling's solution in the cold. Attempts to prepare a crystalline oxime, phenylhydrazone, *p*-bromophenylhydrazone, or a cinchonine salt failed. S. S. Z.

The Oxidation of Sucrose by Nitric Acid. FREDERICK DANIEL CHATTAWAY and HINTON JOHN HARRIS (T., 1922, **121**, 2703—2709).

Cellulose. III. Determination of the Viscosity of Cellulose. MICHIMARO NAKANO (*J. Chem. Ind. Japan*, 1922, **25**, 899—910).—The author has studied the preparation of the cuprammonium solution and the effects of various factors on the viscosity of the cuprammonium solution of cellulose, the result being summarised as follows. The viscosity decreases with time until it attains a constant value. A dilute solution attains a constant value more rapidly than a concentrated one, but with a very dilute solution the value is constant from the beginning. With solutions of the same concentration, the lower the viscosity the less is the difference between the final and initial values; the viscosity increases much more rapidly than the concentration. The relative viscosity increases with the temperature. No appreciable decrease of viscosity due to a small loss of ammonia could be observed. Oxygen and light have the largest effect on the viscosity. The depolymerisation of the molecular aggregate of cellulose is due to the

action of light. Of the various preliminary treatments of cellulose, the thermal treatment is the deciding factor for viscosity. K. K.

Nature of the Swelling Process. VI. Swelling and Partition of Cellulose Acetate in Organic Solvents. F. KNOEVENAGEL, J. HOGREFE, and F. MERTENS (*Koll. Chem. Beihefte*, 1922, **16**, 180—214; cf. A., 1921, i, 402, 709, 710, 771).—The swelling and partition of cellulose acetate in the mixtures, acetic acid–water, acetic acid–benzene, acetone–benzene, nitrobenzene–*iso*-propyl alcohol, ethyl alcohol–benzene, nitrobenzene–benzene, ethyl alcohol–water, acetic acid–nitrobenzene, acetone–nitrobenzene, methyl alcohol–nitrobenzene, acetone–methyl alcohol, and acetic acid–camphor has been investigated. Cellulose acetate soluble in acetone or chloroform or insoluble in acetic acid was used in the various experiments. The present experiments are an extension of those previously published (*loc. cit.*), and show that alcohols, benzene, and water in varying quantities are taken up by cellulose acetate in constant amounts. In these cases, the law of constant combining proportions is applicable, and it is suggested that where this law holds it is well to speak of compounds and to regard the taking up of the liquids as a chemical process. The compounds involved in these cases are in all probability of a higher order than molecular compounds. The valency involved in these cases is shown to be due to electrical forces. The nature of this type of combination is considered, and it is shown that the swelling process consists of a reaction between two molecules and is of a chemical nature. J. F. S.

Hydrocellulose. EMIL HEUSER and WALTER VON NEUENSTEIN (*Cellulosechemie*, 1922, **3**, 89—96).—According to recent theories (Herzog and Jancke, A., 1921, ii, 532; Karrer, A., 1922, i, 231), the cellulose substance is built up of double molecules of anhydrocellobiose, which are systematically arranged in crystal symmetry and held together by special affinities called crystal valencies. These crystal valencies are assumed to be released by all processes which destroy the fibrous structure. The attack on the crystal valencies produces only physical changes, converting the fibrous crystal cellulose into amorphous cellulose, the double anhydrocellobiose molecules remaining intact. The first stage of chemical hydrolysis would involve an attack on the anhydride position of one of the cellobiose residues, without depolymerising the unit, and it is suggested that hydrocellulose is thus formed, consisting of cellobiose–anhydrocellobiose differing from the simple amorphous cellulose as regards the open carbonyl group, but not in molecular dimensions. Further hydrolysis involves the first stage of depolymerisation with formation of free cellobiose, accompanied or closely followed by the second stage, with formation of dextrose. Girard's hydrocellulose produced from fibrous cellulose is a mixture of cellulose and true hydrocellulose, but the hydrocellulose produced by Knoevenagel and Busch's method (A., 1922, i, 636) from viscose cellulose is a homogeneous hydrocellulose, because it is formed from cellulose in which the crystal valencies

have already been resolved. This view is supported by the preparation of highly methylated derivatives by Denham and Woodhouse's method. Ordinary cotton cellulose, on repeated methylation, gave a product corresponding with dimethylcellulose, almost completely insoluble in cold water and in organic solvents. The product from the pure hydrocellulose of Knoevenagel and Busch, with the same methoxyl content, was completely soluble in these media and behaved as a uniform substance. Girard's hydrocellulose yielded a mixed product, partly soluble like that from the pure hydrocellulose and partly insoluble like that from ordinary cotton. In no case was a trimethylated derivative obtained. The dimethylhydrocellulose from Knoevenagel and Busch's product yielded on acetylation principally monoacetyldimethylhydrocellulose soluble in organic solvents and with relatively low melting point. Determinations of molecular weights of these derivatives gave low but inconclusive results.

J. F. B.

Plant Colloids. XIV. Physico-chemical Analysis of Agar Jellies. M. SAMEC and V. ISAJEVIĆ (*Koll. Chem. Beihefte*, 1922, 16, 285—300; cf. A., 1922, i, 921).—Agar-agar is shown to contain a not inconsiderable quantity of electrolytes, which are so closely combined with the organic substances that neither dialysis nor electro-dialysis is sufficient to remove them from the residue of the gum. The chief constituents of agar ash are sulphuric acid and calcium, and a little silicic acid is also present. On boiling the agar solution under pressure, the sulphuric acid passes into an easily dialysable form. Simultaneously with this, the whole of the physico-chemical properties of the solution change, so that a causal connexion between the sulphur content and the power of forming jellies is deduced. Gelose-sulphuric acid is a typical constituent of agar, and in this the sulphuric acid is in all probability present as an ester. The mean molecular weight of this substance is about 9000. It is a monobasic acid and contains one atom of sulphur in each molecule. Agar jellies reach the maximum of their tenacity at the neutral point.

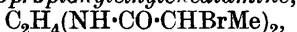
J. F. S.

Preparation of Aliphatic Dialkylaminoalkyl Compounds. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (Brit. Pat. 169185, addition to 167781 (cf. A., 1922, i, 529).—The condensation described in the main patent can be carried out by causing an alkali hydroxide to act on a mixture, in molecular proportions, of a dialkylhalogeno-alkylamine, and a substance of the general formula $R \cdot CO \cdot CHR' \cdot X$ such as ethyl acetoacetate. Further, a purer product is obtained if the reaction mixture is mixed with benzene and shaken with ammonia before drying and distilling. Ethyl diethylaminoethylacetoacetate, prepared in this way from diethyl-chloroethylamine and ethyl acetoacetate, boils at 130—132°/10 mm.

G. F. M.

New Compounds of Diamines. II. PETER BERGELL (*Z. physiol. Chem.*, 1922, 123, 280—289).—The following compounds

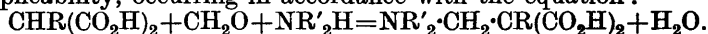
have been prepared from ethylenediamine and the necessary acid chloride :—*di-α-bromopropionylethylenediamine*,



white, glistening needles, m. p. 203°, *dichloroacetylenehydrazine*, long, rectangular or rhombic prisms, m. p. 171—172°, *di-β-naphthalenesulphonyldiethylenediamine*, fine needles. From pentamethylenediamine, *di-α-bromopropionylpentamethylenediamine*, and *di-β-naphthalenesulphonylpentamethylenediamine*, m. p. 147°. From these halogenated compounds, on heating with ammonia, the corresponding amino-derivatives are formed, but were not isolated. On treating that obtained from dibromopropionylpentamethylenediamine with β-bromopropionyl bromide, *di-α-bromopropionyl-dialanylpentamethylenediamine*, m. p. 180°, is obtained. W. O. K.

Dialkylaminoalkyl Compounds. M. BOCKMÜHL and A. SCHWARZ (U.S. Pat. 1429922).—Ethyl α-(diethylaminoethyl)-acetoacetate, b. p. 132—135°/10 mm., is prepared by mixing 136 parts of diethylaminoethyl chloride with 130 parts of ethyl acetoacetate and gradually stirring into the mixture 57—58 parts of powdered alkali hydroxide, cooling, treating with benzene, shaking the benzene solution with ammonia, drying and distilling. As an alternative method, alkali hydroxide may be gradually introduced into diethylaminoethyl bromide hydrobromide and ethyl acetoacetate. The corresponding α-dimethyl ester, b. p. 124°/12 mm., may be similarly prepared from dimethylaminoethyl chloride. Ethyl diethylaminobutylacetoacetate, b. p. 138°/10 mm., is prepared from diethylaminochlorobutanol, ethyl acetoacetate, and powdered alkali hydroxide. CHEMICAL ABSTRACTS.

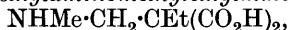
β-Aminodicarboxylic Acids and Aminopolycarboxylic Acids. C. MANNICH and ERIC GANZ (*Ber.*, 1922, 55, [B], 3486—3504).—In a previous communication (A., 1920, i, 719), Mannich and Kather have described the preparation of ω-dimethylamino-dimethylmalonic acid from methylmalonic acid, dimethylamine, and formaldehyde. The reaction is now shown to be of general applicability, occurring in accordance with the equation :



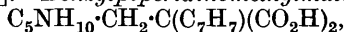
The reaction is generally effected by mixing concentrated solutions of formaldehyde and of a monosubstituted malonic acid which has been half neutralised by the requisite base and preserving the mixture in ice. In general, the new acid separates spontaneously or after addition of alcohol or acetone; if this is not the case, there is little likelihood of a successful preparation owing to the instability of the products. The nature of the substituent introduced into the malonic acid has but little influence on the course of the change, provided that it is aliphatic or fatty aromatic; with aromatic constituents, the primarily formed dicarboxylic acid suffers immediate loss of carbon dioxide. Secondary bases, such as dimethylamine and piperidine, are more suitable than primary bases or ammonia with which frequently more than one hydrogen atom becomes involved in the reaction.

The β -amino-dicarboxylic acids are generally unstable and decompose readily in substance or in solution with the production of α -substituted acrylic acids. The change is conveniently effected by boiling them in neutral solution. It has not been found possible to discover conditions under which carbon dioxide is evolved without elimination of the basic group. On the other hand, the conversion of the aminodi- into the aminomono-carboxylic acid appears to be possible through the esters, since the dicarboxylic acids when treated with alcoholic hydrogen chloride give esters of the mono-carboxylic acids which can be hydrolysed by aqueous hydrochloric acids to the acid hydrochlorides. The place of the monosubstituted malonic acids may be taken by ethanetricarboxylic acid, $\text{CH}(\text{CO}_2\text{H})_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, but not apparently by ethanetetracarboxylic or methylenedimalonic acid. Cyanoacetic acid may also be used.

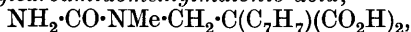
The following substances are described: *Dimethylaminomethylethylmalonic acid*, $\text{NMe}_2 \cdot \text{CH}_2 \cdot \text{CEt}(\text{CO}_2\text{H})_2$, plates, m. p. 101° (decomp.), which is readily decomposed into α -ethylacrylic acid, b. p. 179 – 180° . *Methylaminomethylethylmalonic acid*,



m. p. about 136° (decomp.), and its benzoyl derivative, plates, m. p. 142° (decomp.). *Dimethylaminomethylallylmalonic acid*, rhombic plates, m. p. 85° (decomp.), its chloroplatinate and α -allylacrylic acid, b. p. 76 – $78^\circ/16$ mm. (the barium, lead, and silver salts are described). δ -Phenylpropyl- α -dimethylaminomethylmalonic acid, $\text{CH}_2\text{Ph} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{C}(\text{CH}_2 \cdot \text{NMe}_2)(\text{CO}_2\text{H})_2$, small, colourless needles, m. p. about 115° (decomp.) [from δ -phenylpropylmalonic acid, dimethylamine, and formaldehyde], and δ -phenyl- α -methylenevaleric acid, $\text{CH}_2\text{Ph} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{C}(\text{CH}_2) \cdot \text{CO}_2\text{H}$, m. p. 45° (silver salt, leaflets). *Benzyl dimethylaminomethylmalonic acid*, needles, m. p. 88° , and α -benzylacrylic acid, $\text{CH}_2 \cdot \text{C}(\text{CH}_2\text{Ph}) \cdot \text{CO}_2\text{H}$, m. p. 68° [the latter acid yields a dibromide, $\text{CH}_2\text{Ph} \cdot \text{CBr}(\text{CH}_2\text{Br}) \cdot \text{CO}_2\text{H}$, needles, m. p. 145° ; it is oxidised by potassium permanganate in faintly alkaline solution to α -benzylglyceric acid, $\text{OH} \cdot \text{CH}_2 \cdot \text{C}(\text{OH})(\text{CH}_2\text{Ph}) \cdot \text{CO}_2\text{H}$, prisms, m. p. 127°]. *Benzylpiperidinomethylmalonic acid*,



decomp. about 121° , and its sparingly soluble lead and barium salts; the acid is converted by alcoholic hydrogen chloride at the atmospheric temperature into ethyl α -benzyl- β -piperidinopropionate hydrochloride, $\text{C}_5\text{NH}_{10} \cdot \text{CH}_2 \cdot \text{CH}(\text{C}_7\text{H}_7) \cdot \text{CO}_2\text{Et} \cdot \text{HCl}$, plates, m. p. 185° , which is hydrolysed by concentrated hydrochloric acid to α -benzyl- β -piperidinopropionic acid hydrochloride, small plates, m. p. 146° . *Benzylmethylaminomethylmalonic acid*, small needles, m. p. about 150° (decomp.), its benzoyl derivative, m. p. about 138° (decomp.), and nitroso-compound, plates, m. p. about 122° (decomp.); [the sodium salt of the acid is transformed by potassium cyanate into benzylmethylcarbamidomethylmalonic acid,



small plates, m. p. about 98° (decomp.), which when heated in boiling xylene passes into α -benzyl- β -methylcarbamidopropionic acid, $\text{NH}_2 \cdot \text{CO} \cdot \text{NMe} \cdot \text{CH}_2 \cdot \text{CH}(\text{CH}_2\text{Ph}) \cdot \text{CO}_2\text{H}$; the latter substance is converted by boiling acetic anhydride into 2 : 4-diketo-5-benzyl-1-methyl-

hexahydropyrimidine, $\text{CO} \begin{smallmatrix} \text{NH} - \text{CO} \\ \text{NMe} \cdot \text{CH}_2 \end{smallmatrix} \text{CH} \cdot \text{CH}_2\text{Ph}$, small needles, m. p. 78°]. *Benzylallylaminomethylmalonic acid*, $\text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{C}(\text{CH}_2\text{Ph})(\text{CO}_2\text{H})_2$, needles, m. p. 138° (decomp.), and its sparingly soluble *lead* and *barium* salts.

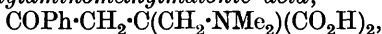
According to experimental conditions, benzylmalonic acid is converted by ammonia and formaldehyde into *iminobismethylbenzylmalonic acid*, $\text{NH}[\text{CH}_2 \cdot \text{C}(\text{CH}_2\text{Ph})(\text{CO}_2\text{H})_2]_2$, small plates, m. p. 107° (decomp.), or *benzylaminomethylmalonic acid*,



lustrous leaflets, m. p. about 148° (decomp.); either substance is transformed in boiling neutral aqueous solution into α -benzylacrylic acid.

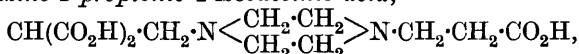
β -*Dimethylamino- α -phenylpropionic acid*, $\text{NMe}_2 \cdot \text{CH}_2 \cdot \text{CHPh} \cdot \text{CO}_2\text{H}$, needles, m. p. 143°, prepared from phenylmalonic acid, dimethylamine, and formaldehyde at 0°, is transformed by being heated into atropic acid, m. p. 106°. Phenylmalonic acid, ammonia, and formaldehyde yield β -amino- α -phenylpropionic acid, which is isolated as the *hydrochloride*, m. p. 185°; it is converted by phenylacetyl chloride to a small extent into β -phenylacetylaminomethylmalonic acid, small needles, m. p. 185°, the main product of the reaction being, however, phenylacetamide. Phenylmalonic acid, ammonium chloride, and formaldehyde give β -iminobis- α -phenylpropionic acid, $\text{NH}(\text{CH}_2 \cdot \text{CHPh} \cdot \text{CO}_2\text{H})_2$, which is isolated as the *hydrochloride*, m. p. 112°; it passes into atropic acid when boiled in neutral solution.

Phenacyldimethylaminomethylmalonic acid,

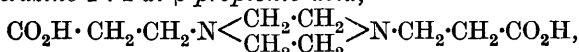


needles, m. p. about 148° (decomp.), and *phenacylmethylaminomethylmalonic acid*, m. p. 105° (decomp.), are obtained in the usual manner; the sparingly soluble *lead* and *barium* salts of the latter acid are mentioned.

Piperazine-1-propionic-4-isosuccinic acid,

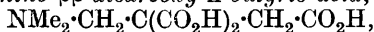


leaflets, m. p. about 227° (decomp.), after becoming discoloured at 200°, is prepared from malonic acid, piperazine, and formaldehyde, and is converted by hot aqueous hydrochloric acid into *piperazine-1:4-di- β -propionic acid*,



which is isolated as the *dihydrochloride*, m. p. 261—262° (decomp.).

Ethanetricarboxylic acid, dimethylamine, and formaldehyde yield γ -dimethylamino- $\beta\beta$ -dicarboxy-n-butyric acid,



needles, m. p. about 135° (decomp.), which passes in boiling aqueous solution by loss of carbon dioxide into γ -dimethylamino- β -carboxy-n-butyric acid, $\text{NMe}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, m. p. 158°. The latter acid is transformed into itaconic acid by treatment of its crystalline *methiodide* with potassium hydroxide.

The action of formaldehyde on dimethylammonium cyanoacetate is accompanied by the evolution of carbon dioxide; the product of the action consists doubtless of β -dimethylaminopropionitrile, $\text{NMe}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CN}$. Its isolation could not be effected, but its presence is established by the formation of acrylic acid when the crude product is treated with hydrogen chloride.

H. W.

A Synthesis of Aminohydroxydicarboxylic Acids. C. MANNICH and M. BAUROTH (*Ber.*, 1922, **55**, [B], 3504—3509).—A synthesis of β -aminodicarboxylic acids from monosubstituted malonic acids, formaldehyde, and amines has been described by Mannich and Kather (A., 1920, i, 719) and Mannich and Ganz (preceding abstract). If, under otherwise similar conditions, the alkylmalonic is replaced by tartronic (hydroxymalonic) acid, aminohydroxydicarboxylic acids are produced. These, like the compounds described previously, are unstable substances, and when warmed with water undergo simultaneous decomposition in two directions; thus dimethylaminomethyltartronic acid becomes transformed on the one hand by simple loss of carbon dioxide into β -dimethylamino- α -hydroxypropionic acid, and, on the other, by loss of carbon dioxide and dimethylamine, into pyruvic acid. β -Dimethylamino- α -hydroxypropionic acid is not an intermediate compound in the latter change, since it is stable under the experimental conditions adopted.

Dimethylaminomethyltartronic acid, $\text{OH}\cdot\text{C}(\text{CH}_2\cdot\text{NMe}_2)(\text{CO}_2\text{H})_2$, plates, m. p. about 115° (decomp.), is prepared by the action of formaldehyde at 0° on a concentrated aqueous solution of tartronic acid which has been half neutralised by dimethylamine. It yields β -dimethylamino- α -hydroxypropionic acid, $\text{NMe}_2\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$, which is analysed in the form of its *hydrochloride*, rodlets, m. p. 145 — 146° . *Methylaminomethyltartronic acid*,

$\text{OH}\cdot\text{C}(\text{CH}_2\cdot\text{NHMe})(\text{CO}_2\text{H})_2$,

aggregates of coarse needles, m. p. about 153° (decomp.), when rapidly heated, is similarly prepared from tartronic acid, formaldehyde, and methylamine and is converted by hot water and hydrochloric acid into β -methylamino- α -hydroxypropionic acid *hydrochloride*, transparent pyramids, m. p. 155 — 156° . *Aminomethyltartronic acid*, $\text{OH}\cdot\text{C}(\text{CH}_2\cdot\text{NH}_2)(\text{CO}_2\text{H})_2$, coarse crystals, m. p. about 138° (decomp.), is decomposed by hot water into pyruvic acid in small amount; β -amino- α -hydroxypropionic acid does not appear to be produced. *Piperidinomethyltartronic acid* crystallises in leaflets, m. p. about 190° (decomp.).

H. W.

The Carbamide Rearrangement. TENNEY L. DAVIS and H. W. UNDERWOOD, jun. (*J. Amer. Chem. Soc.*, 1922, **44**, 2595—2604).—It is shown that carbamide, thiocarbamide, and guanidine and their derivatives undergo the "urea rearrangement." Carbamide yields ammonia and isocyanic acid, and the other compounds yield derivatives of ammonia and of isocyanic acid. Such rearrangement forms the basis of a number of syntheses. *s*-Disubstituted aromatic carbamides may conveniently be prepared by

heating carbamide with primary aromatic amines. In the aliphatic series, the reaction succeeds, but the products are more difficult to isolate, and the process is being further studied. The similarity between guanidine and carbamide, and between cyanamide and isocyanic acid in respect to a number of their reactions is pointed out. It is considered that the polymerisation of cyanamide to dicyanodiamide, when its aqueous solution is evaporated, is believed to be a case of the "urea dearrangement."

The explanation of the formation of melamine, when aqueous ammonia and dicyanodiamide are heated together, previously given (A., 1922, i, 118), is probably wrong. A portion of the dicyanodiamide is hydrolysed by the action of the ammonia to yield, first, guanylcarbamide and later guanidine, and the latter dearranges to form cyanamide, which combines with the unaltered dicyanodiamide to yield melamine.

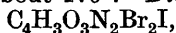
W. G.

Trihalogenated Pyvurins. M. GARINO (*Gazzetta*, 1922, 52, ii, 207—220).—Various compounds analogous to Fischer's tribromopyvurin (A., 1887, 918) have been prepared, pyruvic acid being converted into the dichloro- or dibromo-derivative and this treated with carbamide in presence of sulphuric acid to give the dihalogenated pyvureide, which yields the trihalogenated pyvurin when subjected to the action of a halogen. The stability of these compounds, and also their solubility in water, 95% alcohol, or ether, diminish as the chlorine is replaced by bromine, and no derivative with more than one atom of iodine could be obtained. When treated carefully with dilute alkali solution, the trihalogenated pyvurins yield the corresponding analogues of chloroform, the readiness with which this decomposition occurs increasing as the atomic weight of the halogens present increases. Pharmacological experiments on mammals of various species show that, whereas trichloropyvurin passes almost unchanged through the organism, the tribromo-compound is decomposed with formation of bromoform and produces prolonged narcosis.

Dichloropyvureide, $\text{CCl}_2\text{:C} \begin{smallmatrix} \text{NH}\cdot\text{CO} \\ | \\ \text{CO}\cdot\text{NH} \end{smallmatrix}$, prepared from dichloropyruvic acid, is a white, pulverulent substance, m. p. 286° , subliming unchanged at about 170° .

Trichloropyvurin, $\text{CCl}_3\cdot\text{CO}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, crystallises in soft, lustrous plates, m. p. 242° (decomp.), and gives the phenylcarbylamine reaction with potassium hydroxide and aniline; with potassium hydroxide and β -naphthol it gives a greenish-blue coloration and with thymol a reddish-violet coloration. It readily forms supersaturated solutions in water.

Dichlorobromopyvurin, $\text{C}_4\text{H}_3\text{O}_3\text{N}_2\text{Cl}_2\text{Br}$, forms lustrous, white scales, m. p. 236° (decomp.). *Chlorodibromopyvurin*, $\text{C}_4\text{H}_3\text{O}_3\text{N}_2\text{ClBr}_2$, forms white, lamellar crystals, m. p. 238° (decomp.). *Dichloroiodopyvurin*, $\text{C}_4\text{H}_3\text{O}_3\text{N}_2\text{Cl}_2\text{I}$, forms yellow crystals, m. p. about 230° (decomp.), and begins to yield iodine vapour at about 150° or, if very slowly heated, at about 170° . *Dibromoiodopyvurin*,



forms white crystals turning yellow in the light, m. p. 197° (decomp.), and begins to emit iodine at about 105°. T. H. P.

Preparation of Chlorobromoiodypyurin. M. GARINO and I. MUZIO (*Gazzetta*, 1922, 52, ii, 226—232).—Chloropyruvic acid (cf. Genvresse, *Bull. Soc. chim.*, 1892, [iii], 7, 83), prepared by the action of sulphuryl chloride on pyruvic acid, forms white, rhombohedral crystals (+H₂O), m. p. 55°, and decomposes between 122° and 155°; the anhydrous acid, m. p. about 45°, is very unstable. *Chlorobromopyruvic acid*, CHClBr·CO·CO₂H, forms white, tabular crystals, m. p. 105°.

Chlorobromopyvureide, $\text{CClBr}\cdot\text{C} \begin{smallmatrix} \text{NH}\cdot\text{CO} \\ \text{CO}\cdot\text{NH} \end{smallmatrix}$, forms a light, white precipitate, and begins to sublime at about 120°. *Chlorobromoiodypyurin*, CClBrI·CO·CO·NH·CO·NH₂, prepared by treating the preceding compound with iodine in presence of iodic acid and carbon tetrachloride, forms white crystals, m. p. 233° (decomp.), and begins to emit iodine at 160°. It is highly stable in the dry state, but readily decomposes in solution, especially under the influence of light. In presence of potassium hydroxide, it gives a violet coloration with thymol and a blue coloration with β-naphthol; with potassium hydroxide and aniline, it forms phenylcarbylamine. When treated with potassium hydroxide under certain conditions, it yields ammonium oxalurate and chlorobromoiodomethane, which is being investigated further. T. H. P.

Electrolytic Dissociation of Dicyanodiamide in Aqueous Solution. NAOTO KAMEYAMA (*J. Coll. Eng. Tokyo*, 1922, 11, 185—191).—By measuring the conductivity of solutions of sodium hydroxide and dicyanodiamide at 25°, the hydrolysis of sodium dicyanodiamide in 0·1 mol. solution was found to be 94·5%. In more dilute solutions, hydrolysis is almost complete. The dissociation constant at 25° is $0\cdot6 \times 10^{-14}$. The basic properties of dicyanodiamide are very feeble, the hydrochloride, if it exists at all, being completely hydrolysed in aqueous solution. G. F. M.

Attempts to Prepare Carbonyl Cyanide and a Method of Obtaining Unsaturated Amino-acids. OTTO DIELS, HUGO GÄRTNER, and RICHARD KAACK (*Ber.*, 1922, 55, [B], 3439—3448).—Attempts are described to prepare carbonyl cyanide, CO(CN)₂, by the ozonisation of suitable derivatives of malononitrile; these, however, have not been completely successful. A synthesis of unsaturated amino-acids from ethyl cyanoethoxyacrylate has been effected.

Ethoxymethylenemalononitrile, OEt·CH:C(CN)₂, large, colourless crystals, m. p. 65—66° after previous softening, is prepared by the protracted heating of a solution of malononitrile and ethyl orthoformate in acetic anhydride. It is converted by boiling water into *hydroxymethylenemalononitrile*, m. p. 135° (decomp.) [*hydrochloride*, C₄H₃ON₂Cl, lustrous needles, m. p. 121° (decomp.)], and by ammonia (25%) into *aminomethylenemalononitrile*, pale yellow crystals, m. p.

146°. Ozonisation of ethoxymethylenemalononitrile dissolved in glacial acetic acid under varied conditions of temperature and concentration has not led to conclusive results, but, in certain circumstances, a crystalline material has been isolated in very small amount, the properties of which are such as might be expected to be shown by carbonyl cyanide. Ozonisation of ethyl cyanoethoxyacrylate dissolved in ethyl acetate leads to the production of an ozonide which is decomposed by warm water with formation of oxalic acid. Benzylidenemalononitrile is unexpectedly resistant towards the action of ozone.

Malononitrile reacts energetically with acetaldehyde at 0° in the presence of a drop of piperidine, and gives 1 : 3-dimethylcyclobutane-2 : 2 : 4 : 4-tetranitrile, $(\text{CN})_2\text{C} \begin{smallmatrix} \text{CHMe} \\ \text{CHMe} \end{smallmatrix} \text{C}(\text{CN})_2$, small, colourless needles, m. p. 184—185°. In the presence of ethyl alcohol, the same substances yield ethylidenebismalononitrile, $\text{CHMe}:[\text{CH}(\text{CN})_2]_2$, colourless, prismatic crystals, m. p. 113—114°, which is decomposed by warm water with formation of acetaldehyde. Methylenebismalononitrile, large prisms, m. p. 136—137°, is prepared by the action of formaldehyde (40%) on a solution of malononitrile in alcohol. It dissolves in boiling water to a clear solution from which spindle-like crystals, m. p. about 192—195° after darkening at about 130°, separate; the filtrate from these crystals, if again boiled for a short time, deposits lustrous leaflets, m. p. 231—233° after darkening at about 200°. The composition of the two compounds is identical, but their further investigation has not been possible owing to lack of material.

Ethyl ethoxymethylenecyanoacetate is converted by benzylamine in ethyl-alcoholic (95%) solution into ethyl α -cyano- β -benzylaminoacrylate, $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{CH}\cdot\text{C}(\text{CN})\cdot\text{CO}_2\text{Et}$, thick, colourless needles, m. p. 103—104°, which is slowly transformed by a solution of sodium in boiling ethyl alcohol (96%) into β -benzylaminoacrylic acid, $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{H}$, colourless, unctuous leaflets, m. p. 97—98°, b. p. 105—106°/12 mm. (the sodium and silver salts are described). β -Anilinoacrylic acid, m. p. 156°, is prepared similarly and in poor yield from ethyl cyanoanilinoacrylate.

Ethyl cyanoethoxyacrylate is converted by cautious treatment with hydrazine hydrate into ethyl cyanohydrazinoacrylate, $\text{NH}_2\cdot\text{NH}\cdot\text{CH}\cdot\text{C}(\text{CN})\cdot\text{CO}_2\text{Et}$, slender, colourless needles, m. p. 96—97°, which, with acetone, yields the compound, $\text{CMe}_2\cdot\text{N}\cdot\text{NH}\cdot\text{CH}\cdot\text{C}(\text{CN})\cdot\text{CO}_2\text{Et}$, rhombohedra, m. p. 78—79°. H. W.

Possible Asymmetry of Aliphatic Diazo-compounds. III. P. A. LEVENE and L. A. MIKESKA (*J. Biol. Chem.*, 1922, **54**, 101—103).—When fused with benzoic acid, ethyl diazosuccinate yields ethyl benzoylmalate, b. p. 147—148°/3 mm., 143°/2 mm. The products from two preparations had $[\alpha]_D^{20} + 0.22^\circ$ and $+ 0.12^\circ$, respectively. The authors regard the rotations obtained as additional evidence of the existence of optically active diazosuccinic esters (cf. A., 1922, i, 818). E. S.

***s*-Diisopropylhydrazine and its Derivatives. II.** HARRY L. LOCHTE, WILLIAM A. NOYES, and JAMES R. BAILEY (*J. Amer. Chem. Soc.*, 1922, **44**, 2556—2567; cf. A., 1922, i, 329).—*s*-Diisopropylhydrazine has been carefully purified and some of its physical constants have been redetermined with the following results: b. p. 124.5°/750 mm., d_4^{25} 0.7844, n_D^{25} 1.4125. It gives an *oxalate*, m. p. 200°, and a *semicarbazide* derivative, m. p. 100°. If the dry hydrochloride is mixed with a 30% excess of dry powdered copper oxide in a stoppered flask and after a week the mixture is distilled, 2:2'-azopropane, b. p. 88.5°/750 mm., d_4^{25} 0.7408, n_D^{25} 1.3890, is obtained. This compound is readily reduced to the symmetrical hydrazine, but weak oxidising agents have no effect on it. When left in contact with solid sodium or potassium hydroxides, it is partly converted into acetoneisopropylhydrazone.

isoPropylhydrazine, $\text{CHMe}_2\cdot\text{NH}\cdot\text{NH}_2$, b. p. 106—107°/750 mm., may be prepared by one of four methods, namely, hydrolysis of the azo-derivative, hydrolysis of acetoneisopropylhydrazone, direct reduction of an equimolecular mixture of acetone, hydrazine hydrate, and hydrochloric acid, or by hydrolysis of isopropylsemicarbazide. The third method, that of catalytic reduction, as in the case of the *s*-hydrazine, is the most practical one. The base is very unstable and is best isolated as its *hydrochloride*, m. p. 114°, and gives a *dibenzoyl* derivative, m. p. 161.5°, and a *phenylthiosemicarbazide*, m. p. 141.5°. When the free base is mixed with an equimolecular amount of dry acetone and an equal volume of absolute alcohol is added *acetoneisopropylhydrazone*, b. p. 132—134°, d_4^{25} 0.8225, n_D^{25} 1.4360, is obtained.

The *mononitroso*-derivative, b. p. 65—66°/6—8 mm., d_4^{25} 0.9440, n_D^{25} 1.4420, of *s*-diisopropylhydrazine has been isolated and its *sodium* salt prepared.

It is suggested that some of the above methods may serve for the preparation of a number of *s*-secondary hydrazines, azoparaffins, monoalkylhydrazines, and mixed hydrazo- and azo-paraffins.

W. G.

A New Method for the Introduction of an Ethyl Group. The Reaction between Organomagnesium Haloids and Ethyl Sulphate. HENRY GILMAN and RACHEL E. HOYLE (*J. Amer. Chem. Soc.*, 1922, **44**, 2621—2626).—Ethyl sulphate reacts with organomagnesium haloids in which the group MgX is attached to carbon, oxygen, or nitrogen, and in all the cases examined this group was replaced by the ethyl group. The yields of the reaction in a number of cases were decidedly good, and the process should be of value, not only in synthetic chemistry, but also as a trustworthy method for the determination of the mechanism of certain reactions.

W. G.

The Preparation and Properties of Trimethylstannane. CHARLES A. KRAUS and WILLARD N. GREER (*J. Amer. Chem. Soc.*, 1922, **44**, 2629—2633).—Metallic sodium acts on trimethylstannic chloride in liquid ammonia to give *sodium trimethylstannide*, SnMe_3Na , and this in turn is decomposed by ammonium

nitrate or chloride in the same solvent to give *trimethylstannane*, SnMe_3H , an oily liquid, b. p. $60^\circ/750.3$ mm. The stannane is reconverted by the action of sodium in liquid ammonia to sodium trimethylstannide and with hydrochloric acid in aqueous solution it gives trimethylstannic chloride and hydrogen. W. G.

The Mutual Influence of Substituents in Poly-substituted Benzenes. E. KLEUCKER (*Ber.*, 1922, 55, [B], 2941).—The conclusion to which the author has been led that the mutual influence of substituents in ortho- and para-disubstituted benzenes is explicable in the same manner as that between groups at the ends of open-chain, conjugated unsaturated compounds (A., 1922, i, 734) has been reached previously by Angeli (*Atti R. Accad. Lincei*, 1921, [v], 30, ii, 344), whose communication at the time of the author's work was not generally available. H. W.

Equilibrium in the System *m*-Dinitrobenzene-Urethane. NICOLAI ANTONOVICH PUSHIN and ALEXANDRA FIOLETOVA (T., 1922, 121, 2822—2823).

The Action of Thionyl Chloride on Substituted Benzene-sulphonyl Chlorides. J. POLLAK and ZOSIA RUDICH (*Monatsh.*, 1922, 43, 209—224).—By the action of thionyl chloride on *m*-xylene-2:4-disulphonyl chloride, Pollak and Schadler obtained a substance which appeared to be 2:4-dichloro-*m*-phthaloyl chloride (A., 1918, i, 497). To investigate this type of reaction further, the action of thionyl chloride on *o*- and *p*-toluenesulphonyl chlorides has now been studied. At 200° , *p*-toluenesulphonyl chloride is converted into *p*-chlorobenzylidene chloride, and at 240° almost quantitatively into *p*-chlorobenzoyl chloride; *o*-toluenesulphonyl chloride was converted into *o*-chlorobenzoyl chloride at 240 — 250° , but under no conditions was *o*-chlorobenzylidene chloride formed. The possibility that chlorobenzotrichlorides are first formed and then hydrolysed by adventitious moisture is shown to be excluded. Toluene itself, on the other hand, gives benzotrichloride and no benzylidene chloride when heated in a sealed tube with thionyl chloride. By the action of thionyl chloride on *o*-xylene-4:6-disulphonyl chloride at 250° , a compound, $\text{C}_8\text{H}_4\text{Cl}_6$, m. p. 78° , was obtained, which may be a dichlorodi(dichloromethyl)benzene. At 320° , a crystalline compound, m. p. 193 — 196° , was formed, which may be a more highly chlorinated derivative of *o*-xylene.

The dichloro*isophthalic* acid obtained by Pollak and Schadler by the action of thionyl chloride on *m*-xylene-2:4-disulphonyl chloride has been further investigated and found to be 2:6-dichloro*isophthalic* acid; its *methyl* ester has m. p. 97 — 98° . The reaction appears, therefore, not to consist simply in replacement of chlorosulphonyl groups by chlorine, but a further rearrangement of the substituting groups is involved. At 260° , *m*-xylene-2:4-disulphonyl chloride is converted by thionyl chloride into a compound, $\text{C}_8\text{H}_2\text{Cl}_6$, m. p. 113 — 114° , and at 320° into a still more highly chlorinated product.

p-Anisolesulphonyl chloride reacts with thionyl chloride at 250°

to give a compound, $C_7H_2OCl_6$, m. p. 214° , probably *chloromethoxy-pentachlorobenzene*.
E. H. R.

Esters of the Hydroxyalkylarylamines. I. Acid Sulphuric Esters of the Simple Monohydroxyethylarylamines. KENNETH HERBERT SAUNDERS (T., 1922, 121, 2667—2675).

p-Cymene. IV. The Chlorination of 2-Amino-p-cymene. ALVIN S. WHEELER and I. V. GILES (*J. Amer. Chem. Soc.*, 1922, 44, 2605—2612; cf. A., 1919, i, 490; 1920, i, 751; 1922, i, 332).—When 2-acetamido-p-cymene is chlorinated in solution in carbon tetrachloride 5-chloro-2-acetylamido-p-cymene, m. p. $109-111^\circ$, is obtained and on hydrolysis yields 5-chloro-2-amino-p-cymene, b. p. $240-250^\circ$, from which the *hydrochloride*, the *sulphate*, and the *benzoyl* derivative, m. p. 137.5° , are prepared. When the hydrochloride is diazotised and the diazo-compound boiled with water, 5-chlorocarvacrol, b. p. $158/52$ mm., is obtained, and when the diazo-compound is treated with cuprous cyanide in an excess of potassium cyanide and the resulting nitrile hydrolysed, it yields 4-chloro-2-methyl-5-isopropylbenzoic acid, m. p. 125° . When the hydrochloride is diazotised with half the equivalent amount of sodium nitrite, 2 : 2'-diazamino-5 : 5'-dichloro-p-cymene, m. p. $135-137^\circ$, is obtained.

The diazotised base couples readily with hydroxy-compounds. The resulting azo-dyes, in which a sulphonic group is present, act as direct dyes when employed in weak acetic acid solution. The others are developed dyes. The colours produced on wool and silk are fast to light and washing. The brilliancy of some is striking, and is undoubtedly due to the presence of the chlorine atom. The following are described. 4(5'-Chlorocarvacrylazo)phenol, m. p. 196° ; 4(5'-chlorocarvacrylazo)resorcinol, m. p. 188° (decomp.); 4(5'-chlorocarvacrylazo)salicylic acid, m. p. 165° , and its sodium salt; 4(5'-chlorocarvacrylazo)- α -naphthol, m. p. 128° (decomp.); 1(5'-chlorocarvacrylazo)- β -naphthol, m. p. 163° ; 4(5'-chlorocarvacrylazo)-1-naphthol-2-sulphonic acid and its sodium salt; 2(5'-chlorocarvacrylazo)-1-naphthol-4-sulphonic acid, m. p. 246° , and its sodium salt; 1(5'-chlorocarvacrylazo)-2-naphthol-7-sulphonic acid, m. p. 228° (decomp.).

The constitution of the chloroaminocymene was proved as follows. The chloroacetamidocymene was oxidised by means of potassium permanganate in the presence of magnesium sulphate and yielded 5-chloro-2-acetamido-4-isopropylbenzoic acid, m. p. $207-209^\circ$, and this on hydrolysis gave 5-chloro-2-amino-4-isopropylbenzoic acid, m. p. 159° , giving a *hydrochloride*, m. p. 178° . Finally chloroaminocymene was diazotised and the product, by means of the Sandmeyer reaction, was converted into a dichloro-p-cymene, which, on oxidation in a sealed tube with nitric acid at 180° for ten hours, yielded 2 : 5-dichloroterephthalic acid, m. p. 305° .

W. G.

α -Naphthylnitroamine and its Transformations. E. BAMBERGER (*Ber.*, 1922, 55, [B], 3383—3392).— α -Naphthylnitroamine differs from other members of this group, which do not contain a

chromophoric group and are colourless, in having a yellow colour. It is converted in a normal manner by mineral acids into 2-nitro- α -naphthylamine, but in alkaline solution it is transformed in an unusual manner into β -naphthaquinone- α -diazide, the reaction probably following the course: $C_{10}H_7 \cdot NH \cdot NO \rightarrow C_{10}H_7 \cdot N \cdot NO \cdot OH \rightarrow C_6H_4 \begin{smallmatrix} C(N_2 \cdot OH) \cdot C \cdot OH \\ | \\ CH = CH \end{smallmatrix} \rightarrow C_6H_4 \begin{smallmatrix} C(N_2) \cdot CO \\ | \\ CH = CH \end{smallmatrix}$. The peculiar

behaviour of α -naphthylnitroamine probably depends on the feebly acidic nature of its isonitroso-form, and its consequent ready formation by the hydrolysis of its salts and subsequent isomerisation to the quinonediazide.

[With LEO SCHLEIN.]—The conversion of α -naphthylamine by successive diazotisation and oxidation with potassium ferricyanide into α -naphthylnitroamine (cf. *Diss. Zürich*, 1894) is described in detail; the substance forms golden-yellow crystals, m. p. 123—124° when rapidly heated. The *ammonium*, *lead*, *silver*, *calcium*, and *barium* salts were prepared. The nitroamine is converted by sodium methoxide and methyl iodide into α -naphthyl-N-methylnitroamine, $C_{10}H_7 \cdot NMe \cdot NO_2$, almost colourless, vitreous crystals, m. p. 54·5—55°.

α -Naphthylnitroamine is transformed by aqueous potassium hydroxide at the atmospheric temperature into β -naphthaquinone- α -diazide [β -hydroxy- α -diazonaphthalene], golden-yellow needles, m. p. 94—94·5°; preliminary experiments appear to show that a similar change does not take place with β -naphthylnitroamine.

Reduction of α -naphthylnitroamine by sodium amalgam and water leads to the formation of naphthalene, α -naphthylamine, β -naphthol, and ammonia. The production of β - (instead of α)-naphthol is explained by the established relationship of α -naphthylnitroamine to β -naphthaquinone- α -diazide.

α -Naphthylnitroamine is converted by nitrous acid in the presence of glacial acetic acid and subsequent treatment with an alkaline solution of β -naphthol into α -naphthylazo- β -naphthol, m. p. 228—229°. H. W.

The Mechanism of the Bromination of Phenol in Aqueous Solution. HARRY BAINES (T., 1922, 121, 2810—2813).

Reduction of Polynitrophenols by Hydrogen Sulphide in Presence of Ammonia. L. CHAS. RAIFORD (*Science*, 1921, 53, 218; cf. A., 1920, i, 156).—Reduction of 2:4-dinitrophenol by hydrogen sulphide and ammonia results, in contradiction of previous statements, in the production of isomeric substances. A. A. E.

Methyl Sulphites of Secondary Aromatic Aliphatic Amines. M. BOCKMÜHL and K. WINDISCH (U.S. Pat. 1426348).—*Sodium N-ethoxyphenylmethylaminomethyl sulphite*, m. p. 265°, is prepared by heating a mixture of formaldehyde solution, sodium hydrogen sulphite solution, *N*-methylphenetidine, and ethyl alcohol, collecting the product, and redissolving it in dilute ethyl alcohol. The corresponding *ethyl* derivative is similarly obtained from ethylphenetidine. *Sodium 1-phenyl-2:3-dimethylpyrazol-5-one-4-ethylaminomethyl sulphite*, m. p. (in water of crystallisation) 80—90°, is obtained by

adding a hot solution produced by the interaction of formaldehyde and sodium hydrogen sulphite to ethylaminoantipyrine, concentrating the solution in a vacuum, and purifying with aqueous acetone.

CHEMICAL ABSTRACTS.

Researches on Residual Affinity and Co-ordination. XII. Cobaltammine and Ferric Lakes of Dinitrosoresorcinol. GILBERT T. MORGAN and JOHN EWART MOSS (T., 1922, 121, 2857—2866).

Preparation of New Guaiacol Compounds. PHARM-AZEUTISCHE INDUSTRIE G. M. B. H. and RUDOLF HAUSCHKA (Austrian Pat. 86131; from *Chem. Zentr.*, 1922, iv, 710).—Silicon tetrachloride or other reactive silicon compound is allowed to react with guaiacol. From silicon tetrachloride and guaiacol, *dichlorodiguaiacylsilicomethane*, $\text{SiCl}_2(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{OMe})_2$, and *tetraguaiacylsilicomethane*, $\text{Si}(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{OMe})_4$, are obtained, and can be partly separated by distillation in a vacuum. The former is a viscid substance, but by solution in ether and evaporation can be obtained in colourless or greyish-green crystals; it is slowly decomposed by water with separation of silicic acid. The latter is a viscid liquid which by long heating in a vacuum gives off guaiacol vapour and forms *polyguaiacylsilicon*, $\text{Si}_{10}(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{OMe})_{22}$, a thick, honey-like syrup, b. p. $220^\circ/20$ mm. G. W. R.

Action of Aromatic Alcohols on Phenols in the Presence of Aluminium Chloride. RALPH C. HUSTON (*Science*, 1920, 52, 206—207).—At relatively low temperatures, benzyl alcohol reacts with phenol in presence of aluminium chloride, giving a 40—50% yield of *p*-benzylphenol. The corresponding methyl and ethyl ethers were obtained in slightly better yields. A. A. E.

Synthesis of certain Primary Alcohols from Unimolecular Formaldehyde and Grignard's Reagents. KARL ZIEGLER and PAUL TIEMANN (*Ber.*, 1922, 55, [B], 3406—3416).—An extension of previous work (cf. A., 1921, i, 394).—An ethereal solution of 4-bromo-1-methylnaphthalene is treated successively with activated magnesium powder and gaseous formaldehyde whereby it is transformed into 1-methyl-4-hydroxymethylnaphthalene, small, colourless needles, m. p. $74\text{--}75^\circ$ (*phenylurethane*, needles, m. p. 103°); the yield is 40—50% of that theoretically possible, and is greatly dependent on the quality of the magnesium powder. The carbinol is oxidised by the necessary amount of dichromate and sulphuric acid to 1-methylnaphthalene-4-aldehyde, colourless needles, m. p. $33\cdot5\text{--}34^\circ$ (the corresponding *bisulphite compound*, *semicarbazone*, colourless leaflets, m. p. 228° , and *azine*, pale yellow crystals, m. p. $166\text{--}167^\circ$, are described). 1-Bromo-2-methylnaphthalene is transformed in a similar manner into 2-methyl-1-hydroxymethylnaphthalene, m. p. $136\text{--}137^\circ$, in 57% yield (*phenylurethane*, m. p. $127\text{--}128^\circ$). The oxidation of the carbinol to the corresponding aldehyde could not be effected, a part of the original substance being completely burnt, whereas the residue remained unchanged. A solution of

the carbinol in glacial acetic acid is converted by hydrogen chloride and hydrogen bromide, respectively, into 2-methyl-1-chloromethyl-naphthalene, plates, m. p. 61—63°, and 2-methyl-1-bromomethyl-naphthalene, long needles, m. p. 87·5—89°. Reduction by sodium of the latter substance dissolved in moist ether gives 1:2-dimethyl-tetrahydronaphthalene, b. p. 123·5—124·5°/11 mm., $d_4^{23\cdot8}$ 0·9847, $d_4^{23\cdot8}$ 0·9844, d_4^{20} 0·988, $n_D^{23\cdot8}$ 1·55298, $n_D^{23\cdot8}$ 1·55762, $n_D^{23\cdot8}$ 1·57082, $n_D^{23\cdot8}$ 1·58195, n_D^{20} 1·5593, which appears to contain a small proportion of the dihydro-compound.

$\beta\beta$ -Diphenylvinyl bromide, magnesium, and formaldehyde give γ -phenylcinnamyl ($\gamma\gamma$ -diphenylallyl) alcohol, $\text{CPh}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{OH}$, which is isolated through the corresponding hydrogen phthalate (the sodium salt of the latter is described). The alcohol has m. p. 61·5—63°, b. p. 205°/15 mm., 192°/10 mm. The corresponding acetate has b. p. 205°/15 mm., m. p. 36—37·5°, $d_4^{10\cdot9}$ 1·1003, $d_4^{10\cdot7}$ 1·1005, d_4^{20} 1·091, $n_D^{10\cdot7}$ 1·57980, n_D^{10} 1·58592, $n_D^{10\cdot7}$ 1·60189, $n_D^{10\cdot7}$ 1·61734, n_D^{20} 1·5817, whereas the benzoate has m. p. 89—90°. The alcohol is reduced by sodium and ethyl alcohol to $\alpha\alpha$ -diphenylpropane, b. p. 140—141°/13 mm., 280°/760 mm., d_4^{41} 0·9951, d_4^{20} 0·990, n_D^{41} 1·56810, n_D^{20} 1·5605. It is converted by hydrogen bromide in glacial acetic acid solution into $\gamma\gamma$ -diphenylallyl bromide, $\text{CPh}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{Br}$, m. p. 37—39°, which is transformed into γ -phenylcinnamaldehyde (semicarbazone, m. p. 214—215°). γ -Phenyl- β -methylcinnamyl alcohol, $\text{CPh}_2\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{OH}$, crystallises in coarse prisms, m. p. 68—69°, b. p. 184°/11 mm. (benzoate, colourless crystals, m. p. 116°). It is converted by concentrated sulphuric acid in the presence of glacial acetic acid into 1-phenyl-2-methylindene, m. p. 56·5°, its ability to suffer ring closure in this manner being in striking contrast to that of the lower homologue.

p-Dibromobenzene is converted by magnesium and formaldehyde into *p*-bromobenzyl alcohol which is readily oxidised to *p*-bromobenzaldehyde, m. p. 57°, b. p. 105—110°/12 mm. The latter substance is transformed by magnesium methyl bromide into *p*-bromophenyl-methylcarbinol, $\text{C}_6\text{H}_4\text{Br}\cdot\text{CHMe}\cdot\text{OH}$, a colourless, viscous liquid, b. p. 133—134°/15 mm., 127—128°/11 mm., $d_4^{15\cdot2}$ 1·4690, d_4^{20} 1·463, $n_D^{15\cdot2}$ 1·56713, $n_D^{15\cdot2}$ 1·57190, $n_D^{15\cdot2}$ 1·58619, $n_D^{15\cdot2}$ 1·59650, n_D^{20} 1·5697. (The substance can also be prepared from magnesium *p*-bromophenyl bromide and acetaldehyde.) It is transformed by sodium hydrogen sulphate at 150° into *p*-bromostyrene, $\text{C}_6\text{H}_4\text{Br}\cdot\text{CH}\cdot\text{CH}_2$, a colourless, mobile liquid, b. p. 88·5—89·5°/16 mm., 83·5—84·5°/11 mm., m. p. 4·5°, $d_4^{12\cdot9}$ 1·4098, d_4^{20} 1·401, $n_D^{12\cdot9}$ 1·59137, $n_D^{12\cdot9}$ 1·59931, $n_D^{12\cdot9}$ 1·61960, $n_D^{12\cdot9}$ 1·63801, n_D^{20} 1·5961. *p*-Bromobenzaldehyde and magnesium ethyl bromide give *p*-bromophenylethylcarbinol, b. p. 138—139°/11 mm., $d_4^{16\cdot3}$ 1·4085, $d_4^{16\cdot4}$ 1·4084, d_4^{20} 1·404, $n_D^{16\cdot4}$ 1·55779, $n_D^{16\cdot4}$ 1·56227, $n_D^{16\cdot4}$ 1·57505, $n_D^{16\cdot4}$ 1·58577, n_D^{20} 1·5607, which is converted by sodium hydrogen sulphate into *p*-bromopropenylbenzene, $\text{C}_6\text{H}_4\text{Br}\cdot\text{CH}\cdot\text{CHMe}$, m. p. 35°, b. p. 108—110°/11 mm., 238—239°/atmospheric pressure, d_4^{21} 1·3309, d_4^{20} 1·356, n_D^{21} 1·57746, n_D^{20} 1·58391, n_D^{21} 1·60372, n_D^{21} 1·62159, n_D^{20} 1·5934. Magnesium *p*-bromophenyl bromide and acetone give the expected carbinol, which was

not isolated in the homogeneous condition; it is transformed into *p*-bromoisopropenylbenzene, $C_6H_4Br \cdot CMe \cdot CH_2$, b. p. $110^\circ/11$ mm., $228^\circ/\text{atmospheric pressure}$, m. p. 11° , d_4^{25} 1.3592, d_4^{20} 1.350, n_a^{12} 1.57721, n_D^{12} 1.58346, n_B^{12} 1.60497, n_γ^{12} 1.62089, n_D^{20} 1.5835.

The brominated styrenes could only be caused to react incompletely with magnesium. H. W.

Some Condensation Reactions with Di-*p*-dimethylaminobenzhydrol (Michler's Hydrol). MARSTON TAYLOR BOGERT and A. RUDERMAN (*J. Amer. Chem. Soc.*, 1922, **44**, 2612—2621).—Di-*p*-dimethylaminobenzhydrol (Michler's hydrol) condenses with the imides of succinic and phthalic acids to give the corresponding leucauramines, which on hydrolysis by alkali give the amic acids. The condensation may be carried out in either alcoholic solution or concentrated sulphuric acid. Under these conditions, succinimide gives *succinyl-leucauramine*, m. p. 151° (corr.). With nitrous acid, this yields *succinyl-dinitroleucauramine*, m. p. $94-96^\circ$ (decomp.), and on hydrolysis gives *di-p-dimethylaminobenzhydrysuccinamic acid*, m. p. 170° . Phthalimide and Michler's hydrol give in alcoholic solution *phthalyl-leucauramine* in its stable form, m. p. 186.7° (corr.), whilst, if the condensation takes place in concentrated sulphuric acid, a labile form, m. p. 90° , is obtained and on heating is converted into the stable form. When oxidised with lead peroxide this compound gives *phthalyl-leucauraminecarbinol*, m. p. 176° (corr.). *Dinitrophthalyl-leucauramine*, m. p. 104° (decomp.), and *di-p-dimethylaminobenzhydrylphthalamic acid*, m. p. 163.8° (decomp., corr.), were prepared. The amic acid when oxidised by lead peroxide gave the corresponding *carbinol*, m. p. 187° (corr.). Michler's hydrol did not condense with phthalimidine, but with phthalide gave *di-bis-dimethylaminobenzhydrylphthalide*, m. p. 201° (corr.). A condensation product was not obtained from 4-nitrophthalimide, but 3-aminophthalimide yielded *3-leucauraminylphthalyl-leucauramine*, m. p. $219-220^\circ$ (corr.).

Anthraquinone, its α - or β -amino-derivatives, alizarin, thiocarbamide, or benzoylenecarbamide failed to react with the hydrol under the experimental conditions, but dehydrothio-*p*-toluidine condensed readily with the hydrol in alcoholic solution to give *2-di-p-dimethylaminobenzhydrylbenzthiazole*, m. p. $190-191^\circ$ (corr.).

In alcoholic solution, "saccharin" gives a deep blue coloration with the hydrol even in dilute solution, and this reaction appears to be a delicate test for either compound. W. G.

Solubility. VII. The Solubility of Salts of Aromatic Acids. FRITZ EPHRAIM (*Ber.*, 1922, **55**, [B], 3472—3486; cf. A., 1922, ii, 574, and earlier abstracts).—The communication is the first of a series devoted to a study of the solubilities of metallic salts of organic acids and is confined to a qualitative survey of the field. Aqueous solutions of the sodium salts of seventy-three carboxylic or sulphonic acids, generally normal in concentration, are mixed at the atmospheric temperature with equivalent quantities of normal solutions of barium, strontium, calcium, and mercuric

chlorides, magnesium, zinc, ferrous, manganese, cobalt, nickel, copper, and cadmium sulphates, lead and silver nitrates, and the gradual or immediate formation of precipitates or their failure to appear is recorded. The acids used are benzoic, phenylacetic, cinnamic, β -naphthoic, phthalic, naphthalic, *o*- and *p*-chlorobenzoic, 4-chlorophthalic, salicylic, 2- and 4-hydroxy-*m*-toluic, 3-hydroxy-*p*-toluic, 3- and 1-hydroxy- β -naphthoic, 3 : 5-dihydroxybenzoic, *p*-hydroxybenzoic, *p*-methoxybenzoic, *o*-benzoylbenzoic, *o*-*p*-toluoylbenzoic, *o*-*m'*-nitro-*p'*-toluoylbenzoic, *o*- α -naphthoylbenzoic, *o*- and *p*-nitrobenzoic, 4-nitro-2-hydroxybenzoic, 5- and 4-chloro-2-nitrobenzoic, 2-nitro-6-hydroxybenzoic, 3-nitro-4-methoxybenzoic, 4-chloro-3 : 5-dinitrobenzoic, *o*-, *m*-, and *p*-aminobenzoic, 4-amino-2-hydroxybenzoic, and 3-amino-4-methoxybenzoic. The following sulphonic acids are employed: benzene-, 2 : 4- and 3 : 4-dimethylbenzene-, α - and β -naphthalene-, 2 : 5- and 3 : 4-dichlorobenzene-, 1-chloronaphthalene-, 5-dibromonaphthalene-2-, *p*-hydroxybenzene-, 5- and 4-hydroxynaphthalene-1-, 6-hydroxynaphthalene-2-, 5- and 3-nitro-2-methylbenzene-, 4-chloro-3-nitrobenzene-, 3 : 4-dichloro-5-nitrobenzene-, 5-nitronaphthalene-1-, 6-nitronaphthalene-2-, 3 : 5-dinitro-4-methylbenzene-, 3 : 5-dinitro-2 : 4-dimethylbenzene-, and 2-chloro-3 : 5-dinitrobenzene-, sulphanilic, 4- and 3-sulphobenzoic, and 3-sulpho-4-hydroxybenzoic acids. Benzene-1 : 3-di-, naphthalene-2 : 5-, -2 : 7-, and -1 : 5-di-, 1-nitronaphthalene-3 : 6-di-, dibromonaphthalene-2 : 7-di-, 2 : 6-dinitrobenzene-1 : 4-di-, 1-carboxybenzene-2 : 4-di-, naphthalene-1 : 3 : 6-tri-, 1-chloronaphthalene-3 : 6 : 8-tri-, 2-chloronaphthalene-3 : 6 : 8-tri-, and 1-nitronaphthalene-3 : 5 : 7-tri-sulphonic acids are also used.

The barium, lead, and silver salts of the carboxylic acids are without exception sparingly soluble, as are those of copper, except in two cases in which the acids contain vicinal carboxyl groups. The precipitates are usually caseous or voluminous, whereas those of other salts are crystalline. This property appears to be constitutional and not simply attributable to the rapidity of the separation. In many cases, the separation of the precipitates occurs relatively very slowly, although the substances once formed are frequently very sparingly soluble. The phenomenon can scarcely be attributed to simple supersaturation, and it appears more likely that an equilibrium between true and complex or pseudo-salt exists in the solutions. In certain cases in which the initial salt form is sparingly soluble, this change is very obvious. Thus, for example, cadmium phenylacetate is immediately precipitated, but speedily re-dissolves and subsequently crystallises in a different form. Similar observations are recorded with the cadmium and copper salts of 4-hydroxy-*m*-toluic acid, the two varieties of the copper salt being further distinguished by their respective brown and green colours. Further confirmation of the existence of two distinct types of salts is found in the observation that the strontium salts in respect of solubility do not by any means always fall into line between the corresponding barium and calcium salts. Frequently the equilibrium between the two forms is only slowly established; this is well illustrated by the zinc,

manganese, and cobalt salts of naphthalic acid. The observation that separation is expedited by warming the solutions is regarded as strong evidence that a chemical reaction is here involved and that the phenomenon is not simply one of crystallisation.

The great solubility of the magnesium salts, which in many cases exceeds that of the sodium salts, is remarkable. The mercuric salts are generally freely soluble and are only precipitated when the parent acid forms a complete series of sparingly soluble salts or possibilities exist for the formation of internal complexes. The salts of zinc, manganese, ferrous iron, cobalt, nickel, and cadmium have medium solubilities; of these, the cadmium and to a less extent the zinc compounds tend to have the lowest solubilities and to approximate in their behaviour to the copper salts.

The influence of the organic residue on the solubility of the salts is discussed at considerable length. The observations, however, are of a preliminary nature.

The salts of the sulphonic acids are generally more freely soluble than those of the corresponding carboxylic acids. In this respect, the behaviour of naphthalene- β -sulphonic acid is altogether exceptional, since its salts, in particular the magnesium compound, are distinguished by their sparing solubility (cf. A., 1921, i, 508). The introduction of a nitro-group into the molecule appears to increase the solubility of the salts, but the effect is not further enhanced by the introduction of a second nitro-group. As in the case of the carboxylic compounds, the barium and lead salts are generally the most sparingly soluble, whereas the silver salts of the sulphonic acid are relatively soluble. The mercuric salts are, in general, freely soluble, whilst a great increase in solubility is noted in the case of the copper salts. The sodium salts in many cases do not dissolve freely.

The solubility of the salts derived from acids containing a sulphonic and a carboxyl group resembles in general that of the simple sulphonic acid. The introduction of a second sulphonic group into the molecule does not further increase the solubility of the salts.

H. W.

Preparation of Phenylglycine-*o*-carboxylic Acid. HERBERT L. HALLER (*J. Ind. Eng. Chem.*, 1922, **14**, 1040—1044).—The reaction between anthranilic acid and chloroacetic acid for the preparation of phenylglycine-*o*-carboxylic acid was studied. The best yields were obtained under the following conditions: Concentration, 25 g. of anthranilic acid in 200 c.c. of water. Ratio, 2 mols. of anthranilic acid to 1 mol. of chloroacetic acid. Condensing agent, 2.33 mols. of sodium carbonate to 1 mol. of chloroacetic acid. Temperature, 90°. Time of reaction, 1 hour. The use of an alkali carbonate as a condensing agent gives a better yield than an equivalent amount of an alkali hydroxide.

H. C. R.

Preparation of Allyl *p*-Aminobenzoate. SOCIETY FOR CHEMICAL INDUSTRY IN BASLE (Swiss Pat. 92300; from *Chem. Zentr.*, 1922, iv, 711; cf. Adams and Volweiler, A., 1921, i, 416).—

Compounds containing the *p*-nitrobenzoyl group are allylated and the allyl *p*-nitrobenzoate is reduced. For example, *p*-nitrobenzoyl chloride is heated with allyl alcohol at about 80°, or *p*-nitrobenzoic acid is esterified in the presence of hydrogen chloride. The allyl *p*-nitrobenzoate thus obtained is a light yellow oil crystallising on cooling, having m. p. 30° and b. p. 146—152°/3 mm. Allyl *p*-aminobenzoate obtained by reduction of the latter compound forms almost colourless needles, m. p. 54°. It is a local anæsthetic.

G. W. R.

Preparation of Complex Silver Compounds. F. HOFFMANN-LA ROCHE & Co. (D.R.-P. 1356912, Swiss Pat. 90809, 91108, and 91109; from *Chem. Zentr.*, 1922, iv, 711; cf. Myers, A., 1921, i, 843).—Organic or inorganic silver salts are allowed to react with thio-acyl derivatives of aromatic amines. *α*-Thiolacetylamidophenol, an amorphous, yellow powder, m. p. 105°, from chloroacetylamidophenol and sodium persulphide, is allowed to react with silver nitrate solution. The silver *α*-thiolacetylamidophenol obtained contains 37.2% of silver and gives no precipitate with sodium chloride, hydrogen sulphide, or ammonium sulphide solutions. From sodium *α*-thiolacetylamidosalicylate, silver sodium *α*-thiolacetylamidosalicylate is obtained. *α*-Thiolacetylamidosalicylic acid, obtained from chloroacetylamidosalicylic acid and sodium persulphide, is a light yellow powder, m. p. 223°. It gives a sodium salt. Similar products are obtained by the action of silver nitrate on the sodium salts of thiolisovalerylamidosalicylic acid and thiolpropionylamidosalicylic acid, respectively. The latter compound has m. p. 226°. These acids are prepared by the action of sodium persulphide on bromoisovalerylamidosalicylic acid and bromopropionylamidosalicylic acid, respectively.

G. W. R.

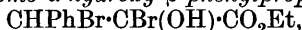
The Resolution of Phenoxypropionic Acid and *o*-Nitrophenoxypropionic Acid into their Active Components. E. FOURNEAU and G. SANDULESCO (*Bull. Soc. chim.*, 1922, [iv], 31, 988—993).—In resolving acids into their optical isomerides, the choice of zohimbine as a base leads to the formation of salts which crystallise readily and are separable without difficulty. Details are given of the separation of the phenoxypropionic acids as salts of yohimbine and of the *o*-nitrophenoxypropionic acids as salts of yohimbine and of cinchonine. In both cases the active form of the acids melt at a lower temperature than the racemic mixtures; *d*- and *l*-phenoxypropionic acids have m. p. 87°, the mixture 115°; the corresponding temperatures for *o*-nitrophenoxypropionic acid being 111—112° and 157°.

H. J. E.

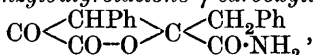
Ethyl Phenylpyruvate. II. H. GAULT and R. WEICK (*Bull. Soc. chim.*, 1922, [iv], 31, 993—1026; cf. A., 1922, i, 1024).—Various reactions of the three isomeric forms of ethyl phenylpyruvate were studied and grouped according to whether they were (a) different in the case of the enolic and ketonic forms, or (b) common to all three forms. Among the former are the color-

ation obtained in presence of ferric chloride, the formation of additive bromine derivatives, the addition of phenylcarbimide yielding the phenylurethane, and the action of hydrochloric acid, which reactions the authors regard as fundamental for distinguishing between the α - and β - and the γ -forms. The reactions common to all three isomerides include formation of esters, lactonisation, and condensation. An attempt to investigate the isomerism of ring-substituted derivatives of ethyl phenylpyruvate was abandoned owing to the difficulty of preparing these substances. The refractive indices of the isomerides were found to be: β , n_D^{20} 1.49735, γ , n_D^{20} 1.49821; the value for the α -ester was not determined by reason of the rapid oxidation of the substance in air. Theoretical consideration of the results indicates that the β -form is enolic, and on chemical grounds the α -ester is considered to be similar, the two being stereoisomerides; it is not possible, as yet, to decide which is the *cis* and which the *trans* form. The γ -ester has, on theoretical grounds, the ketonic form.

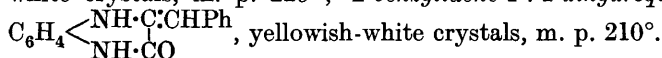
The following substances do not appear to have been previously described: *Ethyl β -bromophenylpyruvate*, $\text{CHPhBr}\cdot\text{CO}\cdot\text{CO}_2\text{Et}$, a mobile, yellow liquid of characteristic odour, b. p. 182—184.5°/20 mm.; *Ethyl $\alpha\beta$ -dibromo- α -hydroxy- β -phenylpropionate*,



a yellow, crystalline solid, m. p. not determined, as the substance is too unstable: it is stated that this is the first instance of the isolation of a brominated enolic compound; *Ethyl α -acetoxyl- β -phenylpropionate*, a colourless oil of pleasant odour, b. p. 161—163°/16 mm.; *Ethyl α -benzoyloxy- β -phenylpropionate*, yellow oil, b. p. 225—226°/15 mm.; *Ethyl α -acetoxycinnamate*, white crystals, m. p. 33.5°; *Ethyl α -benzoyloxy- γ -cinnamate*, white needles, m. p. 87°; *α -Keto- β -phenyl- γ -benzylbutyrolactone- γ -carboxylamide*,



white crystals, m. p. 229°; *2-benzylidene-1:4-dihydroquinoxalone*,



H. J. E.

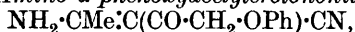
Preparation of an *ar*- β -Tetrahydronaphtholcarboxylic Acid and its Ester and Acyl Derivative. TETRALIN G. M. B. H. (D.R.-P. 357663; from *Chem. Zentr.*, 1922, iv, 761).—An anhydrous alkali salt of *ar*- β -tetrahydronaphthol is treated with carbon dioxide at temperatures above 100°. After acidification, the resulting product is changed into esters or acyl derivatives by the usual methods. The potassium salt of *ar*- β -tetrahydronaphthol, freed from water in a stream of hydrogen at 150—160°, is treated with carbon dioxide under pressure for several hours at 160—170°. After one molecule of carbon dioxide has been absorbed, the product is dissolved in water and acidified with hydrochloric acid. The *β -tetrahydronaphthol- α -carboxylic acid* thus obtained forms colourless needles, m. p. 177—178°. It gives a deep blue coloration with ferric chloride. The *methylester* has b. p. 184—185°/20 mm.; it

has an odour like that of ethyl acetoacetate, and forms a crystalline mass on keeping. By the action of acetic anhydride on the carboxylic acid at 100° in the presence of sulphuric acid, *β*-acetoxytetrahydronaphthalene-*o*-carboxylic acid, m. p. 142—143°, is obtained.

G. W. R.

Certain Acidic Derivatives of "Dinitriles" and *β*-Aminocrotonic Esters. ERICH BENARY and MARTIN HOSENFELD (*Ber.*, 1922, **55**, [B], 3417—3429; cf. Benary and Schmidt, A., 1921, i, 776).—In continuation of previous work, the introduction of the phenoxyacetyl group into imidoacetonitrile, imidobenzoylacetonitrile, and imidotoluoylacetonitrile has been investigated. The use of the ester in the presence of sodium ethoxide leads to the production of a *N*-derivative, whereas *C*-compounds are produced from the acid chloride in the presence of pyridine. The condensation of the ester with these substances in the presence of potassium ethoxide has been described by Meyer (A., 1914, i, 996), but evidence is now adduced to show that his conception of the products as *C*-derivatives is incorrect.

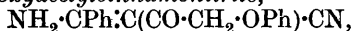
Whereas in the previous instances investigated the production of uniform *C*- or *N*-derivatives has been observed according to the mode of procedure, it is found that cinnamoyl chloride and diacetonitrile give a mixture of about equal quantities of the two isomerides, whereas cinnamic ester and sodium ethoxide give only the *N*-derivative. *β*-Amino-*α*-phenoxyacetylcrotononitrile,



slender, colourless needles, m. p. 167°, is prepared by the action of phenoxyacetyl chloride on imidoacetylacetonitrile in anhydrous ethereal solution in the presence of pyridine. It is converted by *N*-sodium hydroxide solution into *β*-hydroxy-*α*-phenoxyacetylcrotononitrile, $\text{OH} \cdot \text{CMe} \cdot \text{C}(\text{CO} \cdot \text{CH}_2 \cdot \text{OPh}) \cdot \text{CN}$, almost colourless needles, m. p. 138°, the enolic nature of which is established by the isolation of the green copper salt. *β*-Amino-*α*-phenoxyacetylcrotononitrile is converted by phenylhydrazine into 4-cyano-1-phenyl-5-phenoxyethyl-3-methylpyrazole, $\text{CMe} \cdot \begin{smallmatrix} \text{C}(\text{CN}) \\ \diagup \quad \diagdown \\ \text{N} \cdot \text{NPh} \end{smallmatrix} \cdot \text{C} \cdot \text{CH}_2 \cdot \text{OPh}$, colourless needles, m. p.

73—74°, which is also prepared by the action of phenylhydrazine on *β*-hydroxy-*α*-phenoxyacetylcrotononitrile in acetic acid solution. *N*-*β*-Phenoxyacetylamidocrotononitrile, $\text{OPh} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CMe} \cdot \text{CH} \cdot \text{CN}$, m. p. (*α*-form) 96°, (*β*-form) 123° (cf. Meyer, *loc. cit.*), is decomposed by *N*-sodium hydroxide solution with the formation of phenoxyacetic acid, and by phenylhydrazine in acetic acid solution with production of phenoxyacetic acid phenylhydrazide.

β-Amino-*α*-phenoxyacetylcinnamionitrile,



glassy, hexagonal plates, m. p. 152°, is prepared from imidobenzoylacetonitrile, pyridine, and phenoxyacetyl chloride in the presence of ether, and is transformed into *β*-hydroxy-*α*-phenoxyacetylcinnamionitrile, $\text{OH} \cdot \text{CPh} \cdot \text{C}(\text{CO} \cdot \text{CH}_2 \cdot \text{OPh}) \cdot \text{CN}$, lustrous leaflets, m. p. 118°. With phenylhydrazine in acetic acid solution (50%), it gives 4-cyano-1 : 3-diphenyl-5-phenoxyethylpyrazole, slender, colourless

needles, m. p. 158° . β -Phenoxyacetylamidocinnamionitrile, $\text{OPh}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CPh}\cdot\text{CH}\cdot\text{CN}$, m. p. (α -form) 95° (Meyer, *loc. cit.*, gives 87°), m. p. (β -form) 114° , is converted by *N*-sodium hydroxide solution into phenoxyacetic acid, and by phenylhydrazine into phenoxyacetic hydrazone. The product obtained by coupling the β -variety with diazobenzene chloride in alcoholic solution has m. p. 140° (Meyer, *loc. cit.*, gives 110°), and appears to have the composition $\text{C}_{23}\text{H}_{18}\text{O}_2\text{N}_4$; its nitrogen content is greater than that found by Meyer.

β -Amino- α -phenoxyacetyl- β -*p*-tolylacrylonitrile,
 $\text{C}_6\text{H}_4\text{Me}\cdot\text{C}(\text{NH}_2)\cdot\text{C}(\text{CO}\cdot\text{CH}_2\cdot\text{OPh})\cdot\text{CN}$,

large, colourless needles, m. p. 178° , β -hydroxy- α -phenoxyacetyl- β -*p*-tolylacrylonitrile, $\text{C}_6\text{H}_4\text{Me}\cdot\text{C}(\text{OH})\cdot\text{C}(\text{CO}\cdot\text{CH}_2\cdot\text{OPh})\cdot\text{CN}$, colourless crystals, m. p. 141° , and 4-cyano-1-phenyl-3-*p*-tolyl-5-phenoxymethylpyrazole, long needles, m. p. 167° , are obtained by similar methods. β -Phenoxyacetylamido- β -*p*-tolylacrylonitrile, m. p. 148° (cf. Meyer, *loc. cit.*), is decomposed by sodium hydroxide or phenylhydrazine in the manner described for the analogous *N*-compounds.

Ethyl chloroformate, imidoacetylacetonitrile, and pyridine give an unstable substance, $\text{C}_{12}\text{H}_{15}\text{O}_2\text{N}_3$, a pale yellow, crystalline powder, m. p. 129 – 130° (decomp.). It is decomposed by boiling sodium hydroxide solution with the evolution of ammonia and pyridine. When preserved in the presence of water or alcohol, it forms a yellowish-red powder, decomp. 265 – 280° .

Imidoacetylacetonitrile, cinnamoyl chloride, and pyridine in the presence of ether yield a mixture of β -amino- α -cinnamoylcrotononitrile, $\text{NH}_2\cdot\text{CMe}\cdot\text{C}(\text{CO}\cdot\text{CH}\cdot\text{CHPh})\cdot\text{CN}$, colourless needles, m. p. 198 – 199° , and β -cinnamoylaminocrotononitrile,

$\text{CHPh}\cdot\text{CH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CN}$,

colourless, quadratic plates, m. p. 191 – 192° . The latter substance is transformed by *N*-sodium hydroxide solution into ammonia and cinnamic acid, and by bromine in the presence of chloroform into β - α' -bromocinnamoylaminocrotononitrile,

$\text{CHPh}\cdot\text{CBr}\cdot\text{CO}\cdot\text{NH}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CN}$,

a colourless, crystalline powder, m. p. 144 – 145° . β -Amino- α -cinnamoylcrotononitrile is converted by sodium hydroxide solution into β -hydroxy- α -cinnamoylacetone, $\text{OH}\cdot\text{CMe}\cdot\text{C}(\text{CO}\cdot\text{CH}\cdot\text{CHPh})\cdot\text{CN}$ (enolic form), sulphur-yellow needles, m. p. 130° , and by phenylhydrazine into 4-cyano-1-phenyl-5-styryl-3-methylpyrazole, slender, colourless needles, m. p. 134° . β -Amino- α -cinnamoylcrotononitrile dibromide, $\text{CH}_3\cdot\text{C}(\text{NH}_2)\cdot\text{C}(\text{CN})\cdot\text{CO}\cdot\text{CHBr}\cdot\text{CHBr}\cdot\text{Ph}$, crystallises in slender needles, m. p. 220° (decomp.) after darkening at 205° .

β -Amino- α -cinnamoylcinnamionitrile,

$\text{NH}_2\cdot\text{CPh}\cdot\text{C}(\text{CO}\cdot\text{CH}\cdot\text{CHPh})\cdot\text{CN}$,

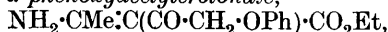
long, colourless needles, m. p. 173° (prepared from imidobenzoyl-acetonitrile, cinnamoyl chloride, and pyridine) is converted in the usual manner into β -hydroxy- α -cinnamoylcinnamionitrile,

$\text{OH}\cdot\text{CPh}\cdot\text{C}(\text{CO}\cdot\text{CH}\cdot\text{CHPh})\cdot\text{CN}$,

lemon-yellow needles, m. p. 149° , and 4-cyano-1:3-diphenyl-5-styrylpyrazole, colourless needles, m. p. 205° (decomp.). β -Cinnamoylaminocinnamionitrile, $\text{CHPh}\cdot\text{CH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CPh}\cdot\text{CH}\cdot\text{CN}$, prepared

from the nitrile, cinnamic ester, and potassium ethoxide, crystallises in long, colourless needles or leaflets, m. p. 134—135°.

Ethyl β-amino-α-phenoxyacetylcrotonate,

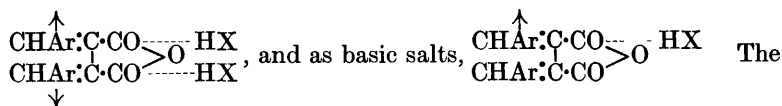


m. p. 159°, is prepared by the action of ethyl β-aminocrotonate or phenoxyacetyl chloride and pyridine in the presence of ether. It is converted by the successive action of phenylhydrazine and alcoholic potassium hydroxide solution into 1-phenyl-3-phenoxy-methyl-5-methylpyrazole-4-carboxylic acid, $\text{N} \begin{smallmatrix} \text{C}(\text{CH}_2 \cdot \text{OPh}) \\ \text{NPh} - \text{CMe} \end{smallmatrix} > \text{C} \cdot \text{CO}_2 \text{H}$,

brown needles, m. p. 178°. *Ethyl β-phenoxyacetylaminocrotonate*, $\text{OPh} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CMe} : \text{CH} \cdot \text{CO}_2 \text{Et}$, prepared by the ester method, crystallises in colourless needles, m. p. 88°. H. W.

Halochromism of the Fulgides. HANS STOBBE and RICHARD DIETZEL (*Ber.*, 1922, 55, [B], 3567—3580).—The absorption spectra of diphenylfulgide, $\text{CHPh} : \text{C} \cdot \text{CO} > \text{O}$, and the corresponding tri-

and tetra-phenyl compounds have been investigated. The substances dissolve in indifferent media such as light petroleum, alcohol, and chloroform, yielding solutions of their own colour in the solid state, whereas in strongly acidic liquids such as mono-, di-, and tri-chloroacetic acids they give solutions of a much darker colour. The isolation of the fulgides from these solutions in the form of their solid molecular compounds has not been accomplished, since they dissociate into their components in the presence of water, even when a large excess of acid is used. The investigation has therefore been confined to their solutions in chloroform and the three chloroacetic acids. The absorption of light is dependent on the strength of the acid; in the weakest of these, the limit of absorption approximates to that observed in chloroform solution. It therefore appears that, even in the presence of an excess of the acid, the fulgide is present partly as the monochloroacetate and partly as fulgide, and that this equilibrium is most markedly displaced in favour of the salt in the trichloroacetic acid solution. The constitution of the fulgide has a regular effect on the absorption of light. The ultra-violet spectra have also been examined. The absorption of solutions of the fulgides in chloroform are characterised by an ultra-violet band in the region of short wave-length and a "colour band" in the visible region. Increase in the number of the phenyl groups has no effect on the former, but causes an increased intensity in the latter and also a considerable displacement towards the red end. In the three chloroacetic acid solutions, the absorption is similar, but differs from that observed in chloroform. In place of the two bands of the latter, the ultra-violet band in the chloroacetic acid solutions disappears and is replaced by a narrow colour band which is very strongly displaced towards the red end. This displacement of the band is characteristic of the transition from a saturated to an unsaturated compound. It appears, therefore, that (in accordance with Pfeiffer's method of formulation) the fulgides function as normal salts,



formulæ, however, are to be regarded only as structural approximations, since they do not take into account the established influence of the number of aryl radicles on the strength of the halochromism.

The colour of the arylfulgides is attributable to the ortho-quinonoid tetrahydrofuran nucleus, $\begin{array}{c} > \text{C}:\text{C}:\text{CO} \\ > \text{C}:\text{C}:\text{CO} \end{array} > \text{O}$, and to the number and nature of the aryl substituents. The effect of the opening of the ring or alteration of its unsaturated character has been examined in the cases of diphenylfulgenic acid, $\text{CO}_2\text{H}\cdot\text{C}(\text{CHPh})\cdot\text{C}(\text{CHPh})\cdot\text{CO}_2\text{H}$, triphenylfulgenic acid, and tetrahydrodiphenylfulgide (dibenzylsuccinic anhydride). The absorption curves of the fulgenic acids in chloroform are precisely similar to those in the chloroacetic acids, so that their molecular condition in the solutions must be almost the same. The halochromism which is so strongly marked with the fulgides has practically disappeared after the opening of the ring and loss of the quinonoid nucleus. A comparison of the absorption curve of tetrahydrodiphenylfulgide with that of diphenylfulgide shows that the former is much more transparent, and also that the narrow ultra-violet band of the latter persists after hydrogenation. On the other hand, the absorption curves of tetrahydrodiphenylfulgide in alcohol and trichloroacetic acid are very similar. In this case, as with the fulgenic acids, halochromism is scarcely perceptible; the carbonyl groups are not in themselves capable of uniting with chloroacetic acid. For this purpose, the ethylenic linkings of the non-hydrogenated fulgide are indispensable; they strengthen the unsaturated nature of the carbon atom, and thus indirectly cause a deepening of the colour. H. W.

Resorcinolphenylsuccinein. ARTHUR LAPWORTH and JOHN ALEXANDER McRAE (T., 1922, 121, 2722—2724.)

A Condensation of Dehydrodeoxycholic Acid. TOMIHIDE SHIMIZU (*Z. physiol. Chem.*, 1922, 123, 159—163).—Dehydrodeoxycholic acid on treatment with hydrogen chloride in alcoholic solution not only is esterified, but also an aldol condensation takes place between a keto-group of one molecule and a methylene group of another, and in addition the hydroxyl group formed in this process is replaced by chlorine, a compound, $\text{C}_{52}\text{H}_{79}\text{O}_7\text{Cl}$, m. p. 204° , being formed. On treatment with sodium ethoxide, this compound is hydrolysed and also loses hydrogen chloride, to yield an unsaturated dibasic acid, $\text{C}_{48}\text{H}_{70}\text{O}_7$, six-sided prisms, m. p. 276° . In addition to the above-mentioned condensation product, the simple ethyl ester, lustrous leaflets, m. p. 108° , can also be isolated, and if methyl alcohol is used instead of ethyl alcohol, no condensation takes place, the sole product being *methyl dehydrodeoxycholate*, fine needles aggregating into leaflets, m. p. 130° . W. O. K.

The Bile Acids. XV. ψ -Choloidanic Acid. HEINRICH WIELAND (*Z. physiol. Chem.*, 1922, **123**, 237—245).— ψ -Choloidanic acid formed, along with choloidanic acid, in the oxidation of deoxybilianic acid has the formula $C_{24}H_{34}O_{10}$. It forms a neutral tetramethyl ester, $C_{28}H_{42}O_{10}$, a *dimethyl* ester, $C_{26}H_{38}O_{10}$, long needles, m. p. 268°, and a *barium* salt, $C_{26}H_{36}O_{10}Ba$, glistening needles. When heated, it loses carbon dioxide and water, to form *pyro- ψ -choloidanic acid*, $C_{23}H_{30}O_6$, lustrous leaflets, m. p. 246° (*hydrate*, $C_{23}H_{30}O_6 \cdot H_2O$, glistening needles, m. p. 115—116°). The dimethyl ester of ψ -choloidanic acid yields, when heated, the neutral ester of a monobasic acid, $C_{23}H_{29}O_5 \cdot OMe$, m. p. 192°. W. O. K.

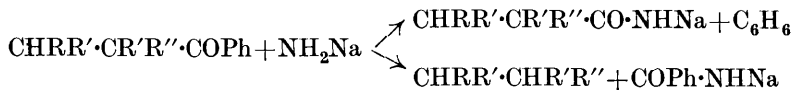
The Bile Acids. XIV. Cilianic Acid, Ciloidanic Acid, and Biloidanic Acid. HEINRICH WIELAND and OTTO SCHLICH-TUNG (*Z. physiol. Chem.*, 1922, **132**, 213—236; cf. A., 1922, i, 838).—Ciloidanic acid, $C_{24}H_{34}O_{13}$, may be oxidised by nitric acid, *d* 1.52, to biloidanic acid, $C_{22}H_{32}O_{12}$. The formula given previously for this acid, $C_{23}H_{34}O_{12}$, is not correct, and it is found that it is identical with norsolanellnic acid. When heated with sulphuric acid, ciloidanic acid loses carbon dioxide and carbon monoxide, to yield a *keto-tetracarboxylic acid*, $C_{22}H_{32}O_9$, needles, m. p. 238°, $[\alpha]_D^{16} + 73.5^\circ$. This keto-carboxylic acid on oxidation by nitric acid (*d* 1.4) yields biloidanic acid in a very pure form, and by this means the new formula has been established. Biloidanic acid when heated in a vacuum loses water and carbon dioxide to yield *pyrobiloidanic acid*, $C_{21}H_{28}O_8$, fine, microscopic prisms, m. p. 193—195°. If this acid is heated with alkali, an internal lactone ring is hydrolysed, and an acid, $C_{21}H_{30}O_9 \cdot H_2O$, is formed. The constitution of the bile acids is discussed in the light of these results, and modifications of the earlier formulæ are suggested. W. O. K.

The Acidity of Gallaldehyde. M. NIERENSTEIN (*Ber.*, 1922, **55**, [B], 3581).—The presumed great acidity of gallaldehyde has been regarded by Rosenmund and Zetzsche (A., 1918, i, 301) as indirect evidence against Nierenstein's observation (A., 1909, i, 402) that gallaldehyde is formed by the hydrolysis of gallotannin. The recognition that the aldehyde is not so acidic as was supposed (Rosenmund and Pfannbuch, A., 1922, i, 1030) invalidates this argument. H. W.

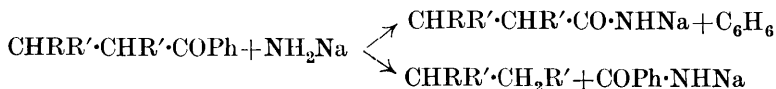
The Condensation of *o*-Halogenoketones with Aldehydes. SVEN BODFORSS (*Ber.*, 1922, **55**, [B], 3581).—A claim for priority against Bauer and Werner (A., 1922, i, 1034; cf. Bodforss, A., 1917, i, 223; 1919, i, 211). H. W.

Some $\alpha\beta\beta$ -Tetra-substituted Propiophenones and the Products they yield on Decomposition with Sodamide. GEORGES ALBESCO (*Ann. Chim.*, 1922, **18**, 216—262; cf. Haller and Bauer, A., 1909, i, 108, 654; 1910, i, 300; Dumesnil, A., 1911, i, 718).—A study of the action of organo-magnesium compounds on phenyl styryl ketone and phenyl methylenedioxystryl ketone with formation of $\beta\beta$ -substituted acetophenones and subsequent substitution

in the α -position with methyl or ethyl groups, resulted in the preparation of the following compounds. *Phenyl α -ethylstyryl ketone*, a viscous liquid, b. p. $208^{\circ}/14$ mm. *β -Phenyl- β -p-tolyl-propiophenone*, colourless crystals, m. p. 96° , b. p. $254^{\circ}/12-13$ mm. *β -Methylenedioxyphenyl- β -methylpropiophenone*, prisms, m. p. 73° . *β -Methylenedioxyphenyl- β -ethylpropiophenone*, colourless prisms, m. p. 58° , b. p. $233^{\circ}/11$ mm. *β -Phenyl- β -methylenedioxyphenylpropiophenone*, crystals, m. p. 97° , b. p. $280^{\circ}/14$ mm. *$\beta\beta$ -Diphenyl- α -dimethylpropiophenone*, m. p. 90° . *$\beta\beta$ -Diphenyl- α -ethylpropiophenone*, m. p. 118° . *β -Phenyl- α -methyl- β -ethylpropiophenone*, crystals, m. p. $54-55^{\circ}$. *β -Phenyl- α -dimethyl- β -ethylpropiophenone*, mobile liquid, b. p. 195° ; *β -phenyl- $\alpha\alpha\beta$ -triethylpropiophenone*, mobile liquid, b. p. $195^{\circ}/760$ mm.; *β -phenyl- β -p-tolyl- α -methylpropiophenone*, colourless crystals, m. p. 116° ; *β -phenyl- β -p-tolyl- α -ethylpropiophenone*, colourless crystals, m. p. 131° , b. p. $252^{\circ}/12$ mm. *β -Phenyl- β -methoxyphenyl- α -methylpropiophenone*, m. p. 128° . *β -Methylenedioxyphenyl- $\alpha\beta$ -dimethylpropiophenone*, m. p. 70° . *β -Methylenedioxyphenyl- $\alpha\alpha\beta$ -trimethylpropiophenone*, colourless, mobile liquid, b. p. 230° . *β -Methylenedioxyphenyl- α -methyl- β -ethylpropiophenone*, an oil, b. p. $236^{\circ}/15$ mm. *β -Methylenedioxyphenyl- α -dimethyl- β -ethylpropiophenone*, an oil, b. p. $235^{\circ}/11$ mm.; *β -methylenedioxyphenyl- $\alpha\beta$ -diethylpropiophenone*, an oil, b. p. $234-235^{\circ}/13-14$ mm. *β -Phenyl- β -methylenedioxyphenyl- α -methylpropiophenone*, needles, m. p. 128° . In those cases in which both β -substituents are of aromatic type, the second α -substitution takes place with difficulty. The action of sodamide on the tetra-substituted derivatives results in fission of the ketone molecule at two different points, the two types of decomposition occurring to the same extent:



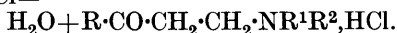
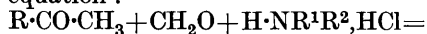
The reaction affords a ready means of preparing tetra-substituted propionic acids. The action of sodamide under the influence of heat on the ketones which are mono-substituted in the α -position results in formation of two products:



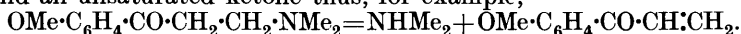
Among the substances obtained by the action of sodamide are the following. *$\beta\beta$ -Diphenyl- $\alpha\alpha$ -dimethylpropionamide*, white crystals, m. p. 120° . *$\alpha\alpha$ -Diphenyl- β -methylpropane*, mobile, colourless liquid, b. p. $145^{\circ}/13$ mm. *γ -Phenyl- β -methylpentane*, mobile, colourless liquid, b. p. 200° . *β -Phenyl- $\alpha\alpha$ -dimethylvaleramide*, viscous liquid, b. p. $180^{\circ}/11$ mm. *δ -Phenyl- γ -ethylhexane*, mobile, colourless liquid, b. p. 205° . *β -Phenyl- $\alpha\alpha$ -dimethylvaleric acid*, crystals, m. p. 82° . *β -Phenyl- $\alpha\alpha$ -diethylvaleric acid*, m. p. $68-69^{\circ}$. *$\beta\beta$ -Diphenyl- α -ethylpropionamide* [α -benzhydrylbutyramide], colourless crystals, m. p. 151° .

H. J. E.

The Synthesis of β -Keto-bases from Fatty-aromatic Ketones, Formaldehyde, and Secondary Amines. C. MANNICH and D. LAMMERING (*Ber.*, 1922, **55**, [B], 3510—3526).— β -Ketonic bases may be prepared from the salts of secondary amines, formaldehyde, and fatty-aromatic ketones in accordance with the equation:



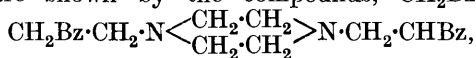
Reaction is usually effected by boiling molar quantities of the salt and concentrated formaldehyde solution with the fatty-aromatic ketone. Frequently, it is advantageous to work in the absence of moisture, for example, by heating the amine salt and ketone with paraformaldehyde in the presence of alcohol, in which case an excess of aldehyde must be used. The synthesis is capable of considerable variation. The ketonic component may be acetophenone, methoxyacetophenone, acetoveratrone, propiophenone, deoxybenzoin, or β -acetyltetrahydronaphthalene, but apparently not *p*-acetylamidoacetophenone, whereas the basic component may be dimethylamine, diethylamine, piperidine, tetrahydroisoquinoline, or piperazine, but not tetrahydroquinoline. The keto-bases and their hydrochlorides are, in general, fairly stable, but are more or less rapidly decomposed at their boiling points into a tertiary amine and an unsaturated ketone thus, for example,



The free bases are sometimes solid, and are then purifiable by crystallisation, and sometimes liquid; in the latter case, they cannot be purified, since they decompose on distillation under diminished pressure. In many cases, they have been further characterised by the formation of oximes, but the process does not occur smoothly when the dimethylamino-group is present in the molecule. The β -keto-bases are most conveniently reduced to the corresponding secondary alcohols by hydrogen in the presence of palladium, but zinc dust and hydriodic acid may also be used. Sodium and alcohol are unsuitable, since loss of the amine residue is caused thereby; aluminium amalgam in the presence of moist ether reduces the ketones to pinacone-like substances. The alcoholic bases, in contrast to the ketonic compounds, are quite stable, and can be distilled under diminished pressure without decomposition.

The synthesis just described allows the ready preparation of substances which contain nitrogen in the γ -position to the benzene nucleus. In contrast to the behaviour of the similar substances containing the nitrogen in the β -position, the compounds,

$OH \cdot C_6H_4 \cdot CO \cdot CH_2 \cdot CH_2 \cdot NMe_2$, and $C_6H_3(OH)_2 \cdot CO \cdot CH_2 \cdot CH_2 \cdot NMe_2$, do not cause any rise in the blood pressure. Anaesthetising properties are shown by the compounds, $CH_2Bz \cdot CH_2 \cdot C_5NH_{10}$,



$CH_2Bz \cdot CH_2 \cdot N < \begin{array}{c} CH_2 \\ CH_2 \cdot CH_2 \end{array} > C_6H_4$, and $CHPhBz \cdot CH_2 \cdot C_5NH_{10}$ (all of which contain the benzoyl group, but not in the form of ester), and by the substances $OMe \cdot C_6H_4 \cdot CO \cdot CH_2 \cdot CH_2 \cdot C_5NH_{10}$,
c* 2

$C_{10}H_{11} \cdot CO \cdot CH_2 \cdot CH_2 \cdot NMe_2$, $C_{10}H_{11} \cdot CO \cdot CH_2 \cdot CH_2 \cdot C_5NH_{10}$, and $OMe \cdot C_6H_4 \cdot CO \cdot CHMe \cdot CH_2 \cdot C_5NH_{10}$. The β -amino-alcohols are not anæsthetics in themselves, but exhibit extremely active properties in the form of their benzoates, being in some cases markedly more potent than cocaine. Unfortunately, they have also an irritant action.

The following individual substances are described. β -Piperidinoethyl phenyl ketone, $C_5NH_{10} \cdot CH_2 \cdot CH_2 \cdot CPh$, a colourless, odourless liquid (*hydrochloride*, m. p. 192—193°, *picrate*, needles, m. p. 180·5°, and *oxime*, needles, m. p. 143°). 1:6-Dipiperidino-3:4-diphenylhexane-3:4-diol,

$C_5NH_{10} \cdot CH_2 \cdot CH_2 \cdot CPh(OH) \cdot CPh(OH) \cdot CH_2 \cdot CH_2 \cdot C_5NH_{10}$, (α -form), m. p. 238° (decomp.) [*hydrochloride*, decomp. about 270°], (β -form), large plates, m. p. 115°. β -Piperidinoethylphenylcarbinol, $OH \cdot CHPh \cdot CH_2 \cdot CH_2 \cdot C_5NH_{10}$, leaflets, m. p. 68—69° (*hydrochloride*, m. p. 138°; *picrate*, needles, m. p. 103°; *benzoate*, flattened needles, m. p. 170°; *p*-nitrobenzoate, brown needles, m. p. 104°; *p*-aminobenzoate, m. p. 118°). β -Tetrahydroisoquinolinoethyl

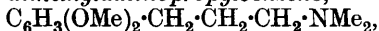
phenyl ketone, $CPh \cdot CH_2 \cdot CH_2 \cdot N \begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} C_6H_4$, a viscous liquid which solidifies in a freezing mixture, and its *hydrochloride*, m. p. 188°. 1:4-Di- β -benzoyl ethylpiperazine, crystalline granules, m. p. 141° (*hydrochloride*, decomp. 190°; *picrate*, needles, decomp. above 190°; *dioxime*, m. p. 245°). *p*-Methoxyphenyl β -dimethylaminoethyl ketone *hydrochloride*, $C_6H_4(OMe) \cdot CO \cdot CH_2 \cdot CH_2 \cdot NMe_2 \cdot HCl$, needles, m. p. 181° (corresponding *picrate*, m. p. 145°); the *hydrochloride* is decomposed at 180°/20 mm., into dimethylamine *hydrochloride* and *p*-anisyl vinyl ketone, b. p. 138—142°/20 mm., m. p. 19° (corresponding *dibromide*, prisms, m. p. 71°). ? 1-Phenyl-3-*p*-anisylpyrazoline, $\begin{array}{c} NPh \text{---} N \\ \diagup \quad \diagdown \\ CH_2 \cdot CH_2 \end{array} > C \cdot C_6H_4 \cdot OMe$, m. p. 105° (from the

vinyl ketone and phenylhydrazine). Anisyl ethyl ketone semicarbazone, m. p. 176°. *p*-Hydroxyphenyl β -dimethylaminoethyl ketone *hydriodide*, pale yellow leaflets, m. p. 205° (from the methoxy-compound and hydriodic acid), and the corresponding *hydrochloride*, pale yellow leaflets, m. p. 189°. *p*-Anisyl- β -dimethylaminoethylcarbinol, b. p. 146—148°/30 mm., m. p. 53° (*hydrochloride*, needles, m. p. 203—204°; *hydrochloride* of the corresponding *benzoate*, m. p. 174°). β -Piperidinoethyl *p*-anisyl ketone, a liquid which solidifies in a freezing mixture (*hydrochloride*, needles, m. p. 216°; *picrate*, short needles, m. p. 165°; *oxime*, needles, m. p. 136°). 1:4-Di-*p*-anisylethylpiperazine, $C_4N_2H_8(CH_2 \cdot CH_2 \cdot CO \cdot C_6H_4 \cdot OMe)_2$, pale yellow leaflets, m. p. 173° after darkening at 171° (the *hydrochloride* darkens without melting above 150°). β -Piperidinoisopropyl *p*-anisyl ketone, $OMe \cdot C_6H_4 \cdot CO \cdot CHMe \cdot CH_2 \cdot C_5NH_{10}$, a liquid prepared from piperidine, *p*-anisyl ethyl ketone, and paraformaldehyde (*hydrochloride*, leaflets, m. p. 178°; *oxime*, m. p. 94°). 3:4-Dimethoxyphenyl- β -dimethylaminoethyl ketone,

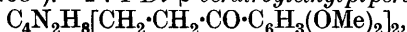
$C_6H_3(OMe)_2 \cdot CO \cdot CH_2 \cdot CH_2 \cdot NMe_2$, a viscous liquid (*hydrochloride*, needles, m. p. 181—182°; *picrate*, needles, m. p. 157°). 3:4-Dihydroxyphenyl β -dimethylaminoethyl ketone (from the *hydrochloride* of the corresponding methoxy-

compound and hydriodic acid), isolated as the *hydriodide*, pale yellow crystals, m. p. 196°, and *hydrochloride*, needles, m. p. 179°.

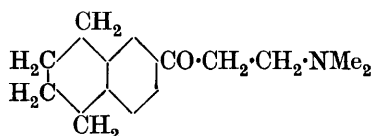
3 : 4-Dimethoxy- γ -dimethylaminopropylbenzene,



a colourless liquid, b. p. 161—164°/30 mm., prepared unexpectedly by the reduction of the corresponding ketone by hydrogen in the presence of palladised animal charcoal (*hydrochloride*, needles, m. p. 195°). β -Piperidinoethyl-3 : 4-dimethoxyphenyl ketone, m. p. 113° (*hydrochloride*, small prisms, m. p. 183°; *picrate*, m. p. 180°; *oxime*, needles, m. p. 168°). 1 : 4-Di- β -veratroylethylpiperazine,



yellow needles, m. p. 168° (*hydrochloride*, short needles which decompose without melting above 150°). Veratryl β -diethylaminoethyl ketone, $\text{C}_6\text{H}_3(\text{OMe})_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NEt}_2$, a colourless liquid (*hydrochloride*, needles, m. p. 140—141°; *picrate*, m. p. 136°; *oxime*, large needles, m. p. 104°). α -Piperidino- β - γ -diphenylpropane- γ -one, $\text{C}_5\text{NH}_{10} \cdot \text{CH}_2 \cdot \text{CHPh} \cdot \text{COPh}$, (from deoxybenzoin, piperidine hydrochloride, and paraformaldehyde), a crystalline powder, m. p. 91° (the *hydrochloride* is very hygroscopic; *nitrate*, short needles, m. p. 117°). β -Tetrahydronaphthyl β -dimethylaminoethyl ketone (annexed formula), a liquid (*hydrochloride*, needles, m. p. 170°; *picrate*, needles, m. p. 156°). β -ar-



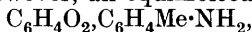
viscous liquid [*hydrochloride*, m. p. (anhydrous) 170°, (+aq.) 85°; *nitrate*, needles, m. p. 134—135°; *oxime hydrochloride*, silky needles, m. p. 211°].

H. W.

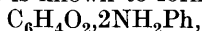
The Influence of Substitution in the Components of Binary Solution Equilibria. XXXVII. The Systems of *p*-Benzoquinone with Phenols, Amines, and Hydrocarbons. ROBERT KREMANN, SEPP SUTTER, FRANZ SITTE, HUBERT STRZELBA, and ALADAR DOBOTZKY (*Monatsh.*, 1922, **43**, 269—313).—A systematic investigation has been made of the additive compounds of quinhydrone character formed by *p*-benzoquinone with a number of aromatic hydroxy-compounds, amines, and hydrocarbons. The method of attack adopted was through the determination of the condition-diagram of the binary system formed between *p*-benzoquinone and the substance under examination. Early experiments on these lines failed to give satisfactory results for two reasons. First, it was not realised that the additive compounds are not formed instantaneously when the two components are fused together, but frequently some considerable time at a higher temperature is needed to establish equilibrium. This phenomenon has not previously been recorded in the case of additive compounds between organic substances. Secondly, at the high temperatures at which fusion occurred, secondary reactions frequently started to some extent, rendering the observations worthless. The latter difficulty

was overcome by the addition to the binary system of a constant quantity of a third inactive substance, for which nitrobenzene was chosen. The ternary system could be treated as a quasi-binary system, and the nitrobenzene, by lowering the temperatures at which fusion and primary crystallisation took place, lessened the chance of the occurrence of secondary reactions between the *p*-benzoquinone and the other component. The existence of the following compounds between quinone and aromatic hydroxy-compounds was established from the occurrence of maxima in the *T*-*x* curves of the equilibrium diagrams: with phenol, $C_6H_4O_2, 2PhOH$; with quinol, $C_6H_4O_2, C_6H_4(OH)_2$; with pyrocatechol, $2C_6H_4O_2, C_6H_4(OH)_2$; with resorcinol, $2C_6H_4O_2, C_6H_4(OH)_2$; with pyrogallol, $3C_6H_4O_2, C_6H_3(OH)_3$.

These compounds can be explained on the assumption that combination takes place between the hydroxy-group and one of the two oxygen fields of force of the benzoquinone. In the cases of pyrocatechol, resorcinol, and pyrogallol, steric hindrance allows only one field of force of each benzoquinone molecule to come into play. The two naphthols both form, at first, equimolecular compounds, $C_6H_4O_2, C_{10}H_7 \cdot OH$, but when the mixtures are heated for some time to a higher temperature, compounds of higher melting point containing two mols. of benzoquinone to one of naphthol are formed. This combination with a second molecule of benzoquinone must be attributed to the benzenoid fields of force. Of the three nitrophenols, 1 : 2 : 4-dinitrophenol, and picric acid, only *p*-nitrophenol forms a compound with quinone, the equimolecular compound, $C_6H_4O_2, OH \cdot C_6H_4 \cdot NO_2$. Triphenylcarbinol forms no compound. Only three systems with amines were studied successfully. *p*-Toluidine, when carefully melted with *p*-benzoquinone, forms a simple mixture giving a eutectic; after warming the mixture some time, however, an equimolecular compound,



is formed. Since aniline is known to form the compound



it is evident that the *p*-methyl group has a similar effect on the combining power of aniline to the *p*-nitro-group on that of phenol. α -Naphthylamine forms an equimolecular compound with *p*-benzoquinone, whilst β -naphthylamine, which at first forms no compound, when warmed for some time forms two compounds, $C_6H_4O_2, C_{10}H_7 \cdot NH_2$ and $2C_6H_4O_2, C_{10}H_7 \cdot NH_2$. No compounds were detected between *p*-benzoquinone and any of the hydrocarbons triphenylmethane, naphthalene, acenaphthene, phenanthrene, fluorene, or with diphenylamine or carbazole, but anthracene forms an equimolecular compound.

E. H. R.

The Catalytic Action of Mercury in the Sulphonation of Anthraquinone. G. W. CLOUGH (*J. Soc. Dyers and Col.*, 1921, 38, 299—300).—After several attempts, the author has failed to confirm the statement of Martinet and Roux (A., 1921, i, 732) that in the sulphonation of anthraquinone by means of fuming sulphuric acid in the presence of mercury as a catalyst, the α -sulphonic acid

is always formed first and that this simultaneously changes into the β -isomeride.

A. J. H.

Bromonitrocamphane. P. M. GINNINGS and W. A. NOYES (*J. Amer. Chem. Soc.*, 1922, **44**, 2567—2573; cf. Forster, *T.*, 1897, **71**, 199, 1030; 1899, **75**, 1141; 1900, **77**, 251; 1901, **79**, 108, 264, 644, 653, 987, 1003; 1902, **81**, 865; 1903, **83**, 78).—Further evidence is given in support of Forster's work on this subject, and definite proof of the structure of bromonitrocamphane anhydride is advanced.

On oxidation with nitric acid, bromonitrocamphane breaks down successively into camphor, camphoric acid, and camphoronic acid. The authors found no evidence of the formation of a hydrate of bromonitrocamphane, as suggested by Forster, during the action of potassium hypobromite on camphoroxime, but did find that a certain amount of hydroxynitrosocamphane was formed. The course of the action of the hypobromite is bromination of the camphoroxime and then oxidation to bromonitrocamphane. The anhydride of the last-named compound is best prepared by dissolving it in light petroleum of low boiling point and adding this to a mixture of concentrated sulphuric acid and light petroleum kept at -10° . The anhydride reacts with Grignard's reagent to give *methylbromonitrocamphane anhydride*, m. p. $117-118^{\circ}$, which yields a *benzoyl* derivative, m. p. $113-114^{\circ}$, and is decomposed by alcoholic sodium hydroxide to give acetylcamphenylcarboxylic acid.

W. G.

Preparation of Polycyclic Hydrocarbons of the Terpene Series. CHEMISCHE FABRIK AUF ACTIEN (VORM. E. SCHERING) (D.R.-P. 353933; from *Chem. Zentr.*, 1922, iv, 499).—Hydrazones of terpene ketones are heated with mercuric oxide in indifferent solvents; or the double salts of the hydrazones with mercuric chloride in the presence of an equivalent amount of alkali are heated in indifferent solvents. Slightly soluble basic mercury compounds are thereby formed which decompose on heating, as, for example, $C_{10}H_{16} \cdot N \cdot NH \cdot Hg \cdot OH = C_{10}H_{16} + N_2 + Hg + H_2O$.

Tricyclene, b. p. 153.5° , m. p. 63.5° , is formed from camphor-hydrazone and mercuric oxide in alcohol after eight hours' heating. *d-Cyclofenchene*, from *d-fenchone*hydrazone, has b. p. $142.5-143.5^{\circ}$, d_{20}^{20} 0.8588, n_D^{20} 1.45134, $[\alpha]_D^{20} +0.45^{\circ}$. *apoCyclene*, from camphenilhydrazone, has b. p. $138-139^{\circ}$, b. p. $120.5/17$ mm., m. p. 40.1° , d_{45}^{45} 0.8694, n_D^{45} 1.44914.

G. W. R.

Oxidation of Sabinene with Chromyl Chloride. GEORGE GERALD HENDERSON, JOHN MCGREGOR ROBERTSON, and DAVID CHRISTIE BROWN (*T.*, 1922, **121**, 2717—2721).

Constituents of some Indian Essential Oils. JOHN LIONEL SIMONSEN and MADYAR GOPAL RAU (*Indian Forest Rec.*, 1922, **9**, 111—146).—I. The oleo-resin of *Pinus khasya* yields 57% of rosin. The turpentine essential oil has d_{30}^{30} 0.8633, n_D^{30} 1.4675, and $[\alpha]_D^{30} +32.83^{\circ}$. On distillation, it gives 70.6%, boiling at $153-159^{\circ}$ consisting of *d*- α -pinene, 11.7% at $159-169^{\circ}$, consisting of a

mixture of α - and β -pinenes, and the higher fractions contain a terpene identical with *d*-longifolene.

II. The oleo-resin of *Pinus excelsa* yields about 68% of rosin. By fractionation of the oil, 87.9% of very pure *d*- α -pinene was obtained, together with *d*-terpineol, a bicyclic sesquiterpene, and a small quantity of a saturated hydrocarbon, $C_{11}H_{22}$, which appeared to be *n*-undecane. The turpentine itself had the constants d_{20}^{30} 0.857, n_D^{30} 1.4627, and $[\alpha]_D^{30} +40.42^\circ$.

III. The essential oil from *Cedrus deodara*, Loudon, has already been examined by Roberts (T., 1916, **109**, 791) and his results are in the main confirmed. The ketone present to the extent of 8–10% was definitely identified as 4-methyl- Δ^3 -cyclohexenyl methyl ketone. The sesquiterpene (40%) was isolated as a colourless oil, b. p. 152–154°/40 mm., d_{20}^{30} 0.9195, n_D^{30} 1.5040, and $[\alpha]_D^{30} +13.86^\circ$. No crystalline derivatives could be obtained, and the substance was not identified. A sesquiterpene alcohol, b. p. 202–204°/55 mm., was also isolated in about 40% yield. It formed a viscid yellow oil, d_{20}^{30} 0.9578, n_D^{30} 1.515, $[\alpha]_D^{30} +38.41$. It gave no crystalline derivatives and could not be further characterised. No phenol, heptioic, or stearic acids were found, but the presence of esters of butyric, hexoic, and an unidentified crystalline acid, m. p. 110°, was confirmed.

IV. The essential oil from the grass *Andropogon Jwarancusa*, Jones (cf. T., 1922, **121**, 2295), collected in Sind has a lower rotation ($[\alpha]_D^{30} +42.8^\circ$), a higher density (0.9228), and a higher refraction (n_D^{30} 1.4858) than that from grass of reputedly the same species grown in the Hazara district (cf. T., 1921, **119**, 1645). It contains only 44% of piperitone, together with 24% of the terpene *d*- Δ^4 -carene, identical with that in the Hazara oil, about 28% of a sesquiterpene alcohol, b. p. 176–177°/31 mm., 2% of an unidentified alcohol having an odour of roses, and small quantities of either free or combined palmitic, decoic, and octoic acids. The oil as a whole closely resembles that from *Cymbopogon Sennaarensis* described by Roberts (T., 1915, **107**, 1465) rather than the Hazara oil.

V. The essential oil from the seeds of *Xanthoxylum alatum*, Roxb., contains more than 85% of *l*- α -phellandrene, together with a small proportion of linalool, and an unidentified sesquiterpene.

VI. The essential oil from the seeds of *Xanthoxylum acanthopodium*, DC. (yield 1.2%), had the following constants: d_{20}^{30} 0.8837, n_D^{30} 1.4746, $[\alpha]_D^{30} +6.54^\circ$, saponification value 60.79, ditto after acetylation 242.5. The chief constituents are dipentene, methyl cinnamate, and more than 50% of linalool. In addition, *l*- α -phellandrene, a small quantity of an aldehyde or ketone, and a mixture of fatty acids consisting probably of hexoic, octoic, and heptioic acids were found.

VII. The essential oil from the seeds of *Xanthoxylum Budrunga*, Wall., is apparently identical with that examined by Semler (A., 1911, i, 1002) and stated by him to have been obtained from *X. alatum*. The terpene named by him xanthoxylene is definitely shown to be *l*-sabinene, as it gave sabinic acid, m. p. 55–57°, on oxidation, 1:4-terpin, on treatment with dilute sulphuric acid,

and terpinene dihydrochloride with hydrogen chloride in acetic acid solution. In addition to this hydrocarbon, terpinene was found in small quantities in the oil, together with an unidentified alcohol. No dimethoxyphloracetophenone could be found in the sample of oil examined.

G. F. M.

Essential Oils. SCHIMMEL & Co. (*Rep. Schimmel & Co.*, 1922, 5—166; from *Chem. Zentr.*, 1922, iv, 763—764).—Descriptions are given of a number of essential oils, many of which have already appeared. Essential oil from *Abies pindrow* (Indian silver fir) has d_{15}^{20} 0.8647, $[\alpha]_D -10^\circ 59'$, n_D^{20} 1.47328, acid number 0.3; ester number 6.5. Indian baldrian oil has d_{15}^{20} 0.9361, $[\alpha]_D -34^\circ 6'$, n_D^{20} 1.48712, acid number 37.3, ester number 39.8, acetyl number 69.1. Essential oil from *Erigeron canadense* has d_{15}^{20} 0.8720, $[\alpha]_D +53^\circ 56'$, n_D^{20} 1.49922, acid number 0.3, ester number 63.5, acetyl number 70.3. Pine needle oil from *Tsuga canadensis* has (Cable, *J. Amer. Pharm. Assoc.*, 1921, 10, 170) d_{15}^{20} 0.9020—0.9234, $[\alpha]_D^{20} -14.80^\circ$ to 21.65° , n_D^{20} 1.4691—1.4704, acid number 0.33—0.71, ester number 103.8—147.35, acetyl number 113.5—171.94. Essential oil from *Tsuga heterophylla* has d_{15}^{20} 0.8444—0.8521, $[\alpha]_D^{20} -6^\circ$ to -20° , n_D^{20} 1.4790—1.4840, acid number 2.57—3.4, ester number 6.7—17.25, acetyl number 19.6—33.4. Spanish oil of thyme has d_{15}^{20} 0.9297, $[\alpha]_D +0^\circ 35'$; it contains 45% of thymol, also amyl alcohol, amylcarbinols, Δ^8 -hexenol, and a new terpene, $C_{14}H_{16}$, of carrot-like odour, b. p. 155 — 156° , with d_{15}^{20} 0.8533—0.8537, $[\alpha]_D +4^\circ 35'$ to $4^\circ 50'$, n_D^{20} 1.46201—1.46231. The latter compound gives a nitrosochloride which decomposes at about 85° , a nitrolpiperidine, m. p. 194 — 195° , and a nitrolamine, m. p. 105 — 108° . The oil also contains camphene, α -pinene, *p*-cymol, γ -terpinene, linalool, *l*-borneol, ψ -terpineol, geraniol, and caryophyllene. Essential oil from *Cicuta virosa*, L., has d_{15}^{20} 0.8909, $[\alpha]_D +16^\circ 32'$, n_D^{20} 1.4848, acid number 3.7, ester number 17.7.

G. W. R.

Caoutchouc. RUDOLF PUMMERER and PETER A. BURKARD (*Ber.*, 1922, 55, [B], 3458—3472).—Caoutchouc dissolved in hexahydrotoluene has been submitted to catalytic hydrogenation in the presence of spongy platinum. In order to obtain a highly depolymerised and therefore highly active material, very dilute solutions (0.2—0.6%) are employed. The reaction occurs at the atmospheric temperature, but is more conveniently studied at 70 — 80° with freshly purified caoutchouc and recently prepared catalyst. With more concentrated solution (even 1%) the hydrogenation is frequently incomplete, possibly owing to poisoning of the catalyst by adsorbed caoutchouc. The caoutchouc absorbs one molecular proportion of hydrogen for each isoprene residue, $(C_5H_8)_x + xH_2 = (C_5H_{10})_x$, and there is no tendency towards further union with hydrogen after this stage is reached. If the caoutchouc molecule contained the isoprene residues in an open chain, a greater absorption of hydrogen would be expected in accordance with the scheme $(C_5H_8)_x + (x+1)H_2 = C_{5x}H_{10x+2}$. The accuracy attained in the experiments permits the conclusion to be drawn that caoutchouc consists either of a ring system or of an unusually long chain of

isoprene residues ($x > 20$). The isolation of the hydrocaoutchouc from the solutions is somewhat difficult, since the product in substance and in solution is readily dehydrogenated to caoutchouc (at any rate in the presence of unavoidable traces of platinum). Precipitation of the colloid by kaolin in the absence of air and subsequent removal of the solvent under diminished pressure in an atmosphere of hydrogen yields *hydrocaoutchouc* as a very pale yellow, elastic skin, which swells and ultimately dissolves in ether and closely resembles ordinary caoutchouc. It certainly retains the high molecular weight.

The autoxidation of hydrocaoutchouc has been quantitatively studied by removing the excess of hydrogen by evacuation from the apparatus in which the substance has been prepared and subsequently agitating the solution with oxygen (in the presence of the platinum). A volume of oxygen, equal to half that of the hydrogen previously used, is rapidly absorbed, after which the action proceeds much more slowly and at approximately the same rate as observed with a similar solution of caoutchouc in hexahydrotoluene. The product of the autoxidation, *isocaoutchouc* II, when freshly prepared, dissolves easily and rapidly in ether without protracted swelling phenomena. When treated with hydrogen and spongy platinum, it rapidly absorbs one molecular proportion of the gas for each isoprene residue, thus showing that bridged linkings are not present in the molecule. In its solubility, *isocaoutchouc* II appears to be more closely allied to Harries's α - and β -*isocaoutchouc* than to caoutchouc.

The absorption of gaseous oxygen by a very dilute solution of caoutchouc in hexahydrotoluene appears to be finished at the atmospheric temperature when a molecular proportion of oxygen has been used for every two isoprene residues. It is immaterial whether the action takes place in the presence or absence of spongy platinum. The tardiness with which absorption by concentrated solutions of caoutchouc occurs is very manifest.

The action of perbenzoic acid on solutions of caoutchouc in chloroform at 0° gives a viscous *caoutchouc oxide*, $(C_5H_8O)_x$, which is insoluble in all media. Products richer in oxygen are obtained in the presence of moisture. Reaction with the theoretical quantity of perbenzoic acid is almost complete after one hour, so that caoutchouc behaves normally towards this reagent.

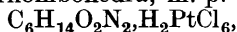
The viscosity of a solution of caoutchouc in benzene at 25° is not changed if the solution is heated to gentle ebullition during eight hours and subsequently cooled rapidly or slowly to 25° ; if therefore a polymerisation equilibrium exists in caoutchouc solutions, it must be very rapidly attained. The coagulation of caoutchouc in boiling benzene is not observed with 2% solutions, but occurs slowly with 4% solutions. It does not take place during ten hours at 50° . The phenomenon is reversible. H. W.

Centaurein ; a New Glucoside obtained from the Roots of *Centaurea Jacea*. MARC BRIDEL and CAMILLE CHARAUX (*Compt. rend.*, 1922, **175**, 833—835).—*Centaurein*, a glucoside

crystallising in small, pale yellow, elongated plates, of no definite m. p., was extracted from the dried roots of *Centaurea Jacea*. It contains 9.96% of water, which is lost at 50° in a vacuum, the glucoside itself remaining unchanged. It has $[\alpha]_D -76.54^\circ$ (-85° anhydrous) in methyl-alcoholic solution and $[\alpha]_D -133.68^\circ$ (-148.47° anhydrous) in 5% sodium hydroxide solution. Hydrolysis takes place slowly in boiling 5% sulphuric acid, the products being dextrose (33.68%) and *centaureidin* (70.77%), both of which were obtained in crystalline form. H. J. E.

Oxalyl Chloride in the Synthesis of the Triphenylmethane Dyes. HARPER F. ZOLLER (*Science*, 1920, 52, 207).—Oxalyl chloride may be used instead of carbonyl chloride or Michler's ketone in the condensation of aniline and its derivatives, preferably in the presence of fused zinc chloride, for the production of triphenylmethane dyes. A. A. E.

δ -Methylornithine and δ -Methylarginine. The Origin of Creatine. IV. K. THOMAS, J. KAPFFHAMMER, and B. FLASCHEN-TRÄGER (*Z. physiol. Chem.*, 1922, 124, 75—102).—Methylarginine, administered to rabbits, does not increase the total creatinine in the urine. The methylarginine required for the experiments was prepared from δ -benzoylornithine (Sørensen, A., 1905, i, 600), which is obtained from ornithuric acid, but is contaminated with 3-benzoylamido-2-piperidone, long, white needles, m. p. 184°. On treatment with *p*-toluenesulphonyl chloride and alkali δ -*p*-toluenesulphonyl- α -benzoylornithine, $C_7H_7 \cdot SO_2 \cdot NH \cdot [CH_2]_3 \cdot CH(NHBz) \cdot CO_2H$, is formed, fine, white needles, m. p. 160—164° (decomp.). If too little alkali be used, 1-*p*-toluenesulphonyl-3-benzoylamido-piperidone, white needles, m. p. 184°, is obtained as a by-product. Methylation of δ -*p*-toluenesulphonyl- α -benzoylornithine with methyl sulphate yields δ -*p*-toluenesulphonyl- α -benzoyl- δ -methylornithine, needles, m. p. 188—189°. Hydrolysis of this compound with acid yields δ -*p*-toluenesulphonyl- δ -methylornithine, thin plates, decomp. 245° (*hydrochloride*, glistening plates, m. p. 288°), whilst reduction with hydriodic acid and phosphonium iodide at 50—60° yields α -benzoyl- δ -methylornithine, $NHMe \cdot [CH_2]_3 \cdot CH(NHBz) \cdot CO_2H$, a microcrystalline white powder, m. p. 215°. On hydrolysis, dl-*methylornithine* is formed, isolated as the *dihydrochloride*, microcrystalline needles or crusts of rhombohedra, m. p. 157° (*chloroplatinate*,



m. p. 206°; *monohydrochloride*, m. p. 215—225°). Along with methylornithine is formed 3-amino-1-methyl-2-piperidone, isolated as the *chloroplatinate*, $(C_6H_{12}ON_2)_2 \cdot H_2PtCl_6$, light yellow, rhombic leaflets, m. p. 210° (*picrate*, $C_{12}H_{15}O_8N_5$, m. p. 207°). The reaction of methylornithine and of aminomethylpiperidone with alkaloid precipitants has been investigated, with particular reference to Winterstein's isomeric lysine.

Treatment of methylornithine with a solution of cyanamide in presence of ammonia yields α -benzoyl- δ -methylarginine, decomp. about 265°, and on hydrolysis with acid this yields dl-*methylarginine*, $NH_2 \cdot C(NH) \cdot NMe \cdot [CH_2]_3 \cdot CH(NH_2) \cdot CO_2H$ [*hydrochloride*,

$C_7H_{16}O_2N_4 \cdot 2HCl$, fine needles, aggregated in clumps, decomp. 215° ; *nitrate*, $C_7H_{16}O_2N_4 \cdot 2HNO_3$, rhombic prisms, m. p. 153° ; *cupri-nitrate*, fine, dark blue needles containing water of crystallisation, which on dehydrating have the formula $(C_7H_{16}O_2N_4)_2 \cdot Cu(NO_3)_2$; *picrates*, $C_7H_{16}O_2N_4 \cdot C_6H_3O_7N_3$, felted needles, decomp. $207-209^\circ$, and $C_7H_{16}O_2N_4 \cdot (C_6H_3O_7N_3)_2$, m. p. 145° . *d*-Arginine also gives a *dipicrate*, $C_6H_{14}O_2N_4 \cdot (C_6H_3O_7N_3)_2$, m. p. $198-199^\circ$. Arginase does not act on methylarginine. W. O. K.

The Reduction of Morphine by Emde's Method. FRANZ FALTIS and THEODOR HECZKO (*Monatsh.*, 1922, **43**, 255—267; cf. Faltis and Krausz, A., 1922, i, 676).—In the first part of the paper the influence of structure on the rupture of cyclic quaternary ammonium bases into tertiary bases by treatment with sodium amalgam (Emde's method, *loc. cit.*) is discussed. The course of the reaction is specially influenced, in condensed systems, by the position of a phenyl group in relation to the ring-nitrogen. In the previous paper the reaction was applied to dimethylapomorphine methochloride. It has now been extended to morphine itself in the form of dimethylmorphine methochloride. The product is identical with the α -dimethylmorphimethine previously obtained by Pschorr (A., 1911, i, 908) by Hofmann's method. The rupture of the ring therefore takes place without reduction, and it is further shown that sodium amalgam has no reducing action on α -dimethylmorphimethine methochloride. E. H. R.

The Pilocarpine Series. I. Nitropilocarpine and Nitro-isopilocarpine. MAX POLONOVSKI and MICHEL POLONOVSKI (*Bull. Soc. chim.*, 1922, [iv], **31**, 1027—1045; cf. Jowett, T., 1900, **77**, 851; 1901, **79**, 580 and 1331; 1903, **83**, 438).—Whilst direct nitration of pilocarpine cannot be effected, the action of excess of concentrated sulphuric acid on pilocarpine nitrate gives an 80% yield of *nitropilocarpine*, $NO_2 \cdot C_{11}H_{15}O_2N_2$, hard, white, prismatic needles, m. p. $135-136^\circ$. The introduction of a nitro-group into the molecule causes pilocarpine to lose its basic character. The authors consider it probable that the entering group is attached to the 5-carbon atom in the iminazole ring. The substance is stable towards many reagents, and does not undergo isomerisation on being heated; it is attacked, however, by alkalis, being partly delactonised and partly isomerised, the change taking place very rapidly in cold alcoholic solution. The alkaline solution on acidification with acetic acid yields a white, crystalline precipitate of *nitropilocarpic acid*, $NO_2 \cdot C_{11}H_{17}O_3N_2$, m. p. 199° , which loses water on being heated at $200-205^\circ$, forming nitropilocarpine. The sodium and barium salts were prepared. Reduction of nitropilocarpine may be effected by various means; three molecules of hydrogen being utilised per molecule of alkaloid, but no reduction derivative was isolated. The stability of pilocarpine is considerably modified by introduction of the nitro-group; the nitro-derivative on prolonged boiling with excess of baryta water is decomposed with formation of barium cyanide and formate and the barium salts of pilopic and homopilopic acids, together with other

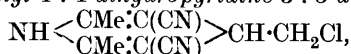
substances. The reaction is very complex owing to the formation of intermediate substances which react further, giving rise to secondary products. Pilopic and homopilopic acids may function either as monobasic, lactonic, or dibasic acids. Barium salts of the former type are obtained from the action of barium carbonate on the acid with subsequent filtration and evaporation to dryness, of the latter on heating the acid with baryta water, excess of which is eliminated with carbon dioxide. The constitution of pilocarpine is discussed but is not yet completely elucidated.

Nitroisopilocarpine, prepared similarly to nitropilocarpine, crystallises in small, white prisms, m. p. 93–94°, and forms salts with dilute alkalis, but is readily relactonised, yielding the original substance. Pilocarpine and *isopilocarpine* suffer similar decompositions with formation of the same products, but there is this difference, homopilopic acid appears to be formed in greater quantity from pilocarpine than is pilopic from nitropilocarpine; with the isomeride and its nitro-derivative the converse is the case. No evidence as to the nature of the isomerism was obtainable from the decomposition products, but it is pointed out that prolonged heating with baryta water may transform nitropilocarpine into its isomeride as a preliminary to decomposition. Both substances, however, yield methylamine at the outset, so that if isomerisation occurs, as suggested, the change affects, not the original substances, but their primary decomposition products. H. J. E.

Phosphates of Strychnine. J. BOUILLLOT (*J. Pharm. Chim.*, 1922, [vii], 26, 406–415).—Strychnine forms two phosphates by the direct union of the acid and the base under suitable conditions. The monobasic phosphate of the formula $C_{21}H_{22}O_2N_2 \cdot H_3PO_4 \cdot 2H_2O$ was obtained by dissolving 3.34 g. of strychnine in 100 c.c. of water containing the calculated quantity of phosphoric acid. On cooling, the salt crystallised in fine needles. The dibasic salt, $(C_{21}H_{22}O_2N_2)_2 \cdot H_3PO_4 \cdot 9H_2O$, was obtained by combination of the theoretical amounts of strychnine and phosphoric acid in 80% alcohol. The hot solution slowly deposited the salt in glistening leaflets. It is but slightly soluble in water, and is partly dissociated by this solvent into the monobasic phosphate and free strychnine. It has $[\alpha]_D -43.13^\circ$ in 80% alcohol. A tribasic phosphate could not be obtained, a solution of the acid and base in the requisite proportions depositing only crystals of the dibasic salt and strychnine. G. F. M.

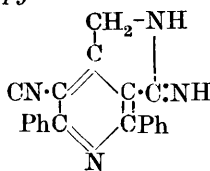
Derivatives of Pyridine obtained from Diacetonitrile and Benzoacetodinitrile. ERICH BENARY and GERTRUD LÖWENTHAL (*Ber.*, 1922, 55, [B], 3429–3434).—In a previous communication (Benary, A., 1921, i, 127), the transformation of ethyl 2:6-dimethyl-4-cyanomethyl-1:4-dihydropyridine-3:5-dicarboxylate into ethyl 5-methyl-3-cyanomethylpyrrole-2-carboxylate has been described. A number of compounds which might possibly suffer a similar conversion of the pyridine into the pyrrole ring have now been examined, but in no case has this change been observed, so that the reaction does not appear to be general.

Imidoacetoacetonitrile and $\alpha\beta$ -dichloroethyl ether yield 2:6-dimethyl-4-chloromethyl-1:4-dihydropyridine-3:5-dicarboxylonitrile,



colourless leaflets, m. p. 170° , which is transformed by a solution of potassium cyanide in methyl alcohol into a mixture of 2:6-dimethyl-4-cyanomethyl-1:4-dihydropyridine-3:5-dicarboxylonitrile, colourless crystals, m. p. 220° , and (?) 2:6-dimethyl-4-carbamido-methyl-1:4-dihydropyridine-3:5-dicarboxylonitrile, colourless leaflets, m. p. 109° . 2:6-Dimethyl-4-cyanomethylpyridine-3:5-dicarboxylonitrile, colourless leaflets, m. p. 230° (decomp.), is conveniently prepared by the action of sodium nitrite on a solution of the corresponding dihydro-compound in glacial acetic acid. The oxidation of 2:6-dimethyl-4-chloromethyl-1:4-dihydropyridine-3:5-dicarboxylonitrile to the pyridine derivative cannot be effected by reason of the unusual lability of the chlorine atom; the action of sodium nitrite on a solution of the compound in glacial acetic acid leads to the production of 3:5-dicyano-2:6-dimethyl-1:4-dihydropyridine-4-aldoxime, $\text{NH} \begin{array}{c} \text{CMe:C(CN)} \\ \text{CMe:C(CN)} \end{array} > \text{CH} \cdot \text{CH} \cdot \text{NOH}$, prismatic needles, decomp. 161° after darkening at about 157° , which is further characterised by its conversion into a benzoate, colourless needles or leaflets, m. p. 186° after softening at 176° , and an acetate, long, colourless needles, m. p. 115° .

2:6-Diphenyl-4-chloromethyl-1:4-dihydropyridine-3:5-dicarboxylonitrile, $\text{NH} \begin{array}{c} \text{CPh:C(CN)} \\ \text{CPh:C(CN)} \end{array} > \text{CH} \cdot \text{CH}_2\text{Cl}$, colourless leaflets, m. p. 235° , prepared from $\alpha\beta$ -dichlorodiethyl ether and imidobenzoylacetonitrile, is not affected by sodium nitrite and glacial acetic acid, but is oxidised by nitric acid to 2:6-diphenyl-4-chloromethylpyridine-3:5-dicarboxylonitrile, long, colourless needles, m. p. 177° . The chlorodihydro-compound is converted by an alcoholic solution of potassium cyanide into 2:6-diphenyl-4-cyanomethyl-1:4-dihydropyridine-3:5-dicarboxylonitrile, pale brown leaflets, m. p. 185° .



Boiling aqueous potassium hydroxide solution converts 2:6-diphenyl-4-chloromethylpyridine-3:5-dicarboxylonitrile into 2:6-diphenyl-4-hydroxymethylpyridine-3:5-dicarboxylonitrile, colourless, slender needles, m. p. 176° , whereas alcoholic ammonia transforms it into a substance, pale brown needles, m. p. 198° , to which, on account of the absence of basic properties, the annexed constitution is ascribed.

H. W.

Some δ -Ketonic Nitriles and their Relation to Cyclic Compounds. E. P. KOHLER, ALICE GRAUSTEIN, and D. R. MERRILL (*J. Amer. Chem. Soc.*, 1922, **44**, 2536—2556; cf. A., 1922, i, 461).—In the presence of a small amount of sodium methoxide and in very dry methyl alcohol, methyl cyanoacetate combines with $\alpha\beta$ -unsaturated ketones and forms γ -ketonic nitriles. In indifferent media, these are rapidly converted by the action of halogen acids

into equilibrium mixtures containing small quantities of these nitriles mixed with isomeric tetrahydropyridine derivatives. This process takes place very rapidly, so that the open-chain compounds and their cyclic isomerides give the same products in reactions that take place in the presence of acids. Where bases are used, the products obtained from the two types are different. The cyclic compounds react very readily with the halogens and by alternately introducing halogen and eliminating halogen acid it is possible to go step by step from the tetrahydropyridine derivative to true pyridines. With the open-chain compounds, the action of halogens results in a mixture of a great number of open-chain and cyclic halogenated compounds, but the action can be controlled. Halogenation in the presence of potassium acetate gives open-chain compounds only, whilst the same process in glacial acetic acid gives mainly a true pyridine derivative. These reactions have been studied in the case of phenyl styryl ketone and *p*-chlorophenyl styryl ketone. The products from the two ketones behave alike, but the products from the chloro-derivatives generally are less fusible and less soluble than those from the chlorine-free substance.

Phenyl styryl ketone and methyl cyanoacetate condense together to give *methyl α-cyano-γ-benzoyl-β-phenylbutyrate*,
 $\text{COPh} \cdot \text{CH}_2 \cdot \text{CHPh} \cdot \text{CH}(\text{CN}) \cdot \text{CO}_2\text{Me}$,

m. p. 76° , together with some of the trimolecular compound, m. p. 226° , formed by the addition of a second molecule of the unsaturated ketone. *Methyl α-cyano-γ-p-chlorobenzoyl-β-phenylbutyrate*, m. p. 126° , and the trimolecular compound, m. p. $230-232^\circ$, were similarly prepared. Using methyl α-cyanopropionate instead of the cyanoacetate, the product in the latter case was *methyl α-cyano-γ-p-chlorobenzoyl-β-phenyl-α-methylbutyrate*, in two stereoisomeric forms, m. p. 108° and 92° , respectively. When hydrolysed in acid medium the esters described above give ester acids, but when carefully hydrolysed with alcoholic potash the cyano-acid is the product. The compounds described are *methyl hydrogen γ-benzoyl-β-phenylethylmalonate*, m. p. 160° (decomp.), *α-cyano-γ-benzoyl-β-phenylbutyric acid*, m. p. 160° (decomp.), and *γ-benzoyl-β-phenylbutyronitrile*, m. p. 76° , obtained by decomposing the latter at 200° .

The tetrahydropyridine derivatives described are *methyl 6-keto-2:4-diphenyltetrahydropyridine-5-carboxylate*, m. p. $165-166^\circ$, and the free acid, m. p. 130° (decomp.); *6-keto-2:4-diphenyltetrahydropyridine*, m. p. 130° ; *methyl 6-keto-4-phenyl-2-p-chlorophenyltetrahydropyridine-5-carboxylate*, m. p. 204° . On careful bromination, these tetrahydropyridine derivatives give monobromo-derivatives, but if the bromination is conducted at too high a temperature the product is contaminated with the corresponding dihydropyridine derivative. *Methyl 3-bromo-6-keto-2:4-diphenyltetrahydropyridine-5-carboxylate* had m. p. $160-161^\circ$, and, on digestion with sodium methoxide in methyl alcohol, gives *methyl 6-hydroxy-2:4-diphenylpyridine-5-carboxylate*, the free acid of which has m. p. 253° (decomp.) and on heating at 260° decomposes, giving 6-hydroxy-2:4-diphenylpyridine. The monobromo-ester described above on further

bromination yields *methyl 3:5-dibromo-6-keto-2:4-diphenyltetrahydropyridine-5-carboxylate*, m. p. 160° (decomp.) and when a solution of this compound in dry methyl alcohol is rapidly saturated with hydrogen bromide it gives ammonium bromide, *methyl $\alpha\gamma$ -dibromobenzoylphenylethylmalonate*, and *methyl $\alpha\gamma$ -dibromo- γ -benzoyl- β -phenylethylmalonamate*, m. p. 180°, an isomeride, m. p. 140°, of which was obtained during the earlier bromination. These two isomerides were decomposed on heating, giving *4-bromo-4-cyano-2-benzoyl-3-phenyltetrahydrofuran*, m. p. 275°. If the further bromination described above is carried out in boiling chloroform, the dibromo-compound loses hydrogen bromide and forms *methyl 3-bromo-6-hydroxy-2:4-diphenylpyridine-5-carboxylate*, m. p. 238—240°, which does not undergo further bromination, but gives a *perbromide*. The free acid has m. p. 270° (decomp.), and on heating gives *3-bromo-6-hydroxy-2:4-diphenylpyridine*. Similar bromination products from the *p*-chlorophenyl derivatives are *methyl 3-bromo-6-keto-4-phenyl-2-p-chlorophenyltetrahydropyridine-5-carboxylate*, m. p. 194°, *methyl 3:5-dibromo-6-keto-4-phenyl-2-p-chlorophenyltetrahydropyridine-5-carboxylate*, m. p. 183°, and *methyl 6-hydroxy-4-phenyl-2-p-chlorophenylpyridine-5-carboxylate*, m. p. 262°.

Bromination of the methyl cyanoacetate additive products in the presence of potassium acetate gave the following compounds: *methyl α -bromo- α -cyano- γ -benzoyl- β -phenylbutyrate*, m. p. 130°; *methyl $\alpha\gamma$ -dibromo- α -cyano- γ -benzoyl- β -phenylbutyrate*, m. p. 177—179°; *methyl α -bromo- α -cyano- γ -p-chlorobenzoyl- β -phenylbutyrate*, in the form of two isomerides, m. p. 91—92° and 123°, respectively; *methyl $\alpha\gamma$ -dibromo- α -cyano- γ -p-chlorobenzoyl- β -phenylbutyrate*, m. p. 193°. Products of bromination in glacial acetic acid are: *methyl 6-bromo-2:4-diphenylpyridine-5-carboxylate*, m. p. 147°, and its free acid, m. p. 206—208°; *methyl 6-bromo-4-phenyl-2-p-chlorophenylpyridine-5-carboxylate*, m. p. 106°.

Chlorination of the same additive products in chloroform solution gave excellent yields of open-chain substitution products. In this way, the authors prepared *methyl α -chloro- α -cyano- β -phenyl- γ -p-chlorophenylbutyrate*, obtained in two stereoisomeric forms, m. p. 80° and 106°, respectively. A chloroform solution of the isomeride with the higher m. p. when saturated with hydrogen bromide and boiled for several hours gave a compound, m. p. 197° (decomp.), which is probably *methyl 5-chloro-6-keto-4-phenyl-2-p-chlorophenyltetrahydropyridine-5-carboxylate*. This ester reacts readily with chlorine and passes into *methyl 3-chloro-6-hydroxy-4-phenyl-2-p-chlorophenylpyridine-5-carboxylate*, m. p. 196°, and on further chlorination into *methyl 3:4:5-trichloro-6-keto-4-phenyl-2-p-chlorophenyltetrahydropyridine-3-carboxylate*.

*cyclo*Propane derivatives are obtained by heating the α -bromoesters described above with potassium acetate in a suitable solvent; by removing hydrogen chloride from α -chloro-compounds, or by eliminating bromine from $\alpha\gamma$ -dibromo-compounds with potassium iodide. These processes gave stereoisomeric *cyclo*propane derivatives of which the following are described: *methyl 1-cyano-*

3-benzoyl-2-phenylcyclopropane-1-carboxylate, the three isomeric forms of which had m. p. 106° , 110° , and $178-180^{\circ}$, respectively; the *free acid*, m. p. 230° (decomp.), corresponding with these esters, and *methyl 1-cyano-2-phenyl-3-p-chlorophenylcyclopropane-1-carboxylate*, the two isomeric forms of which had m. p. 132° and 180° , respectively.

W. G.

α -Diketones of the Indole Group. I. G. SANNA (*Gazzetta*, 1922, 52, ii, 165—170).—In addition to the products already described (Oddo and Sanna, A., 1922, i, 371), the action of oxalyl chloride on magnesium indolyl bromide yields 2:2-indil, 2:3-indil, and 1:2-indil; 3:3-indil is also formed in traces, in some cases, but not at all in others.

3:3-*Indilphenylosazone*, $[C_8H_6N \cdot C(:N \cdot NHPh)]_2$, crystallises in yellow prisms, m. p. 158° (decomp.), and when heated with alcohol and ferric chloride undergoes oxidation to the corresponding osotetrazone.

2:3-*Di-3'-indolylquinoxaline*, $C_6H_4 \begin{smallmatrix} N:C-C_8H_6N \\ N:C-C_8H_6N \end{smallmatrix}$, obtained by the condensation of 3:3-indil with *o*-phenylenediamine, forms masses of brick-red prisms, m. p. 163° (decomp.), and gives the general reactions of the quinoxalines.

3:3-Indil forms a *silver* derivative, $C_{18}H_{10}O_2N_2Ag_2$, as a grey precipitate, and yields indole-3-carboxylic acid when oxidised by means of hydrogen peroxide.

2:2-*Indil* (2:2-*di-indoyl*), $C_{18}H_{12}O_2N_2$, forms pale yellow, tabular prisms, m. p. 273° , and has the normal molecular weight in freezing acetic acid. The *phenylosazone*, $C_{30}H_{24}N_6$, crystallises in yellow, tabular prisms, m. p. 170° (decomp.), and is oxidised by ferric chloride to the corresponding osotetrazone. When oxidised by means of hydrogen peroxide or fused with potassium hydroxide, 2:2-indil yields indole-2-carboxylic acid.

2:3-*Di-2'-indolylquinoxaline*, $C_{24}H_{16}N_4$, crystallises in tufts of red, acicular prisms, m. p. 154° (decomp.), and shows the general reactions of the quinoxalines.

Bis-1:2-indil (*bis-1:2-di-indoyl*) (annexed formula), also obtained from the products of the action of oxalyl chloride on magnesium indolyl bromide, crystallises in yellow scales, m. p. 320° ; when heated in a reflux apparatus with concentrated potassium hydroxide, it yields 2:2-indil, and when fused with potassium hydroxide, indole-2-carboxylic acid.

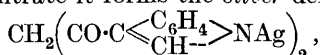
A compound, forming white crystals, m. p. 163° , also occurs among the products of the reaction, but has not been characterised.

T. H. P.

Syntheses of β -Diketones in the Indole Group. I. G. SANNA (*Gazzetta*, 1922, 52, ii, 170—176).—The action of malonyl chloride on magnesium indolyl bromide proceeds similarly to that on magnesium pyrrol bromide (Oddo and Dainotti, A., 1912,

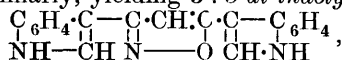
i, 721) and yields di-3-indoylmethane. In many of its reactions this compound behaves, like all β -diketones, as a hydroxy-ketone, but in the solid state and also in solution it appears to exist principally in the normal diketonic form, being transformed, slowly at the ordinary temperature but rapidly when heated, into the keto-enolic modification. Attempts to separate the two tautomeric forms were unsuccessful, but indicated great stability in the normal modification. Since only the 3:3'-compound was obtained in the above reaction, the greater length of the chain in malonyl chloride appears to enhance the tendency to attack in the position of the indole nucleus most remote from the imino-group.

Di-3-indoylmethane, $\text{CH}_2(\text{CO} \cdot \text{C} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CH} \end{smallmatrix} \text{NH})_2$, crystallises in cotton-like masses of minute, white needles, blackening at about 230° , m. p. 287° (decomp.), and is highly resistant to the action of alkali hydroxide or concentrated sulphuric acid. In alcoholic solution it gives with ferric chloride an immediate emerald-green coloration, which tends to darken and to assume a violet reflection. With cupric acetate in alcoholic solution, it gives a greenish-yellow liquid which, on cooling, deposits the *copper* salt, $(\text{C}_{19}\text{H}_{12}\text{O}_2\text{N}_2)_2\text{Cu}$, crystallising in brownish-red prisms, m. p. 254° (decomp.). With ammoniacal silver nitrate it forms the *silver* derivative,



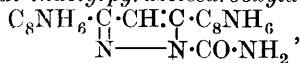
as a white, curdy precipitate; the formation of this compound shows that the hydrogen replaced by the chain is not the iminic hydrogen. Hydrolysis of di-indoylmethane by means of alkali hydroxide yields indole-3-carboxylic acid and 3-indolyl methyl ketone (3-acetylindole).

Di-indoylmethane reacts readily with phenylhydrazine, giving the dehydration product of the monophenylhydrazone, namely, 1-phenyl-3:5-di-indolylpyrazole, $\text{C}_6\text{H}_4 \cdot \text{C} \begin{smallmatrix} | \\ \text{NH} \end{smallmatrix} \text{---} \text{C} \begin{smallmatrix} | \\ \text{CH} \end{smallmatrix} \text{---} \text{C} \begin{smallmatrix} | \\ \text{NPh} \end{smallmatrix} \text{---} \text{C} \begin{smallmatrix} | \\ \text{CH} \end{smallmatrix} \text{---} \text{C}_6\text{H}_4$, which crystallises in yellow prisms resembling knife-blades, m. p. 236° (decomp.), and is converted into the corresponding pyrazoline base when reduced by means of sodium. The reaction with hydroxylamine proceeds similarly, yielding 3:5-di-indolylisooxazole,



which crystallises in yellow prisms, m. p. 219° (decomp.), and exhibits feebly basic properties; restriction of the action of the hydroxylamine results in the formation of a compound which crystallises in slender, red needles, m. p. about 170° (decomp.), and is possibly the mono-oxime of the diketone, as it exhibits reducing properties and yields di-indoylmethane when boiled with dilute hydrochloric acid.

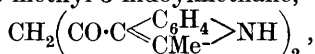
Condensation of di-indoylmethane with semicarbazide results in the formation of *di-indolylpyrazolecarboxylamide*,



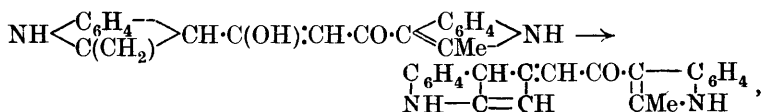
which then takes up a molecule of water and loses ammonia and carbon dioxide, giving 3:5-di-indolylpyrazole, $\text{C}_8\text{NH}_6 \cdot \text{C} \cdot \text{CH} : \text{C} \cdot \text{C}_8\text{NH}_6$, $\begin{smallmatrix} \text{N} & \text{---} & \text{NH} \\ | & & | \end{smallmatrix}$, which forms yellow crystals, m. p. 229° (decomp.), and on reduction with sodium yields the corresponding pyrazoline; the latter, like 1-phenyl-3:5-di-indolylpyrazole, gives a violet coloration with sulphuric acid and potassium dichromate; and a bright purple coloration with nitrous acid.

T. H. P.

Syntheses of β -Diketones in the Indole Group. II. G. SANNA (*Gazzetta*, 1922, 52, ii, 177—184; cf. preceding abstract).—The action of malonyl chloride on magnesium 2-methylindolyl bromide yields di-2-methyl-3-indoylmethane,



which is closely analogous to its lower homologue and exhibits all the reactions characteristic of the β -diketones. It dissolves readily in cold alkali hydroxide solution and is reprecipitated unchanged on addition to the solution of dilute sulphuric acid. With ferric chloride, its alcoholic solution gives an intense emerald-green coloration quickly changing to violet. When boiled with alkali hydroxide solution it gives 2-methylindole-3-carboxylic acid and 2-methyl-3-indolyl methyl ketone, and with phenylhydrazine, hydroxylamine, and semicarbazide it reacts similarly to the lower homologue. The above compound, which must be regarded as the hydroxyketonic form, $\cdot \text{C} \cdot \text{C}(\text{OH}) : \text{CH} \cdot \text{CO} \cdot$, is accompanied by an isomeride which is insoluble in alkali hydroxide solution, yields no coloration in the cold with ferric chloride, is not precipitated by cupric acetate or esterified by phenylcarbimide, and appears to be the normal diketonic form containing the grouping $\cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO} \cdot$. In addition to these two compounds, a third, which is formed in small proportion, has the composition of an anhydro-compound and may be formed by dehydration of the mixed keto-enolic modification :



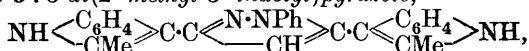
or may represent the result of condensation between the dimethyl-indoylmethane (1 mol.) and 2-methylindole (2 mols.).

Di-2-methyl-3-indoylmethane crystallises in yellow, rhombohedral plates, m. p. 219°, and has the normal molecular weight in freezing acetic acid. The hydroxy-ketonic *tautomeride* forms a yellow, microcrystalline powder or prismatic rods, m. p. 219°, and has the calculated molecular weight in freezing acetic acid, but differs from the preceding compound in its solubility in organic solvents.

From the latter compound the following derivatives are obtainable. The *cupric* derivative, $\text{C}_{21}\text{H}_{16}\text{O}_2\text{N}_2\text{Cu}$, forms a yellow powder

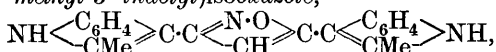
or octahedra with violet reflection, m. p. 220° (decomp.); the silver derivative, $C_{21}H_{16}O_2N_2Ag_2$, was also prepared.

1-Phenyl-3 : 5-di(2'-methyl-3'-indolyl)pyrazole,



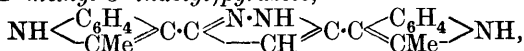
obtained by condensation with phenylhydrazine, crystallises in serrate aggregates of pale yellow prisms, m. p. 192° (decomp.), and on reduction by means of sodium gives the pyrazoline base, $NH \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{CMe} \end{array} \gg C \cdot C \begin{array}{c} \text{N} \cdot \text{NPh} \\ \text{CH}_2 \end{array} \gg CH \cdot C \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{CMe} \end{array} \gg NH$, which, in sulphuric acid solution, gives a bright violet coloration with dichromate or with nitrite.

3 : 5-Di(2'-methyl-3'-indolyl)isooxazole,



prepared by the action of hydroxylamine, crystallises in pale yellow prisms, m. p. 174° (decomp.), and exhibits basic properties more marked than those of the corresponding indole derivative; its hydrochloric acid solution is rendered turbid by ammonia, platinum chloride, or auric chloride.

3 : 5-Di(2'-methyl-3'-indolyl)pyrazole,



obtained by condensation with semicarbazide, crystallises in minute, yellow needles, m. p. 247° (decomp.), and is reduced by sodium to the corresponding pyrazoline derivative, which yields violet colorations when treated in sulphuric acid solution with dichromate or sodium nitrite.

The *anhydro*-compound (see above), $C_{21}H_{18}O_2N_2 \cdot H_2O$, forms short, stout, yellow, hexagonal prisms, m. p. 224° (decomp.).

T. H. P.

Conversion of β -Phenylhydroxylamine into Quinoline Bases.

E. BAMBERGER and H. WEITNAUER (*Ber.*, 1922, **55**, [B], 3376—3382).—Quinoline is prepared in very small yield by the action of glycerol and sulphuric acid on β -phenylhydroxylamine (cf. Hindermann, *Diss. Zurich*, 1897). Replacement of glycerol by acraldehyde, which is generally assumed to be an intermediate product in Skraup's synthesis of quinoline, leads to slightly better results. The intermediate *nitron*, $O:NPh:CH:CH:CH_2$, could only be isolated in an impure, amorphous, resinous form; when heated at a relatively somewhat high temperature and subsequently treated with dilute sulphuric acid, it gives quinoline in quantity which never exceeds 5% of that theoretically possible. Crotonaldehyde and β -phenylhydroxylamine give 2-methylquinoline. Cinnamaldehyde condenses with phenylhydroxylamine to give phenylacryl-*N*-phenylnitron, $O:NPh:CH:CH:CHPh$, yellow needles, m. p. 155—156°, when rapidly heated, which is transformed by a little concentrated sulphuric acid in the presence of glacial acetic acid into 2-phenylquinoline, m. p. 82.5—83°.

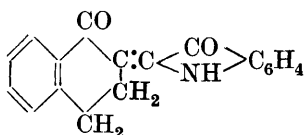
The present synthesis differs from that of Skraup in that it is

not necessary to provide an external source of the necessary oxygen atom, the latter being contained in the phenylhydroxylamine.

H. W.

Reactivity of Methyl Groups in Heterocyclic Bases. WILLIAM HOBSON MILLS and JAMES LEONARD BRIERLEY SMITH (T., 1922, 121, 2724—2737).

Dyes Derived from α -Ketotetrahydronaphthalene [α -Tetralone]. WALTER HERZOG and J. KREIDL (*Ber.*, 1922, 55, [B], 3394—3400).—2-Tetrahydronaphthalene-2'-indoleindigotin [1-Keto-2 : (2')-indoxyltetrahydronaphthalene] (annexed formula) is obtained



when equivalent quantities of α -ketotetrahydronaphthalene and α -isatinanil are heated under a reflux condenser in the presence of light petroleum (b. p. 150—200°). It forms bluish-violet crystals with a bronze reflex, decomp.

about 250°. It is transformed by fuming sulphuric acid into a *sulphonic acid* which gives a pure blue solution in water. With alkali and hyposulphite, it yields a yellow vat from which wool and cotton are dyed in pure blue tones. 1-Keto-2 : 3'-oxy-2'-thionaphthentetrahydronaphthalene, reddish-violet needles, decomp. about 250°, is prepared by the action of 2-ketotetrahydronaphthalene on α -thionaphthenquinoneanil in boiling acetic anhydride solution. It is sulphonated by fuming sulphuric acid. With alkali and hyposulphite, it gives a greenish-yellow vat from which wool is dyed in dark brownish-violet, cotton in reddish-violet shades. Attempts to condense α -ketotetrahydronaphthalene with β -isatinanil were unsuccessful.

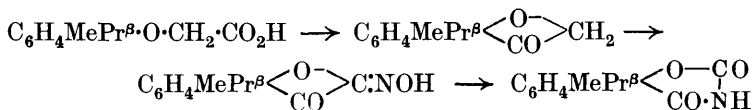
α -Ketotetrahydronaphthalene reacts with terephthalaldehyde in alcoholic solution in the presence of sodium hydroxide to yield the compound $C_6H_4 \left\langle \begin{array}{c} CO \\ | \\ CH_2 \cdot CH_2 \end{array} \right\rangle C_6H_4 \cdot CH : C \left\langle \begin{array}{c} CO \\ | \\ CH_2 \cdot CH_2 \end{array} \right\rangle C_6H_4$, straw-yellow crystals, m. p. (indefinite) 240—255° after darkening at 230°, from which a vat could not be obtained. α -Ketotetrahydronaphthalene, terephthalaldehyde, and 3-hydroxythionaphthen yield mainly a *substance*, small golden-yellow needles, m. p. 192—193° (the constitution of which has not yet been elucidated), and in minor amount the dye $C_6H_4 \left(CH : C \left\langle \begin{array}{c} CO \\ | \\ S \end{array} \right\rangle C_6H_4 \right)_2$.

Cinnamaldehyde and α -ketotetrahydronaphthalene yield β -cinnamylidene- α -ketotetrahydronaphthalene, $C_6H_4 \cdot CO \left\langle \begin{array}{c} CH_2 \cdot CH_2 \end{array} \right\rangle C : CH \cdot CH : CHPh$, large, yellow leaflets, m. p. 132—134°, which becomes polymerised at 220—230°.

H. W.

1 : 3-Benzoxazine. I. Conversion of Oximinocoumaranones into 1 : 3-Benzoxazine Derivatives. EFISIO MAMELI (*Gazzetta*, 1922, 52, ii, 184—189).—4-Methyl-7-isopropyl-3-coumaranone, obtained from thymoxyacetic acid, when treated with nitrous acid, gives 2-oximino-4-methyl-7-isopropylecoumaranone,

which is converted by the action of phosphorus pentachloride into 2 : 4-diketo-5-methyl-8-isopropyl-1 : 3-benzoxazine :



This reaction represents the ordinary Beckmann transposition of the type $\text{R} \cdot \text{C} \begin{array}{c} \text{CO} \cdot \text{R}' \\ \text{NOH} \end{array} \rightarrow \text{R} \cdot \text{C} \begin{array}{c} \text{OH} \\ \text{N} \cdot \text{CO} \cdot \text{R}' \end{array} \rightarrow \text{R} \cdot \text{C} \begin{array}{c} \text{CO} \\ \text{NH} \cdot \text{CO} \cdot \text{R}' \end{array}$ which

has been observed, together with that of the type $\text{R} \cdot \text{C} \begin{array}{c} \text{CO} \cdot \text{R}' \\ \text{NOH} \end{array} \rightarrow$

$\text{R} \cdot \text{C} \begin{array}{c} \text{COR}' \\ \text{N} \end{array} + \begin{array}{c} \text{COR}' \\ \text{OH} \end{array}$, with certain other nitrosoketones. The action of phosphorus pentachloride on cyclic oximinoketones, such as oximinocamphor and oximinohydrindones, results in the opening of the nucleus.

The above transposition is the first observed instance of the transformation of a pentagonal furan ring into a hexagonal oxazine ring. The constitution of 2:4-diketo-5-methyl-8-isopropyl-1:3-benzoxazine is confirmed by its conversion, when heated with dilute aqueous or alcoholic sodium hydroxide solution, into *o*-thymotamide, which was prepared also by the action of ammonia on ethyl thymotate.

2 : 3-Diketo-5-methyl-8-isopropyl-1 : 3-benzoxazine, $\text{C}_{12}\text{H}_{13}\text{O}_3\text{N}$, crystallises in a mass of slender, white needles or scales, m. p. 152—153°, decomposing at 177°, and with ferric chloride in either aqueous or benzene solution gives no coloration in the cold and a straw-yellow coloration when heated; it yields no coloration with concentrated sulphuric acid and is not precipitated by picric acid in alcoholic solution. The potassium salt, $\text{C}_{12}\text{H}_{12}\text{O}_3\text{NK}$, forms a voluminous, white precipitate, the methyl ester, white needles, m. p. 129°, and the ethyl ester, a white, crystalline powder, m. p. 104°.

o-Thymotamide, $\text{OH} \cdot \text{C}_6\text{H}_2\text{MePr}^\beta \cdot \text{CO} \cdot \text{NH}_2$, forms bundles of white needles, m. p. 137°, decomposing at 205°, and gives with ferric chloride a blue coloration in aqueous solution and a green or violet coloration, changing to reddish-violet when heated in benzene solution. It remains unchanged when boiled with concentrated hydrochloric acid, gives no coloration with sulphuric acid, and is not precipitated by picric acid in alcoholic solution. T. H. P.

Dyes derived from $\alpha\alpha'$ -Dicyanodibenzyl Diketone. SIKHI-BHUSHAN DUTT and NIRMAL KUMAR SEN (T., 1922, 121, 2663—2667).

The Substituted Thiocarbamides. III. The Synthesis of Thiazolidine and Thiazan Derivatives. F. B. DAINS, R. Q. BREWSTER, J. S. BLAIR, and W. C. THOMPSON (*J. Amer. Chem. Soc.*, 1922, 44, 2637—2643).—Arylallylamines react with thiocarbimides to give α -allyl- $\alpha\beta$ -diarylthiocarbamides, and these, by the action of acetyl chloride or on heating with hydrochloric acid, suffer rearrangement to 2 : 3-disubstituted thiazolidines. The

following are described. $\alpha\beta$ -Diphenyl- α -allylthiocarbamide, m. p. 91° ; α -phenyl- β -p-bromophenyl- α -allylthiocarbamide, m. p. 123° ; α -phenyl- β -p-tolyl- α -allylthiocarbamide, m. p. 107° ; β -phenyl- α -p-tolyl- α -allylthiocarbamide, m. p. 91.5° ; β -p-bromophenyl- α -p-tolyl- α -allylthiocarbamide, m. p. 121° ; $\alpha\beta$ -di-p-tolyl- α -allylthiocarbamide, m. p. 113° ; 2-phenylimino-3-phenyl-5-methylthiazolidine, m. p. 98° , and its *picrate*, m. p. 168 — 169° ; 2-p-bromophenylimino-3-phenyl-5-methylthiazolidine, m. p. 106° ; 2-p-tolylimino-3-phenyl-5-methylthiazolidine, an oil, and its *picrate*, m. p. 188° ; 2-phenylimino-3-p-tolyl-5-methylthiazolidine, m. p. 72 — 73° , and its *picrate*, m. p. 164 — 166° ; 2-p-bromophenylimino-3-p-tolyl-5-methylthiazolidine, m. p. 81° , and 2-p-tolylimino-3-p-tolyl-5-methylthiazolidine, an oil, and its *picrate*, m. p. 140° .

Arylaminoethanols were also found to unite with arylthiocarbimides and arylcarbimides, and the resulting thiocarbamides and carbamides either by the action of heat alone or under the influence of halogen acids lost water and formed thiazolidines and oxazolidines of known structure. New compounds thus prepared are 2-o-tolylimino-3-phenylthiazolidine, m. p. 94° ; 2-p-tolylimino-3-phenylthiazolidine, m. p. 113° ; 2-phenylimino-3-o-tolylthiazolidine, m. p. 92° ; and 2-phenylimino-3-phenyloxazolidine, m. p. 124° . In a similar manner, the arylaminopropanols gave thiocarbamides, which, under the influence of acids, condensed to a six-membered thiazan ring. The arylpropanols were obtained by heating trimethylene chlorohydrin with the amine for several hours at 130° . Thus p-tolylamine gave p-tolyl- γ -hydroxypropylamine. Thiocarbamides and thiazans thus prepared are $\alpha\beta$ -diphenyl- α -propanolthiocarbamide, m. p. 130° ; 2-phenylimino-3-phenylthiazan, m. p. 139° ; $\alpha\beta$ -di-p-tolyl- α -propanolthiocarbamide, m. p. 142° ; 2-p-tolylimino-3-p-tolylthiazan, m. p. 111° ; β -phenyl- α -p-tolyl- α -propanolthiocarbamide, m. p. 146° ; α -phenyl- β -p-tolyl- α -propanolthiocarbamide, m. p. 127° ; 2-phenylimino-3-p-tolylthiazan, m. p. 139° , and 2-p-tolylimino-3-phenylthiazan, m. p. 94° .

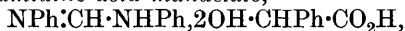
γ -Chloro- α -aryl-amino- β -hydroxypropanes combined with thiocarbimides to give thiocarbamides, which could not be isolated, owing to loss of hydrogen chloride and the consequent closure of the thiazan ring with the production of 5-hydroxythiazans, of which the following are described. 2-Phenylimino-5-hydroxy-3-p-tolylthiazan, m. p. 175° ; 2-p-tolylimino-5-hydroxy-3-p-tolylthiazan, m. p. 142° , and its *hydrochloride*, m. p. 204° , and *picrate*, m. p. 195° ; 2-phenylimino-5-hydroxy-3-p-anisylthiazan, m. p. 157° , and its *picrate*, m. p. 135° ; 2-phenylimino-5-hydroxy-3-p-chlorophenylthiazan, m. p. 171° ; 2-phenylimino-5-hydroxy-3-phenylthiazan, m. p. 175° , and its *picrate*, m. p. 150° , and phenylurethane derivative, m. p. 185° .

W. G.

Isonitriles. IV. Reaction with Organic Acids. M. PASERINI (*Gazzetta*, 1922, 52, ii, 250—257; cf. A., 1921, i, 743, 895; 1922, i, 731).—At the ordinary temperature, aromatic isonitriles [carblyamines] react with certain organic acids yielding carbon monoxide and salts of substituted formamidines. Thus, with benzoic,

mandelic, lactic, and salicylic acids, phenylcarbylamine gives salts of diphenylformamidine composed of two mols. of the acid and one mol. of the base. Acetic acid, however, yields, not diphenylformamidine, but a syrupy liquid probably containing formanilide and possibly also acetanilide. From *p*-carbylaminoazobenzene and lactic acid, the acid lactate of 4 : 4'-bisazobenzeneformamidine is obtained, together with formyl-*p*-aminoazobenzene. The arylformamidine salts formed in these reactions are accompanied by oily compounds which yield aniline and alkali formates when heated with alkali hydroxide and are probably formanilides. According to Nef (A., 1892, 1438), the action of hydrogen chloride on phenylcarbylamine in anhydrous ethereal solution yields the additive compound $(\text{NPh}:\text{CHCl})_2\cdot\text{HCl}$. The formation of this compound is not detectable, although it may occur as an intermediate stage, in the action of hydrogen chloride and acetone or methyl ethyl ketone on phenylcarbylamine or *p*-carbylaminoazobenzene, the only products observed being the monohydrochlorides of the corresponding arylformamidines. Thus, hydrochloric acid in presence of ketones acts like organic acid in absence of ketones or aldehydes.

Diphenylformamidine acid mandelate,



crystallises in colourless needles, m. p. 126° , and, when suspended in water, yields part of its acid to the latter. The *acid lactate*, $\text{C}_{13}\text{H}_{12}\text{N}_2\cdot 2\text{C}_3\text{H}_6\text{O}_3$, forms long, colourless needles, m. p. 136° , and when treated with water, yields the *normal lactate*, which crystallises in colourless needles, m. p. 151° . *Diphenylformamidine salicylate* crystallises in large plates, m. p. 165° , softening at 160° , and the *benzoate* in colourless needles, m. p. $175\text{--}176^\circ$.

4 : 4'-*Bisazobenzeneformamidine acid lactate*, $\text{C}_{25}\text{H}_{20}\text{N}_6\cdot 2\text{C}_3\text{H}_6\text{O}_3$, crystallises in flat, orange needles, m. p. 153° , and the free base, $\text{C}_{25}\text{H}_{20}\text{N}_6$, in lustrous, orange needles, m. p. $196\text{--}197^\circ$.

Diphenylformamidine picrate, $\text{C}_{13}\text{H}_{12}\text{N}_2\cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3$, is formed by the action of picric acid on phenylcarbylamine. T. H. P.

The Additive Formation of Four-membered Rings. I. The Synthesis and Division of Derivatives from 1 : 3-Dimethindiazidine. CHRISTOPHER KELK INGOLD and HENRY ALFRED PIGGOTT (T., 1922, 121, 2793—2804).

Barbituric Acid. WALTER BOCK (*Ber.*, 1922, 55, [B], 3400—3405).—An aqueous solution of barbituric acid gives a bright yellowish-red coloration with a piece of wood. The reaction is shown distinctly at a dilution of 1 in 1000; it is not disturbed by the presence of free mineral acids. Barbituric acids, substituted in position 5, do not appear to give the reaction.

5-Bromobarbituric acid, decomp. $212\text{--}215^\circ$ after previous softening, can be prepared directly from the parent acid dissolved in water and bromine (four-fifths molecular proportion) at $50\text{--}60^\circ$. It is transformed by further treatment with bromine into 5 : 5-dibromobarbituric acid, prisms, decomp. $220\text{--}221^\circ$, or leaflets, decomp. $235\text{--}237^\circ$, which appear to be chemically identical. The

prismatic form is also obtained by the action of bromine on benzylidenobarbituric acid. Whereas the salts of monobromobarbituric acid are stable towards water, the free acid is readily decomposed, yielding mainly hydurilic acid; barbituric acid is also produced, but the presence of parabanic acid could not be established with certainty. 5:5-Dibromobarbituric acid is not greatly affected by a short treatment with boiling water, but by longer action is converted into alloxan and ultimately into hydurilic and barbituric acids; since the latter may be regarded as reduction products of alloxan it appears that other substances arising from the simultaneous oxidation of another part of the latter must also be present.

Aqueous solutions of barbituric acid and *p*-benzoquinone give an intense dark red colour which is perceptible at a dilution of 1 in 10,000. When equivalent proportions of the components are used, a definite product cannot be isolated and the colour disappears after short boiling. When, however, the acid and benzoquinone are taken in the molecular proportion 1:2, a tribasic acid, $C_{26}H_{20}O_{15}N_4$, an amorphous, black powder which decomposes without melting when heated, is obtained (the barium salt was analysed). The quinone appears to act to some extent as an oxidising agent.

H. W.

Nitroso-2-hydroxyindazole. E. BAMBERGER (*Ber.*, 1922, 55, [B], 3371—3375).—In a previous communication, Bamberger and Demuth (A., 1902, i, 650) have shown that 2-hydroxyindazole is obtained by the action of alkali hydroxide on *o*-azidobenzaldoxime, and is converted by nitrous acid into a nitroso-derivative. The latter compound is now proved to be 3-nitroso-2-hydroxyindazole, $C_6H_4 \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{C}(\text{NO}) \end{smallmatrix} \text{N} \cdot \text{OH}$ or $C_6H_4 \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{C}(\text{NO}) \end{smallmatrix} \gg \text{N} \cdot \text{OH}$, since it is converted by reduction with tin foil in the presence of glacial acetic acid into 3-aminoindazole, m. p. 153—154°.

Preliminary experiments appear to show that *o*-hydroxylaminobenzaldoxime is not transformed into 2-hydroxyindazole by the action of alcoholic potash at the atmospheric temperature.

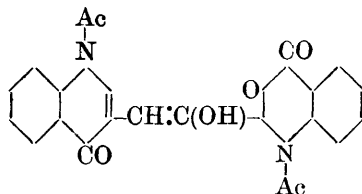
H. W.

Catalytic Reduction of Indigotin. ANDRÉ BROCHET (*Rev. Gen. Mat. Col.*, 1922, 27, 131—136).—Indigotin is rapidly reduced to indigo-white by hydrogenation even at atmospheric pressures, in presence of a reduced nickel catalyst, particularly at slightly elevated temperatures, as, for example, 50—60°, and in presence of sodium hydroxide. The catalyst is added to a suspension of about twice its weight of indigotin in dilute sodium hydroxide solution, and the gas is either bubbled through the liquid with vigorous agitation, or the liquid may be shaken in an atmosphere of the gas. Reduction is complete in one half to one hour, and the nickel recovered from the bleached indigo solution by filtration may be used repeatedly for subsequent hydrogenations. The catalyst retains its activity unimpaired for long periods. Other vat dyes such as “thioindigo,” indanthrene, etc., and also certain

dyes which are not reoxidised by air, such as malachite-green, can in a similar way be converted into their leuco-compounds.

G. F. M.

The Action of Acetic Anhydride on some Furfurylidene-anthranilic Acids. JOHN B. EKELEY and EMMET C. ROGERS (*J. Amer. Chem. Soc.*, 1922, **44**, 2655—2657).—*Furfurylideneanthranilic acid*, m. p. 151° (decomp.) when heated in xylene with excess of acetic anhydride, gave as a final product a compound, m. p. 208°, which is probably the enol form of 1-keto-4-acetyl-3(4': keto-1'-acetyldihydro-2-quinolylacetyl)-dihydro-2:4-benzoxazine (annexed formula). It is probable



that in the first stage of the reaction a furfuryloxazine is formed but suffers a partial decomposition by the acetic acid set free in the reaction, and that the acetyl-anthranilic acid thus formed reacts with the undecomposed oxazine and the resulting carbon chain

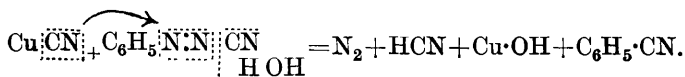
suffers condensation with the carboxyl group of the substituted anthranilic acid to give the quinoline derivative.

2-Bromo-5-furfurylideneanthranilic acid, prepared from 2-bromo-methyl-5-formylfuran and anthranilic acid, does not give the above complex reactions with acetic anhydride.

W. G.

Interaction of Diazonium Salts and Phenols. FREDERICK DANIEL CHATTAWAY and HENRY ROWLAND HILL (*T.*, 1922, **121**, 2756—2760).

An Explanation of Sandmeyer's Reaction. IVO FRANZ KEME (*Chem. Ztg.*, 1922, **46**, 1042).—The replacement of the diazo-group by chlorine, bromine, or cyanogen in the presence of the cuprous salt is explained by supposing that the cyanogen or halogen attached to the copper atom is the one which enters the benzene ring:



This view is supported by the fact that a cuprous salt which contains the group or atom which it is desired to introduce into the benzene ring must always be present.

H. C. R.

Researches on Residual Affinity and Co-ordination. XIII. Cobaltammine and Chromic Lakes of the Azo-salicylic Acids. GILBERT T. MORGAN and J. D. MAIN SMITH (*T.*, 1922, **121**, 2866—2874).

Vat Dyes of the Azo-series. DHIRENDRA NATH MUKERJI (*T.*, 1922, **121**, 2879—2882).

Certain Triphenylmethane Dyes. WALTER A. JACOBS and MICHAEL HEIDELBERGER (*J. Amer. Chem. Soc.*, 1922, **44**, 2626—2628).—Certain dyes of the malachite-green series have been pre-

pared with a view to study their bactericidal action. The dyes were prepared in the usual way by the oxidation of the leuco-compounds with lead peroxide, and the leuco-compounds were prepared either from the corresponding aldehyde and dialkylaniline or from benzhydrol and the substituted aniline. In a number of cases where the chloride and sulphate proved too soluble for convenient manipulation, the nitrate, being less soluble, was prepared. Malachite-green and brilliant-green may be readily isolated and purified in this form. The following derivatives of leucomalachite-green are described: *m*-Acetylamido-, m. p. 154·5—155·5°; *m*-carb-amido-, m. p. 194—196°; *p*-diethylamino-, m. p. 142—144·5°; *o*-chloro-*p*-dimethylamino-, m. p. 170—171·5°; 2-hydroxy-5-benzene-azo-, m. p. 186—187°, and 2-hydroxy-5-*p*-methoxybenzeneazo-, m. p. 187—188°. The derivatives of malachite-green in the form of the following salts were prepared: *p*-Methyl- as its chloride, m. p. 160°; *o*-chloro- as its chloride, m. p. 170°; *p*-chloro- as its nitrate, m. p. 120—175°; *p*-nitro- as its chloride, m. p. 150—155°; *p*-acetyl-methylamido- as its nitrate, m. p. 193—196°; *o*-chloro-*p*-dimethyl-amino- as its chloride, m. p. 185—190°; *m*-carb-amido- as its nitrate, m. p. 185°; *o*-hydroxy- as its chloride, m. p. 195°; *p*-hydroxy- as its chloride, m. p. 185—190°; *o*-methoxy- as its nitrate; *m*-methoxy- as its carbinol, m. p. 147—149·5°; *p*-methoxy- as its chloride, m. p. 125—140°; *o*-ethoxy- as its carbinol, m. p. 178—180°; *p*-ethoxy- as its chloride, m. p. 150°; 3:4-methylenedioxy- as its chloride, m. p. 155—160°; the anhydride from the *o*-hydroxy-acetic acid, m. p. 170—175°, furyl- as its nitrate, m. p. 190°. The m. p. of the salts as given above are also decomposition points. W. G.

The Diazo-reaction in the Carbazole Series. Carbazole-3-diazoimine and -3-diazonium Salts. GILBERT T. MORGAN and HUGH NORMAN READ (T., 1922, 121, 2709—2717).

Electrolytic Preparation of Phenylhydrazine. HIDEO WACHI (Japan Pat. 40194).—Pure phenylhydrazine can be prepared from sodium diazobenzenesulphonate by electrolytic reduction in the presence of sodium hydrogen sulphite. Aniline 25 g., and sodium carbonate 20 g., are dissolved in water 300 g., and sulphur dioxide is passed into the liquid until the solution becomes clear. It is then added, drop by drop, to the calculated quantity of sodium nitrite previously neutralised with acetic acid, to which 50 c.c. of saturated sodium hydrogen sulphite solution has been added. The solution is electrolysed, using spongy zinc or tin rods as electrodes, the operation being conducted at 30—35° during three hours, using a current of 7 volts and a current density 5 amperes per sq. decm. On concentrating the solution and then adding hydrochloric acid to it, phenylhydrazine hydrochloride separates.

K. K.

Action of Ultra-violet Light on Egg-albumin in Relation to the Isoelectric Point. JANET H. CLARK (*Amer. J. Hyg.*, 1922, 2, 322—324; cf. *Amer. J. Physiol.*, 1922, 61, 72).—With solutions of egg-albumin of $P_H > 4.8$, ultra-violet light causes

aggregation and flocculation; otherwise an increase in dispersion results. Changes in charge are accompanied by change in chemical properties. As the p_H becomes less than 4.8, the precipitation on half-saturation with ammonium sulphate increases. Positively, but not negatively, charged particles of albumin are precipitated by sulphate-ions.

CHEMICAL ABSTRACTS.

The Reduction of Methæmoglobin by Ammonium Sulphide.

G. QUAGLIARIELLO (*Arch. di Scien. Biol.*, 1922, **3**, 308—312; from *Physiol. Abstr.*, 1922, **7**, 400).—Ammonium sulphide reduces methæmoglobin slowly in the cold, rapidly on warming, but without the formation of intermediate products. Oxyhæmoglobin is formed after reduction has taken place if the solution is shaken.

W. O. K.

Hæmocyanin. III. The Absorption of Light by Oxyhæmocyanin. G. QUAGLIARIELLO (*Publ. St. Zool. Napoli. Ric. fisiol. chim. biol.*, 1922, **1**, 57; from *Physiol. Abstr.*, 1922, **7**, 405—406; cf. A., 1921, i, 467).—Oxyhæmocyanin from molluscs and arthropods shows one band in the yellow and the beginning of another in the blue. The former band is due to the copper contained in an atomic form in oxyhæmocyanin, and corresponds with λ 579 $\mu\mu$ in molluscs and λ 563 $\mu\mu$ in arthropods. The second band corresponds with λ 475 $\mu\mu$ in both types, and with the second band observed by Dhéré in the ultra-violet. Reduced hæmocyanin does not show any absorption band. Oxyhæmocyanin does not form with potassium ferricyanide any compound analogous to methæmoglobin.

W. O. K.

The Classification of the Nucleic Acids and the Place of Guanylnucleic Acid in the System. R. FEULGEN (*Z. physiol. Chem.*, 1922, **123**, 197—204).—A general review of the nucleic acids and of their nomenclature and classification.

W. O. K.

Guanylnucleic Acid. R. FEULGEN (*Z. physiol. Chem.*, 1922, **123**, 145—158).—In the guanylnucleic acid described by the author (A., 1921, i, 76) and by Hammarsten (*ibid.*, 200), there appears to be a nucleic acid of the type of thymus-nucleic acid in organic combination. There may also be nucleotides containing a pentose.

W. O. K.

The Isoelectric Condition of Gelatin. SIDNEY OWEN RAWLING and WALTER CLARK (T., 1922, **121**, 2830—2843).

The Two Forms of Gelatin and their Isoelectric Points. JOHN ARTHUR WILSON and ERWIN J. KERN (*J. Amer. Chem. Soc.*, 1922, **44**, 2633—2636).—Gelatin, like collagen, shows two minimum points of swelling with change of hydrogen-ion concentration, one at p_H 4.7 and the other at 7.7. These results accord with those of Loeb (A., 1918, i, 317, 318) and those of Davis and Oakes (A., 1922, i, 63) and it is suggested that the two minima represent the isoelectric points of the gel and sol forms of gelatin, respectively.

W. G.

Keratin. II. A. HEIDUSCHKA and E. KOMM (*Z. physiol. Chem.*, 1922, **124**, 37—64; cf. A., 1922, i, 967).—The products obtained by the partial hydrolysis of keratin have been investigated with respect to precipitation by ammonium sulphate and by zinc sulphate, and the limits of precipitation of the various fractions found.

W. O. K.

Mechanism of the Influence of Acids and Alkalis on the Digestion of Proteins by Pepsin or Trypsin. JOHN H. NORTHROP (*J. Gen. Physiol.*, 1922, **5**, 263—274).—The rate of digestion of various proteins by pepsin or trypsin depends on the amount of ionised protein present, being a minimum at the isoelectric point and a maximum at that hydrogen-ion concentration at which the protein is completely combined with acid or alkali to form a salt, and it does not depend on the physical properties of the protein solution.

W. O. K.

Invertase. IV. R. WILLSTÄTTER and W. WASSERMANN (*Z. physiol. Chem.*, 1922, **123**, 181—196).—The invertase of autolysed yeast is much better adsorbed by aluminium or kaolin if the solution containing it is first well diluted. The same holds for precipitation by lead acetate. The facts are applied to the preparation of purified invertase.

W. O. K.

Additive Reactions of the Phosphorus Haloids. V. **The Formation of an Unsaturated Phosphinic Acid.** JAMES B. CONANT and BERNARD B. COYNE (*J. Amer. Chem. Soc.*, 1922, **44**, 2530—2536; cf. A., 1920, i, 454; 1921, i, 69).—The mechanism of the formation of an unsaturated phosphinic acid previously isolated (*loc. cit.*) from acetophenone, phosphorus trichloride, and acetic acid has been established by a study of the corresponding hydroxy- and chloro-phosphinic acids. It is shown that the hydroxy-phosphinic acid which is probably first formed is very readily converted into the chloro-acid by the action of hydrochloric acid, and that the chloro-acid in turn loses hydrogen chloride, giving the unsaturated acid. When acetophenone, phosphorus trichloride, and glacial acetic acid are mixed and the mixture is saturated the next day with dry hydrogen chloride, α -chloro- α -phenylethylphosphinic acid, m. p. 174—175°, is obtained and is readily hydrolysed by water at the room temperature to the hydroxy-acid. When heated above its melting point or more slowly when boiled in aqueous solution, the chloro-acid is converted into α -phenylvinylphosphinic acid (*loc. cit.*). This unsaturated acid on bromination yields $\alpha\beta$ -dibromo- α -phenylethylphosphinic acid, m. p. 186—188°, which when heated above its melting point loses hydrogen bromide, giving β -bromo- α -phenylvinylphosphinic acid, m. p. 133—135°. This acid when treated with aqueous sodium carbonate gives phenylacetylene, and in a similar manner the dibromo-acid gives α -bromostyrene. By the action of water alone, the dibromo-acid is converted into $\alpha\beta$ -dihydroxy- α -phenylethylphosphinic acid, m. p. 143—145°. Phenylvinylphosphinic acid when heated with hydrobromic acid in a sealed tube at 100° for seventeen hours gives

β -bromo- α -phenylethylphosphinic acid. By the action of chlorine, the unsaturated acid gives *$\alpha\beta$ -dichloro- α -phenylethylphosphinic acid*, m. p. 175—178°. W. G.

Organic Arsenic Compounds. [Derivatives of Phenylarsinic Acid.] A. ALBERT (U.S. Pat. 1425929, 1425930, and 1425931).—*p*-Acetylphenylarsinic acid (darkens above 340° without melting) is obtained by dissolving the hydrazone in dilute sodium carbonate solution, adding hydrazine hydrate, and after some time hydrochloric acid. The phenylhydrazone, yellow plates, decomposes above 225°. 4-Hydroxy-3-propionylphenylarsinic acid *p*-nitrophenylhydrazone, yellow needles, decomposes above 235°. The semicarbazone (?) of 3-nitro-1-hydroxyacetylphenylarsinic acid becomes brown above 240°. *p*-Aminoguanidinoacetylphenylarsinic acid decomposes above 300°. *p*-(Acetylvinyl)phenylarsinic acid semicarbazone, thick needles, becomes brown above 330°. *p*-Formylphenylarsinic acid diethylhydrazone decomposes above 140°; the phenylmethylhydrazone, feathery needles, has m. p. 295° (decomp.). Semicarbazide and 3-hydroxy-4-acetylphenylarsinic acid yield a light yellow product. Carbohydrazide and *p*-benzoylphenylarsinic acid yield a white, crystalline compound, almost unchanged at 360°. Similar compounds are obtained from malonylhydrazide and oxalylhydrazide.

Treatment with sodium hyposulphite, phosphorous acid, phosphorus trichloride, hydrogen iodide, sulphur dioxide, or sodium hydrogen sulphite effects selective reduction of the arsenic yielding derivatives of trivalent arsenic, or of arsenobenzene.

CHEMICAL ABSTRACTS.

The Preparation of Sulpharsphenamine. CARL VOEGTLIN and J. M. JOHNSON (*J. Amer. Chem. Soc.*, 1922, **44**, 2573—2577).—The new compound, designated as *sulpharsphenamine*, was not obtained in the pure state. It is prepared from arsphenamine (1 mol.), formaldehyde (2 mols.), and sodium hydrogen sulphite (4 mols.). In its preparation, the following conditions must be observed. The solution of arsphenamine must be complete before the formaldehyde is added; about sixty seconds must be allowed for the formaldehyde to act before the addition of the sulphite, which should be freshly prepared from sodium carbonate and sulphur dioxide and should be added in two portions with an interval of seven minutes between the additions. The sulpharsphenamine is best precipitated by pouring the solution in a fine stream into five volumes of 95% alcohol and is dried by washing with absolute alcohol. It gives its free acid on decomposition with glacial acetic acid. The presence of the side chain $\cdot\text{NH}\cdot\text{CH}_2\cdot\text{O}\cdot\text{SO}_2\text{Na}$ as distinct from the side chain $\cdot\text{NH}\cdot\text{CH}_2\cdot\text{O}\cdot\text{SONa}$ as present in nearsphenamine is shown by its behaviour towards the indigocarmine test of Reinking, Dehnelt, and Labhardt (cf. A., 1905, i, 261). W. G.

Examination of Nearsphenamine [Neosalvarsan]. II. The Constitution of the French Drugs. A. DOUGLAS MACALLUM (*J. Amer. Chem. Soc.*, 1922, **44**, 2578—2582).—Using the technique

previously described (A., 1921, ii, 420), the author has examined a number of samples of French neosalvarsan. He finds rather more variation in these samples than in American products. The most noticeable physical characteristic of the French compounds is that, unlike the neosalvarsans, which are soluble in neutral and alkaline solution alone, they dissolve unchanged in weakly acid media as well. The French compounds darken and decompose at relatively higher temperatures, are less affected by atmospheric oxygen, and are of lower toxicity and also of lower trypanocidal activity than the American preparations. Details of analyses are given.

W. G.

An Arsenical Glucoside: Diglucosidodiaminodihydroxyarsenobenzene. A. AUBRY and E. DORMOY (*Compt. rend.*, 1922, **175**, 819—822; cf. Sokorin, A., 1888, 807; Marchlewski, A., 1894, i, 104, 511; Irvine and Moodie, T., 1908, **93**, 95; Irvine and Gilmour, T., 1908, **93**, 1429).—Diaminodihydroxyarsenobenzene combines with dextrose, yielding a pale yellow, crystalline powder which was shown to be diglucosidodiaminohydroxyarsenobenzene. The substance is readily soluble in water, the solution being lævoptatory, $[\alpha]_D -560^\circ$. When kept, it is slowly hydrolysed; after twenty days less than 40% remains unchanged. The hydrolysis may be retarded by addition of dextrose. A monoglucoside is formed as an intermediate hydrolysis product. In a discussion of the constitution, the authors point out that the glucose may be linked to the amino- or to the phenolic groups; the reactions of the substance indicate the former position.

H. J. E.

Physiological Chemistry.

The Comparative Concentrations of Alcohol in Human Blood and Urine at Intervals after Digestion. WALTER R. MILES (*J. Pharm. Expt. Ther.*, 1922, 20, 265—319).—Estimations of the alcohol in the whole blood, plasma, and urine of men who had consumed a known quantity of alcohol show a greater concentration in the plasma than in the whole blood. At first, the concentrations in the blood and in the urine are approximately the same, but soon that of the urine becomes appreciably greater, and exceeds that of the plasma. W. O. K.

Factors which Determine the Concentration of Calcium and of Inorganic Phosphorus in the Blood-serum of Rats. BENJ. KRAMER and JOHN HOWLAND (*Bull. Johns Hopkins Hosp.*, 1922, 33, 313—317).—The normal concentration of calcium in the serum of rats is from 9.5 to 10.5 mg. per 100 c.c. and that of phosphorus from 7 to 8.5 mg. per 100 c.c. These values were not increased by changes in the diet or by treatment with ultra-violet

light. By lowering the amount of calcium or phosphorus in the food sufficiently, the concentration of the same in the serum could be diminished by as much as 50%. Subsequent addition of fish-liver oils to the food brought the values back to normal. The same result could be obtained, with phosphorus, by illumination with light of wave-length less than 3000 Å. A similar effect could be obtained by starvation for a few days.

CHEMICAL ABSTRACTS.

Sodium Chloride and Selective Diffusion in Living Organisms. JACQUES LOEB (*J. Gen. Physiol.*, 1922, 5, 231—254).—Sodium chloride, calcium chloride, and cerium chloride inhibit the diffusion of strong acids into the egg of *Fundulus* as shown by the decrease in the mortality among the eggs immersed in the acid on the addition of the chloride, and also by the decrease in the rate of fall of the hydrogen-ion concentration. $M/8$ sodium chloride corresponds with $M/1,000$ calcium chloride or $M/30,000$ cerium chloride in producing this inhibition. Weak, undissociated acids are but feebly inhibited by these chlorides, if at all. The diffusion of strong alkalis is accelerated by sodium chloride, and more so by calcium chloride. Sodium chloride in moderate concentration accelerates also the diffusion of potassium chloride into the egg of *Fundulus*, whilst calcium chloride does not.

W. O. K.

Dextrose in Eggs of Vertebrates. G. GORI (*Atti R. accad. fisiocrit. Siena*, 1920, 21, 711—716; from *Chem. Zentr.*, 1922, iii, 927).—Dextrose is absent from the yolks of eggs of *Torpedo* and of fishes: the amount of urea present is insufficient to obscure the reaction. Using material dried first at 45° and then in a vacuum, dextrose was found to be absent from mammalian ova, present, combined and free, in birds' eggs, and present in the free state in amphibian eggs.

G. W. R.

The Synthetic Formation of Kynurenic Acid in the Surviving Liver. Z. MATSUOKA and S. TAKEMURA (*J. Biochem. [Japan]*, 1922, 1, 175—180).—Kynurenic acid is produced by the perfused liver of dogs when either tryptophan or indolepyruvic acid is added to the blood. It is suggested that indolepyruvic acid is probably an intermediate step in the transformation of tryptophan into kynurenic acid. This hypothesis is based on the fact that the same amount was produced (0.1285 and 0.1202 g.) with 1 g. of either the tryptophan or indolepyruvic acid in the perfusing mixture.

CHEMICAL ABSTRACTS.

Some Compounds Extracted from Human Skeletal Muscles. R. ENGELAND and W. BIEHLER (*Z. physiol. Chem.*, 1922, 123, 290—294).—The following compounds have been isolated from human skeletal muscles: carnitine, $C_7H_{15}O_3N$; neosine, $C_6H_{17}O_2N$; myokynine, $C_{11}H_{28}O_3N_2$; and *mirgeline* isolated as the *chloroaurate*, $C_{11}H_{22}O_3N_2 \cdot HAuCl_4$, light yellow, nodular crystals.

W. O. K.

The Pharmacology of Cell Breathing. II. The Function of Iron in Cell Breathing. III. The Dependence of Cell Respiration on the Hydrogen-ion Concentration. PH. ELLINGER and N. LANDSBERGER (*Z. physiol. Chem.*, 1922, **123**, 246—263, 264—279).—Amino-acids are oxidised by oxygen in presence of an emulsion of zinc sulphide-copper phosphor in a gelatin solution, as they are in presence of charcoal (Warburg, A., 1921, i, 230; 1922, i, 190), or by an emulsion of broken-up goose erythrocytes. Potassium cyanide decreases the velocity of oxidation in the case of the goose cells, but at the same time it is itself oxidised. The rate of absorption of oxygen shows a minimum at a low concentration of potassium cyanide and the same phenomenon is observed in the case of isolated frog's muscle if potassium cyanide is applied. The oxidation is parallel to the fluorescence and phosphorescence of the cells under ultra-violet illumination. This is taken to indicate that the efficiency of the cells in catalysing oxidation is connected with the ability of the iron to lose an electron, and so activate the oxidisable material. The rate of consumption of oxygen with charcoal or with cells depends on the hydrogen-ion concentration, and this effect seems to be exerted primarily on the amino-acid which is being oxidised. W. O. K.

The Presence of Aldol in the Urine of Diabetics. ROBERT FRICKE (*Z. physiol. Chem.*, 1922, **124**, 1—7).—Aldol in the urine of diabetics is only partly detected by the "dimedon" method previously employed (A., 1922, i, 300; ii, 326). Improvements are described which render the method more sensitive and accurate. W. O. K.

The Sugar Content of Cerebrospinal Fluids. K. MIFUJI (*J. Tokyo Med. Soc.*, 1921, **35**, No. 10; *Japan Med. World*, **2**, 78).—The normal sugar content of the spinal fluid of the Japanese averages 0.052%. The factor obtained by dividing the blood-sugar content by the spinal fluid sugar content is largest in children and least in the senile cases. In the atrophic form of beri beri the sugar content of both liquids is practically the same as normal, but in the cedematous form they are both increased. In epidemic cerebrospinal meningitis the blood-sugar content is as high as the maximum normal (0.114%) but that of the spinal fluid is remarkably decreased. In epilepsy the spinal fluid sugar content in the intermissions of an attack was low, 0.021%, but returned to normal eighteen hours after the attack. CHEMICAL ABSTRACTS.

Pharmacology and Therapeutics of Iodides. E. D. OSBORNE (*J. Amer. Med. Assoc.*, 1922, **79**, 615—617; from *Physiol. Abstr.*, 1922, **7**, 453).—After the administration of sodium iodide by the mouth, there is an increase in the concentration of sodium in the blood, whilst only a trace of iodine was found in the serum proteins when these were precipitated by tungstic acid or alcohol. On the other hand, after oral administration of potassium iodide, there is no increase of potassium in the blood, but an increase of sodium, whilst 7 to 26% of the iodine given was found in the serum proteins. W. O. K.

Urea. A. MARIE (*Compt. rend. Soc. Biol.*, 1922, **86**, 998; cf. *ibid.*, 1922, **86**, 72).—Intravenous injections of adrenaline hydrochloride produce a considerable increase in the urea content both of the blood and of the parenchyma of the liver freed completely from blood. Adrenaline has also been found to suppress the decomposition of urea in vitro when added to a soja bean extract. Although the vegetable urease may be entirely unlike the hepatic urease, the test-tube experiments lead to the conclusion that the increase in urea content observed after an injection of adrenaline is likewise due to a suppression of the hydrolysis of urea.

CHEMICAL ABSTRACTS.

The Separation of Ethereal Sulphates in Rabbits after Administration of Phenol, *p*-Bromophenol, and Bromobenzene. H. RHODE (*Z. physiol. Chem.*, 1922, **124**, 15—36).—If phenol is administered to rabbits (0.2 g. per kg.), 12% is eliminated in the urine as the ethereal sulphate, whereas if cystine, taurine, or sodium sulphite is administered at the same time, 33%, 17%, and 27%, respectively, of the phenol is eliminated. Thiosulphate and sulphate are without influence on the elimination of the phenol. In the cases of *p*-bromophenol and of bromobenzene, the effect of the simultaneous administration of cystine is to decrease the output of ethereal sulphates, the explanation apparently being that phenylmercapturic acid is formed in both cases. This indicates that the bromobenzene in the animal organism is first of all oxidised to *p*-bromophenol.

W. O. K.

Pharmacology of Benzyl Compounds. II. CARL NIELSEN and JOHN A. HIGGINS (*J. Lab. Clin. Med.*, 1922, **7**, 579—588; cf. *ibid.*, 1921, **6**, 388).—The observations suggest that the relaxing power of benzyl esters on the smooth muscle fibres of the intestine as a rule is dependent on the benzyl content and on the rate of hydrolysis of the benzyl compound.

CHEMICAL ABSTRACTS.

Chemistry of Vegetable Physiology and Agriculture.

The Relation of the Reaction and of Salt Content of the Medium to Nitrifying Bacteria. CAROLYN S. MEEK and CHARLES B. LIPMAN (*J. Gen. Physiol.*, 1922, 5, 195—204).—Nitrifying bacteria are particularly resistant to hydroxyl-ions, surviving in a medium of P_H 13 and yielding their characteristic products in a medium of P_H 11. Sodium sulphate is not nearly so toxic to these products as sodium chloride or sodium carbonate. W. O. K.

Nitrification. IV. The Carbon and Nitrogen Relations of the Nitrite Ferment. AUGUSTO BONAZZI (*J. Bact.*, 1921, 6, 479—499).—A study of the functions of autotrophic carbon assimilation and nitrogen nutrition of the nitroso-ferment. These functions are

intimately connected and mutually interdependent, the bacterial cell being able to assimilate the abundant stores of nitrogen in a nutritive solution in the absence of free carbon dioxide, even although a carbonate as such be present in the medium. Consequently the process of nitrogen oxidation which follows the absorption and leads to the formation of nitrous acid and its salts is dependent on the presence of this free carbon dioxide.

CHEMICAL ABSTRACTS.

Ergosterol in Yeast. A. WINDAUS and W. GROSSKOPF (*Z. physiol. Chem.*, 1922, **124**, 8—14).—Ergosterol is extracted from yeast in a yield of about 0.15% and purified as ergosteryl acetate, m. p. 180—181°. On reduction with palladium black and hydrogen, this acetate unites with six hydrogen atoms to form *ergostanyl acetate*, $C_{29}H_{50}O_2$, small, white needles, m. p. 103°, which on hydrolysis yields *ergostanol*, $C_{27}H_{48}O$, fine leaflets, m. p. 129°. By treatment of ergostanol with phosphorus pentachloride, and subsequent reduction with sodium in amyl alcohol, the hydrocarbon, *ergostane*, $C_{27}H_{48}$, white leaflets, m. p. 72—73°, $[\alpha]_D^{20} + 24.5^\circ$, is obtained, which is not identical with sitosane, ψ -cholestane (coprostanane), or cholestane. Ergostanol, on oxidation with chromic anhydride, yields *ergostanone*, fine white needles, m. p. 56—57°. W. O. K.

Comparison of α - and β -Glucose in Fermentation. RICHARD WILLSTÄTTER and HARRY SOBOTKA (*Z. physiol. Chem.*, 1922, **123**, 164—169).—No difference can be detected in the rate of fermentation of α - and β -glucose. This cannot be due to an equilibrium between the two forms being set up quickly, as the rate of this change under the conditions of the experiment is much slower than the rate of fermentation. W. O. K.

The Selective Fermentation of Mixtures of Sugars. RICHARD WILLSTÄTTER and HARRY SOBOTKA (*Z. physiol. Chem.*, 1922, **123**, 170—175).—Although glucose, fructose, and a mixture of these are all fermented by yeast with approximately the same velocity, yet on fermenting a mixture the glucose ferments more quickly than the fructose. This is apparently because the glucose is more active in the initial stages of fermentation whilst the final stages of the reaction are the same for both sugars. These final stages, however, are the slowest and so they decide the rate of the reaction as a whole. The same holds for the fermentation of a mixture of the α - and β -forms of glucose (see preceding abstract). W. O. K.

Selective Fermentation with Yeast Trained to Ferment Galactose. RICHARD WILLSTÄTTER and HARRY SOBOTKA (*Z. physiol. Chem.*, 1922, **123**, 176—180).—Yeast may be trained so that it will ferment galactose more rapidly than glucose, but it is found that such a yeast will still preferentially ferment glucose out of a mixture of glucose and galactose. An explanation of this phenomenon is indicated on the lines suggested in the preceding abstract. W. O. K.

The Influence of Copper Salts on the Yield of *Sterigmato-cystis nigra* [*Aspergillus niger*]. MARIN MOLLIARD (*Compt. rend.*, 1922, 175, 838—841).—The retarding action of solutions containing copper on the growth of *A. niger* renders direct comparison with the control solution of no value as the two may be at different stages of development. The author has compared the yield—i.e., the ratio of the weight of mycelium obtained to that of sugar consumed—in a control solution and one containing copper sulphate of a concentration of 1/3750, making allowance for the slower growth in the latter. The general result of the presence of copper is diminution of yield, but during a considerable portion of the time the reverse effect was observed. H. J. E.

Some Aspects of Selective Absorption. W. J. V. OSTERHOUT (*J. Gen. Physiol.*, 1922, 5, 225—230).—Analysis of the cell sap of the marine alga *Valonia* shows much more potassium and less sodium, magnesium, calcium, and sulphate-ion than exists in the surrounding sea-water, whilst the chloride is approximately constant. The organic material in the cell sap is small, and this seems to exclude the possibility of accounting for the high concentration of potassium by the assumption that it combines with some organic compound. W. O. K.

Fixation and Polymerisation of Formaldehyde in the Dark by Green Plants. Carbon Dioxide Assimilation by Plants. TH. SABALITSCHKA (*Z. angew. Chem.*, 1922, 35, 684—685).—Experiments with the nasturtium and the water-weed, *Elodea canadensis*, showed that these plants are capable of fixing formaldehyde and polymerising it to carbohydrates even in the absence of light. The plants were placed in an enclosed space and deprived of carbon dioxide. The sugar and starch content of the leaves was determined after some decrease had occurred below the normal by reason of the exclusion of carbon dioxide, and some of the plants were then exposed to formaldehyde either in the form of vapour or in solution in the case of the water weed, whilst others were kept for comparison. After some days the carbohydrates in the leaf were again estimated; as an example of the results, in one case 462 mg. of sugar and 1048 mg. of starch per 100 g. of leaf were found after treatment with formaldehyde, compared with 144 mg. of sugar and 495 mg. of starch in the blank experiment. The quantity of these substances in the formaldehyde experiment was actually higher than at the commencement, whereas in the control experiment the carbohydrates had continued to decrease. This shows that the plants were able to replenish their stock of carbohydrate, depleted by the absence of carbon dioxide, by making use of the formaldehyde, and that the polymerisation takes place in the absence of sunlight. Further, it provides additional evidence for the hypothesis that formaldehyde is an intermediate product of the photosynthesis of carbohydrates from carbon dioxide and water. G. F. M.

Anthocyanin Pigments and Phlobatannins in Plants. ST. JONESCO (*Compt. rend.*, 1922, 175, 904—907; cf. Combes, A., 1922, i, 206).—The red leaves of *Prunus Pissardii*, dried and powdered, were extracted with ethyl ether. The solution, on evaporation, yielded two separate substances: one, soluble in water and crystallising in tablets and needles, the other soluble in ethyl alcohol but not in water, and obtained as a yellow, amorphous substance on evaporation. Various reactions given by the former indicate that it is a tannin; the latter being precipitated by addition of water gives somewhat ambiguous results with aqueous reagents. It is, however, not converted into a red pigment when heated with dilute acids. Further extraction of the dried leaves with ethyl acetate and amyl alcohol yielded the anthocyanidins and pseudo-bases. The latter are readily transformed into anthocyanidins under the influence of dilute hydrochloric acid, their colour changing from yellow to red. The anthocyan constituents—i.e., the total of the pigments present in the various organs—are divided into anthocyanins, red, violet, or blue substances not extracted by amyl alcohol, anthocyanidins, red substances existing uncombined and readily soluble in amyl alcohol, and a third group of substances, the pseudo-bases, yellow in colour, which the author proposes to designate leuco-anthocyanidins. H. J. E.

The Action of Hexamethylenetetramine on Higher Vegetation. E. NICOLAS and G. NICOLAS (*Compt. rend.*, 1922, 175, 836—838).—Solutions of hexamethylenetetramine, the concentration of which lies between 0.1 and 0.3 g. per litre, are utilised as food by beans, but on increasing the concentration a toxic effect is produced. In the former case, the action is shown by increase in weight of the plant and by the enhanced leaf development. H. J. E.

The Chemical Constituents of Green Plants. XXII. The Presence of Succinic Acid and of Oxalic Acid in the Currant (*Ribes rubrum*). HARTWIG FRANZEN and FRITZ HELWERT (*Z. physiol. Chem.*, 1922, 124, 65—74; cf. A., 1922, i, 310).—By converting the acids in the filtrate from the lead acetate precipitate from the currant into their esters and subsequently into the hydrazide or the benzylidene compounds, the presence of succinic acid, malic acid, and citric acid has been demonstrated. Other acids, some unsaturated, are present in traces, including probably oxalic acid, and possibly lactic acid. W. O. K.

Colouring Matter of the Fruit of *Gardenia florida*, L. TETSUJI MUNESADA (*J. Pharm. Soc. Japan*, 1922, No. 486, 666—671).—The colouring matter of the fruit of *Gardenia florida*, L., from China when extracted with water (cf. Kasyer, A., 1885, 59), and decomposed with dilute hydrochloric acid in a current of carbon dioxide, yielded an amorphous powder which is identical with crocetin from saffron (cf. Decker, A., 1914, i, 979). It gave a potassium salt, $C_{10}H_{13}O_2K$, orange-yellow crystals, sodium salt,

short, yellowish-red needles, and ammonium salt, reddish-yellow needles. K. K.

Preservative Principles of Hops. I. FRANK LEE PYMAN, HAROLD ROGERSON, and THOMAS KENNEDY WALKER (*J. Inst. Brewing*, 1922, 28, 929—934).—Attempts were made to isolate crystalline hop-bitter acids by fractional extraction with alkalis of increasing strength of an ethereal solution of the soft resins, obtained by extraction of ground hops with light petroleum. Lupulon was isolated in small yield in colourless prisms, m. p. 94.5—95.5°. No humulon was obtained by this method, and the only other crystalline compounds isolated were lactic acid, $C_{15}H_{30}O_2$, a saturated fatty acid previously found only in the fungus *Agaricus integer*, and small quantities of the constituents of the wax, hentriacontane, ceryl alcohol, and cerotic acid.

G. F. M.

Nitrogenous Constituents of the Fruit of Chayote (*Sechium edule*). KIYOHISA YOSHIMURA (*J. Biochem. [Japan]*, 1922, 1, 347—351).—The fruit of *Sechium edule* (a member of the *Cucurbitaceæ*) was examined with the following results: Water 95.973% and dry substance 4.027%. The dry substance contained: crude protein 16.264%, fat 1.169%, crude fibre 7.311%, nitrogen-free extract 68.392%, ash 6.864%, total nitrogen 2.602%, protein nitrogen 1.56%, and non-protein nitrogen 1.041%; that is, of the total nitrogen 59.99% was protein and 40.009% non-protein. 20 Kg. of the fresh fruit were pressed and then extracted twice with hot water; from the extract were isolated: a small quantity of adenine and choline, 0.7 g. of arginine (as nitrate), and about 1.5 g. of guanidine (as chloraurate). K. K.

The Mannan of Vegetable Ivory. II. Hemicelluloses. HANS PRINGSHEIM and KARL SEIFERT (*Z. physiol. Chem.*, 1922, 123, 205—212; cf. A., 1912, i, 833).—Mannan, prepared from vegetable ivory shavings by the action of 5% sodium hydroxide solution, is treated with acetic anhydride containing hydrogen bromide, when it yields *mannan triacetate*, $C_8H_7O_9(OAc)_3$, a white, amorphous, non-hygroscopic substance, $[\alpha]_D^{25} -27.4^\circ$ in acetylene tetrachloride. Mannan, on treatment with acetic anhydride containing a small amount of concentrated sulphuric acid, yields a white, amorphous substance, from which on hydrolysis and treatment with phenylhydrazine, mannosephenylhydrazone can be obtained, besides a quantity of glucosazone and also apparently the osazone of a disaccharide. W. O. K.

Relation of certain Nutritive Elements to the Composition of the Oat Plant. J. G. DICKSON (*Amer. J. Botany*, 1921, 8, 256—274).—A study of the growth and composition of *Avena sativa aristata* in relation to climate and nutrition. The content of calcium oxide is reduced proportionally to its reduction in the culture solution; it is also greatly reduced by deficiency of phosphorus or nitrogen. The extent to which the content of phos-

phorus of the grain and straw is reduced by reduction in the proportion of phosphate or potassium in the culture solution, and increased by similar reduction of calcium or nitrogen, has been determined. The content of phosphorus of both grain and straw is modified by seasonal differences except for plants grown in solutions deficient in phosphorus. The content of calcium of the grain is modified even when solutions deficient in calcium are employed, whilst that of the straw shows no consistent response to climate.

CHEMICAL ABSTRACTS.

The Comparative Assimilability of Tricalcium Phosphate and the Phosphates of Aluminium and Iron. CH. BRIOUX (*Compt. rend.*, 1922, 175, 1096—1099).—In soils containing little or no calcium carbonate, a considerable proportion of the phosphoric acid exists as ferric or aluminium phosphate. Experiments with six different species of plants showed that, measured by the production of dried organic matter, the use of equivalent quantities of tricalcium, ferric, and aluminium phosphates results in the highest yields being obtained in the case of aluminium and the lowest with iron, although the last-named gives results considerably above the control yield. The author points out that the usual solvents for "available phosphate" give results which are inconsistent with those of his experiments, although 1% citric acid is more trustworthy than others which have been recommended.

H. J. E.

The Availability of Mineral Plant Food (A Modification of the Present Hypothesis). NORMAN M. COMBER (*J. Agric. Sci.*, 1922, 12, 363—369).—The conception that plants can take up from the soil only mineral matter which is in solution is criticised. Three main objections are advanced, namely, the difficulty of correlating the composition of the soil solution with the amount of mineral matter taken up by the plant; the absence of any explanation of the intake of iron by plants, and the difficulty of explaining the availability of phosphates. A modified hypothesis is presented in which the absorption of colloids by plant roots is assumed. The possibility of a definite union of root hairs with solid mineral particles is discussed, and the subsequent dissolution of the mineral particle by the organic matter of the root hair is suggested.

A. G. P.

Theory of Soil Acidity. J. N. MUKHERJEE (*Nature*, 1922, 110, 732).—Experimental evidence is adduced in support of the author's view (*A.*, 1922, ii, 689) concerning the origin of soil acidity. Silica has been found to adsorb appreciable quantities of acetic, citric, hydrochloric, and nitric acids so strongly that on repeated washing the adsorbed substance cannot be removed and the aqueous extract soon becomes neutral. Treatment with aqueous potassium chloride then results, however, in the development of acidity. Simultaneous experiments on electro-osmosis indicate that the anions of the acids, and not their entire molecules, are adsorbed on the surface by chemical forces, and it is suggested that an equivalent

number of kations form a mobile second sheet of the double layer, the forces acting on these being mainly electrical in nature.

A. A. E.

Sulphur Changes in Soil. KURT LANTZSCH (*Intern. Mitt. Bodenk.*, 1922, **12**, 22—35).—Nutrient solutions containing calcium sulphate and inoculated with soil extract showed no formation of sulphide after forty-seven days. The ratio $\text{CaO} : \text{SO}_3$ was, however, changed slightly in some cases. Nutrient solutions to which 20 g. of soil were added to 200 c.c. and allowed to remain under anaerobic conditions for sixty days showed no appreciable formation of sulphides when titrated with iodine solution. A solution containing 0.09% of potassium sulphide together with asparagine and other nutrients developed an odour of butyric acid and lost a small amount of sulphur. A somewhat similar solution containing no organic carbon showed a production of nitrogen dioxide and ammonia when ammonium chloride was the only source of nitrogen; when sodium nitrate was used instead, nitrogen dioxide and ammonia were not produced. In each case, however, some of the sulphur was oxidised to sulphate in the inoculated solutions, whilst the control gave negative results. The control tubes were treated with 0.2 c.c. of 40% formaldehyde solution per 100 c.c. of solution.

CHEMICAL ABSTRACTS.

The Depletion of Soils by Chemical Denudation. MILTON WHITNEY (*Science*, 1922, **56**, 216—218).—The information hitherto collected concerning the rate of chemical denudation of soil and rock material has been based mainly on the translocation of material in true solution, disregarding all matter in colloidal solution. The results have shown that the loss of silica, alumina, and iron is surprisingly small in comparison with that of potassium. It is indicated, however, that in the breaking down of silicates to a point at which potassium goes into solution, silica, alumina, and iron also go into colloidal solution in the same proportion as they bear to the potassium content in the original material. This view is supported by the fact that when finely ground silicates are brought into contact with water, soluble salts go into solution (as determined by conductivity or chemical test) and at the same time there is released a relatively large amount of colloidal material. Further investigation on these lines is necessary before it will be possible to state whether chemical erosion is a selective process which might change the chemical composition of the soil, or whether, by the materials leaving the soil in about their original ratios, there is no material change in the composition of the soil on which water has acted.

A. A. E.

Organic Chemistry.

The Influence of the Structure of Organic Compounds on their Sulpho-chromic Oxidation. L. J. SIMON (*Compt. rend.*, 1922, 175, 1070—1072; cf. A., 1922, ii, 867, 868).—Among the substances which are completely oxidised by the sulpho-chromic mixture are certain straight-chain compounds, phenolic derivatives, and ring-substituted aromatic acids. In other cases, molecular structure influences the extent of oxidation, *e.g.*, methyl benzoate is completely, whilst toluic or phenylacetic acid is only partly, oxidised. From a study of a considerable number of such examples, it is seen that this method of oxidation indicates structural differences and may be used to investigate such problems as tautomerism or intramolecular change. The author has devised a formula based on the number of carbon atoms present in the molecule and the number which escape oxidation, and regards the "oxidation deficit" which it furnishes as a first step towards a new method of structural investigation. H. J. E.

Oxidation of Tertiary Hydrocarbons. P. A. LEVENE and F. A. TAYLOR (*J. Biol. Chem.*, 1922, 54, 351—362).—Further examples are given of the preparation of tertiary hydrocarbons by the malonic ester synthesis (cf. Levene and Cretcher, A., 1918, i, 250). The various stages of the syntheses are represented by the following series of compounds. Revised constants are given for certain compounds which have previously been described.

Ethyl ethylbutylmalonate [previously prepared, but not characterised, by Raper (T., 1907, 91, 1837)], b. p. 128—129°/7 mm., d_4^{20} 0·9646, n_D^{20} 1·4284. *Ethylbutylmalonic acid*, $C_9H_{16}O_4$, m. p. 115°. α -Ethylhexoic acid, b. p. 228—229° (Raper gave 225°); *ethyl- α -ethylhexoate*, $C_{10}H_{20}O_2$, b. p. 189—191°, d_4^{20} 0·8628, n_D^{20} 1·4128. β -Ethylhexyl alcohol, $C_8H_{18}O$, b. p. 181—183°, d_4^{20} 0·8328, n_D^{20} 1·4328; β -ethylhexyl iodide, $C_8H_{17}I$, b. p. 89—90°/11 mm., d_4^{20} 1·3365. γ -Methylheptane, b. p. 120—122° (cf. Clarke, A., 1909, i, 349), d_4^{20} 0·7069, n_D^{20} 1·3980.

Ethyl α -methylheptylmalonate, $C_{15}H_{28}O_4$, b. p. 157—158°/10 mm., d_4^{20} 0·9496, n_D^{20} 1·4324. β -Methylnonoic acid, $C_{10}H_{20}O_2$, b. p. 147—148°/12 mm., d_4^{20} 0·9012, n_D^{20} 1·4342; *ethyl β -methylnonoate*, $C_{12}H_{24}O_2$, b. p. 115°/13 mm., d_4^{20} 0·8653, n_D^{20} 1·4240. γ -Methylnonyl alcohol, $C_{10}H_{22}O$, b. p. 103—103·5°/9 mm., d_4^{20} 0·8342, n_D^{20} 1·4361; γ -methylnonyl iodide, $C_{10}H_{21}I$, b. p. 115°/10 mm., d_4^{20} 1·2515. γ -Methylnonane, $C_{10}H_{22}$, b. p. 165·5—166·5°, d_4^{20} 0·7354, n_D^{20} 1·4126.

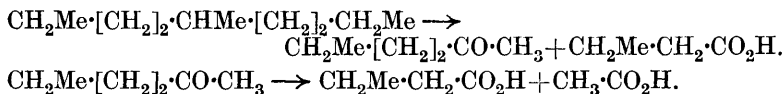
ϵ -Methylnonane (β -butylhexane of Levene and Cretcher, *loc. cit.*), b. p. 164—166°, d_4^{20} 0·7319, n_D^{20} 1·4116.

ϵ -Propylnonane, $C_{12}H_{26}$, b. p. 204—205°, d_4^{20} 0·7559, n_D^{20} 1·4228, was obtained by reduction of δ -butyloctyl iodide (cf. Levene and Cretcher).

Ethyl butylmalonate, b. p. 122°/12 mm. (cf. Adams and Marvel,

A., 1920, i, 283), d_4^{20} 0.9745, n_D^{20} 1.4222. *Ethyl butylheptylmalonate*, $C_{18}H_{34}O_4$, b. p. 177—178°/12 mm., d_4^{20} 0.9318, n_D^{20} 1.4366; *butylheptylmalonic acid*, $C_{14}H_{26}O_4$, needles, m. p. 117°. α -*Butylnonoic acid*, $C_{13}H_{26}O_2$, b. p. 179°/13 mm., d_4^{20} 0.8860, n_D^{20} 1.4403; *ethyl α -butylnonoate*, $C_{15}H_{30}O_2$, b. p. 115°/1 mm., d_4^{20} 0.8560, n_D^{20} 1.4290. β -*Butylnonyl alcohol*, $C_{13}H_{28}O$, b. p. 112—114°/0.5 mm., d_4^{20} 0.8359, n_D^{20} 1.4430; β -*butylnonyl iodide*, $C_{13}H_{27}I$, b. p. 121—123°/0.5 mm. ϵ -*Methyldodecane*, $C_{13}H_{28}$, b. p. 225.5—227°, d_4^{20} 0.7576, n_D^{20} 1.4244.

When ϵ -methylnonane was oxidised with alkaline permanganate, acetic and butyric acids were identified amongst the products of the reaction; the presence of some formic acid was also detected. Apparently the oxidation proceeds mainly according to the following scheme :



E. S.

The Formation of Hydrocarbons during the Action of Potassium on Ethyl Acetate. HELMUTH SCHEIBLER, HEINRICH ZIEGNER, and EMIL PEFFER (*Ber.*, 1922, **55**, [B], 3921—3931).—The action of potassium on an ethereal solution of ethyl acetate has been shown to lead to the formation of ethyl potassioacetate, $CH_2:C(OK) \cdot OEt$ (cf. Scheibler and Voss, A., 1920, i, 366; Scheibler and Ziegner, A., 1922, i, 426). In addition, acidic substances are produced which will be described subsequently, and neutral compounds which are the subject of the present communication.

Potassium and ethyl acetate in varied proportions are allowed to react in the presence of ether and the products are decomposed either by sulphuric acid (30%) or carbon dioxide. The neutral portions are freed from admixed ester and ketones by successive treatment with concentrated potassium hydroxide solution at 80° and sodium hydrogen sulphite and are subsequently distilled, whereby a series of fractions boiling over the range 120—260° are isolated. The carbon and hydrogen content of these increases with increasing boiling point at the expense of the oxygen content. The analytical composition of the fraction b. p. 210—240°/atmospheric pressure agrees with that required by the formula $C_{12}H_{22}$, whereas that of the fraction b. p. above 250° harmonises with the formula $C_{12}H_{24}$. The constitution of the substances has not been elucidated. The insolubility of the bulk of the product in concentrated sulphuric acid indicates the absence of olefines, and the low hydrogen content makes it unlikely that paraffins are present. It is most probable that the hydrocarbons are homologues of benzene or mono- or poly-*cycloparaffins*.

Only traces of hydrogen are evolved in the gaseous state during the action of potassium on ethyl acetate. It appears that the liberated hydrogen reduces a portion of the ethyl potassioacetate extensively and that in the course of the change intermediate

substances are produced which are more readily hydrogenated than ethyl potassioacetate, a considerable proportion of which remains after complete solution of the potassium.

The fractions boiling below 200° consist mainly of hydrocarbons, but appear to contain a certain proportion of ethers; their instability towards alkaline permanganate indicates the unsaturated nature of one or both components.

The formation of hydrocarbons is not observed when potassium is replaced by sodium under otherwise identical conditions.

H. W.

The Chlorination of Methane. ARTHUR SCHLEEDÉ and CURT LUCKOW (*Ber.*, 1922, **55**, [B], 3710—3726).—The chlorination of methane has been studied by passing mixtures of the gases through electrically heated quartz or glass tubes. Inflammation occurs when the gases are used in molar proportions, but the flame gradually dies out; it is permanent when an excess of chlorine is employed. If, on the other hand, an excess of methane is used, ignition is not observed; under these conditions chlorine is only quantitatively utilised if the temperature is not below a certain minimum depending on the precise composition and rate of flow of the mixture. The phenomena are not greatly affected by the presence of catalysts or by an increase of temperature of 100° above the minimum. The products of the reaction are freed from hydrogen chloride by passage through warm concentrated potassium hydroxide solution (water is unsuitable, since it dissolves appreciable amounts of methyl chloride) and are subsequently condensed at a temperature not exceeding -110° . (The vapour tensions of methyl chloride below -30° , of methylene chloride and chloroform below 0° , and of carbon tetrachloride below -20° have been measured.) Methyl chloride can be conveniently separated from the condensate by Stock's method of fractional distillation in a high vacuum, but the process is inapplicable to the separation of methylene chloride, chloroform, and carbon tetrachloride, which are therefore estimated approximately by the technical distillation method.

The results may be summarised as follows. When the velocity of passage of the gaseous mixture per unit of surface exceeds a certain value, and a large increase of the heating (catalysing-surface is not also provided, the reaction tends more and more towards a steady ignition, and increased formation of higher products is observed which takes place particularly at the expense of the chloroform. The greater the velocity of the gas, the greater must be the catalysing surface. If the rate of flow is below the ignition value (or a suitable increase of the heating surface is provided) higher products are not formed in appreciable amount, but the relative proportions of the chlorinated methanes are not those which would be expected from a step-wise reaction. When the rate of flow is below the ignition value, marked changes resulting in the production of carbon tetrachloride and higher products are only observed when the catalysing surface is enormously increased (for example, by the use of activated charcoal). This result is

not appreciably modified when the minimum temperature is exceeded by as much as 100° , when the heating zone is increased or diminished, or when catalysts, such as ferric chloride, molybdenum pentachloride, or antimony pentachloride are present. On the other hand, the results obtained are not in harmony with the values calculated from Martin's formula (*Z. Elektrochem.*, 1921, **27**, 150). If the rate of flow is considerably below the ignition value an increased production of chloroform and carbon tetrachloride or substances of similar boiling point at the expense of methyl and methylene chlorides is observed.

The causes which are operative in producing results differing so greatly from those of a step-wise reaction are discussed in detail. The most probable are the dissociation of methane and subsequent changes such as those represented by the equations $\text{CH}_3\text{Cl} + \text{CH}_4 = \text{C}_2\text{H}_6 + \text{HCl}$, $\text{CH}_2\text{Cl}_2 + \text{CH}_4 = \text{CH}_2\text{Cl}\cdot\text{CH}_3 + \text{HCl}$, $\text{CH}_3\text{Cl} + \text{CH}_3\text{Cl} = \text{CH}_2\text{Cl}\cdot\text{CH}_3 + \text{HCl}$, and $\text{CH}_2\text{Cl}_2 + \text{CH}_3\text{Cl} = \text{CH}_2\text{Cl}\cdot\text{CH}_2\text{Cl}$ (or $\text{CH}_3\cdot\text{CHCl}_2$) + HCl .

The preparation of methyl chloride from methane and carbonyl chloride (cf. Hochstetter, A., 1916, i, 625) has been re-examined. The action appears to be due to greatly diluted chlorine. H. W.

The Thallous Alkyloxides. R. DE FORCAND (*Compt. rend.*, 1923, **176**, 20—23).—Thallous ethoxide was prepared by the method of Lamy (*Ann. Chim. Phys.*, 1863, **67**, 395; 1864, **3**, 373), and was isolated as an oily liquid, d 3.55. It reacts with other alcohols to give the corresponding alkyloxides. In this way the author has prepared the *monothallium* derivatives of *ethylene glycol*, $\text{OH}\cdot\text{C}_2\text{H}_4\cdot\text{OTl}$, and of *glycerol*, $\text{C}_3\text{H}_5(\text{OH})_2\cdot\text{OTl}$, both of which separate as yellow solids, and *thallous phenoxide*, which is white and micro-crystalline. Thallous hydroxide may be similarly prepared. For the preparation of thallous acetate, the ethoxide is the best starting point, and for the neutral sulphate the hydroxide is best used.

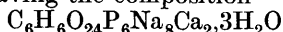
W. G.

The Alkylglycerols. Preparation of Alkylvinylcarbinols [Alkylallyl Alcohols]. RAYMOND DELABY (*Compt. rend.*, 1922, **175**, 967—970; cf. Lespieau, A., 1911, i, 347).—Homologues of glycerol were obtained by the action of magnesium alkyl compounds on acraldehyde, yielding unsaturated secondary alcohols. These were brominated and the resulting bromohydrins converted into diacetins by means of potassium acetate; hydrolysis under pressure, or alcoholysis by methyl alcohol of the diacetins, then yielded the alkylglycerols. The alkylallyl alcohols obtained in the first stage have the following properties. Δ^{α} -Buten- γ -ol (methylvinylcarbinol), b. p. $94-96^{\circ}$; d_4^{20} 0.854; d_4^{22} 0.835; n_D^{20} 1.4087 (cf. Wohl and Losanitsch, A., 1908, i, 934). Δ^{α} -Penten- γ -ol (ethylvinylcarbinol), b. p. $37^{\circ}/20$ mm.; d_4^{20} 0.839; n_D^{27} 1.4182 (cf. Wagner, A., 1885, 370). Δ^{α} -Hexene- γ -ol (propylvinylcarbinol), b. p. $133.5-134^{\circ}$; d_4^{20} 0.851; d_4^{22} 0.834; n_D^{26} 1.4215. Δ -Heptene- γ -ol (butylvinylcarbinol), b. p. $153.5-154^{\circ}$; d_4^{20} 0.852; d_4^{22} 0.835; n_D^{24} 1.4275. These alcohols yielded crystalline allophanates, m. p. $151-152^{\circ}$, $152-153^{\circ}$, $139.5-140^{\circ}$, and $156.5-157^{\circ}$, respectively. Δ^{α} -Heptene- γ -ol was

resolved into its optical isomerides by Pickard and Kenyon's method (T., 1911, 99, 45). H. J. E.

Alkylglycerols: Transformation of Alkylvinylcarbinols into Alkylglycerols. RAYMOND DELABY (*Compt. rend.*, 1922, 175, 1152—1154; cf. preceding abstract).—Experimental details of the transformation of brominated alkylvinylcarbinols into diacetins and of the hydrolysis of the latter into homologues of glycerol are described. *Propylglycerol*, m. p. 60—62°, b. p. 167·5—168°/14 mm., and *butylglycerol*, m. p. 52—54°, b. p. 175—175·5°/17 mm., are hygroscopic, crystalline substances; their *triacetates* have b. p. 157—159°/15 mm., and b. p. 174°/21 mm. respectively. Methylglycerol has b. p. 162·5—163·5°/15 mm. (cf. Lieben and Zeisel, A., 1881, 710); ethylglycerol has b. p. 165—166°/15 mm. (cf. Wagner, A., 1889, 231). The method gives yields corresponding with 60% of the secondary alcohol used. H. J. E.

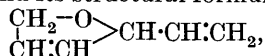
Preparation of Inositol Polyphosphate. SVIGEL POSTERNAK (Swiss Pat. 91727; from *Chem. Zentr.*, 1922, iv, 837—838; cf. A., 1921, i, 225).—A solution of inositol is heated with excess of orthophosphoric acid in the presence of sufficient excess of phosphoric oxide to combine with the water produced in esterification. The resulting products are dissolved in dilute sodium hydroxide solution and the sodium metaphosphate is changed into sodium pyrophosphate by heating at 100°. The latter salt is fractionally crystallised out from the viscid solution of the sodium salt of inositol polyphosphate. Other metallic inositol polyphosphates may be obtained from the sodium salt by double decomposition. Calcium, magnesium and ferric salts are mentioned and a crystalline calcium sodium salt having the composition



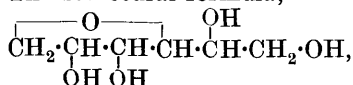
is also obtained; it probably occurs in seeds.

G. W. R.

Cyclic Derivatives of Mannitol. P. VAN ROMBURGH and J. H. N. VAN DER BURG (*Proc. K. Akad. Wetensch. Amsterdam*, 1923, 25, 335—340).—The unsaturated oxide, $\text{C}_6\text{H}_8\text{O}$, produced by heating the hexaformate of mannitol is shown to be identical with 2-vinyldihydrofuran and its structural formula,

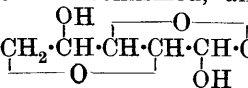


confirmed. The reduced oxide, $\text{C}_6\text{H}_{12}\text{O}$, prepared by reduction of $\text{C}_6\text{H}_8\text{O}$ with hydrogen under a pressure of two atmospheres in the presence of palladium sol, is shown to be identical with 2-ethyl-tetrahydrofuran. The structural formula,



proposed by van Romburgh and van Maanen (*Diss. Utrecht*, 1909) for mannitan is confirmed, and that similarly proposed

for isomannide, $\text{CH}_2\text{—CH—CH—CH—CH}_2$, shown probably to be



correct. *iso*Mannide increases the electrical conductivity of an aqueous solution of boric acid only very slightly. The increase in the case of mannitol and mannitan, respectively, is considerable (cf. Böeseken, A., 1921, i, 843). J. S. G. T.

Investigations on the Dependence of Rotatory Power on Chemical Constitution. XIV. The Normal Aliphatic Ethers of *d*- β -Octanol. JOSEPH KENYON and REGINALD ARTHUR McNICOL (T., 1923, 123, 14—22).

The Ability of $\alpha\gamma$ -Glycols to Form Acetone [*iso*Propylidene] Compounds. J. BÖESEKEN and P. H. HERMANS (*Ber.*, 1922, 55, [B], 3758—3760).—Trimethylene glycol unites with acetone to form an *isopropylidene* ether, a mobile liquid with a camphoraceous odour, b. p. 123—125°, d_{16}^{20} 0.9587, n_D^{25} 1.4252, the isolation of which is rendered difficult by the unfavourable position of the equilibrium of the reaction, glycol + acetone \rightleftharpoons *isopropylidene* + water, and by the considerable volatility of the compound with the vapours of acetone. The relatively difficult formation of an *isopropylidene* compound from trimethylene glycol is due, not only to the presence of the hydroxyl groups in the $\alpha\gamma$ -position and the consequent necessity of forming a six- instead of a five-membered ring, but also, and chiefly, to the unfavourable steric position of these groups. Instances in which the hydroxyl groups are more favourably placed are found in anhydroenneaheptitol (Mannich and Brose, A., 1922, i, 1118) and pentaerythritol, which yields *mono*- and *di-isopropylidene* compounds, m. p. 116° and 135°, respectively.

The place of hydrogen chloride in the condensations may be taken by other acids which are soluble in acetone. Good results are obtained with $\frac{1}{4}$ — $\frac{1}{2}$ % of concentrated sulphuric acid, which is subsequently neutralised with a considerable excess of recently-ignited, finely-divided lime. H. W.

Preparation of an Ester of Trichloroethyl Alcohol. FAR-BENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 358125; from *Chem. Zentr.*, 1922, iv, 888).—The alcohol is converted by the usual methods into the corresponding carbamate. For example, trichloroethyl alcohol dissolved in anhydrous ether is treated with carbamide hydrochloride, or the alcohol dissolved in benzene in the presence of quinoline is treated with carbonyl chloride, and the *trichloroethyl chloroformate* thus formed treated with ammonia. *Trichloroethyl carbamate* forms white needles, m. p. 64—65°. It is a soporific. G. W. R.

A New Phosphoric Ester Produced by the Action of Yeast Juice on Hexoses. ROBERT ROBISON (*Biochem. J.*, 1922, 16, 809—823).—The new ester is prepared in the following way. Lævulose or dextrose is fermented with yeast-juice and constant additions of disodium hydrogen phosphate. When the inorganic phosphate is no more utilised, barium acetate is added to the fermentation mixture, which is then neutralised and precipitated with an equal volume

of alcohol. The precipitate is then extracted with 10 parts of cold water, reprecipitated several times with basic lead acetate, purified by treatment with mercuric acetate, and finally precipitated with alcohol as the barium salt. Hexosemonophosphoric acid has $[\alpha]_D^{20} +25.0^\circ$ in water. The metallic salts with the exception of the basic salts of the heavy metals are all readily soluble in water and are amorphous. A crystalline brucine salt was obtained. The phenylhydrazine salt of the osazone of hexosemonophosphoric acid is not identical with the isomeric compound obtained from the hexosediphosphoric acid. On hydrolysis by acids or by emulsin, the hexosemonophosphoric acid yields free phosphoric acid and a dextrorotatory substance from which glucosazone is obtained. The rotatory power of this product of degradation is, however, less than that of dextrose.

S. S. Z.

Preparation of Thiohydriens. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (Brit. Pat. 185403).—Propylene thiohydrin or mixtures of this with ethylene thiohydrin are obtained by heating propylene chlorohydrin or mixtures of this with ethylene chlorohydrin such as are obtained by the action of hypochlorous acid on olefine gas mixtures, with aqueous sodium sulphide solutions, the product being isolated by evaporating the water in a vacuum, separating the sodium chloride by pressing, and distilling the crude thiohydrin under reduced pressure. *Propylene thiohydrin* boils at $120^\circ/4$ mm., and probably has the constitution $S(CH_2\cdot CHMe\cdot OH)_2$. The thiohydriens are useful as solvents in dye printing. G. F. M.

Varying Valency of Platinum with Respect to Mercaptanic Radicles. SIR PRAFULLA CHANDRA RÂY (T., 1923, 123, 133—141).

Stability of Sodium Formate, Acetate, and Oxalate towards Oxidation under Pressure. HANS SCHRADER (*Ges. Abh. Kenntnis Kohle*, 1920, 5, 193—199; from *Chem. Zentr.*, 1922, iii, 1154).—At 160° , no oxidation of these salts takes place in three hours. Oxidation takes place freely at 210° and rapidly at 260° . Sodium formate and sodium oxalate are oxidised equally quickly, whilst sodium acetate is more slowly attacked. The presence of sodium carbonate or sodium hydroxide has no marked effect. Intermediate stages between the three organic acids and carbon dioxide were not observed. No oxalate was formed from formate, neither was oxalate or formate formed from acetate.

G. W. R.

Investigations on the Dependence of Rotatory Power on Chemical Constitution. XIII. The Spatial Configuration of the Unbranched Aliphatic Chain. ROBERT HOWSON PICKARD, JOSEPH KENYON, and HAROLD HUNTER (T., 1923, 123, 1—14).

The Anodic Preparation of Pure Lead Tetra-acetate, Tetrapropionate and Silver Diacetate. C. SCHALL and W. MELZER (*Z. Elektrochem.*, 1922, 28, 474—477).—The specific conductivities and the corresponding temperature coefficients of solutions of

anhydrous and crystalline lead diacetate in acetic acid have been measured, and the products obtained on electrolysis of these solutions examined. When the water content of the mixture is less than 0.6%, very little change is observable at the anode, and when greater than 2%, the anodic product is mainly lead dioxide. At intermediate concentrations of water, pure lead tetra-acetate may be obtained in good yield if the apparatus is surrounded by ice. The pure salt may be prepared also from a solution of the diacetate in 99.4% acetic acid in the presence of dry sodium acetate. Small amounts of lead tetrapropionate and silver diacetate may be similarly obtained.

W. E. G.

Relationship between the Iodine Values and Refractive Indices of some Hardened Vegetable Oils. J. J. SUDBOROUGH, H. E. WATSON, and D. Y. ATHAWALE (*J. Ind. Inst. Sci.*, 1922, 5, v, 47—69).—Samples of cotton-seed, linseed, arachis, mohua (*Bassia latifolia*), sesamé, sardine, castor, hongay (*Pongamia glabra*), and coconut oils were refined and hydrogenated at 180°, using nickel catalysts, and the relationship between iodine value and refractive index was determined. Except in the case of castor and hongay oils, the relationship between the two constants is independent of the time and of the type of catalyst used. In the case of the first six oils mentioned, the curves representing the relationship between iodine value and refractive index lie very close together and may be represented by the equation $n_D^{60} = 1.4468 + 1.03 \times 10^{-4} + (I.V.) + 7.3 \times 10^{-8} (I.V.)^2$ to an accuracy of about 0.0005. The refractive indices at 60° of the above six oils, when completely hardened, are practically identical at the value 1.4468. The refractive indices of hardened coconut oil are much lower than those of other oils with the same iodine value. In the case of castor oil, the relationship between the iodine value and the refractive index is not independent of the type of catalyst or of the time of hardening owing to the varying extent to which the hydroxyl groups are reduced. It is possible that the case of hongay oil is similar, although its acetyl value is only 24.

H. C. R.

The Catalytic Decomposition of Castor Oil. A. MAILHE (*Compt. rend.*, 1923, 176, 37—39).—When passed over aluminium and copper turnings, castor oil undergoes decomposition, the products varying with the temperature. The products are hydrocarbons and heptaldehyde. Below 600°, the hydrocarbons formed are almost entirely homologues of methane, but above 600° aromatic hydrocarbons, such as benzene, toluene, and *m*-xylene, are also formed.

W. G.

The Transition from the Colloidal to the Crystalloidal State. Solutions of Potassium Oleate. LOUIS LEIGHTON BIRCUMSHAW (*T.*, 1923, 123, 91—97).

Dissociation Constants of Sulphoacetic and α -Sulphopropionic Acids. H. J. BACKER (*Proc. K. Akad. Wetensch. Amsterdam*, 1923, 25, 359—363).—Values of the respective molecular conductivities at 25° of aqueous solutions of sulphoacetic acid,

mono- and di-sodium sulphoacetates, sulphopropionic acid, mono- and di-sodium sulphopropionates, propionanilide- α -sulphonic acid, and sodium propionanilide- α -sulphonate, in dilutions corresponding with 1 g. mol. per 16, 32, 64, 128, 256, 512, and 1024 litres have been determined. The mean values of the respective dissociation constants of sulphoacetic and α -sulphopropionic acids calculated therefrom are 8.9×10^{-5} and 6.0×10^{-5} J. S. G. T.

The *cis*- and *trans*-Iridodichloro-oxalates. Optical Resolution of the *cis*-Potassium Salt. MARCEL DELÉPINE (*Compt. rend.*, 1922, 175, 1408—1411).—Potassium iridodichloro-oxalate, $K_3[IrCl_2(C_2O_4)_2]$, as prepared by Vêzes and Duffour (cf. A., 1909, i, 762) was found to occur in the *cis*- and *trans*-forms, and the *cis*-form was resolved into its two optical isomerides by means of its strychnine salt. The *l*-salt is the less soluble and has $[\alpha]_D -23.8^\circ$. The active salts are more soluble than the racemic mixture. The *trans*-salt is not resolved by means of its strychnine salt. The *cis*- and *trans*-isomerides are capable of being transformed into one another under suitable temperature conditions. W. G.

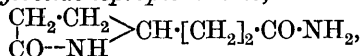
Investigations on the Dependence of Rotatory Power on Chemical Constitution. XVI. The Di- α -octyl Esters of the Saturated Dicarboxylic Acids. LESLIE HALL (T., 1923, 123, 32—44).

The Syntheses of γ -Hydroxy- and α -Amino- γ -hydroxypimelic Acids. HERMANN LEUCHS and WERNER NAGEL (*Ber.*, 1922, 55, [B], 3950—3960).—The compounds are prepared from the lactone ester,

the lactone ester, $\begin{array}{c} \text{CO} \text{---} \text{O} \\ | \quad \diagup \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} > \text{CH} \cdot \text{CH}_2 \cdot \text{CH}(\text{CO}_2\text{Et})_2$, described by

Leuchs and Möbis (A., 1909, i, 361). Attempts to halogenate the lactone ester, or the corresponding acid in the malonic residue and subsequently to eliminate the carbethoxy- or carboxy-group did not lead to satisfactory results, since only impure, non-crystalline products could be obtained which, even after re-esterification, could not be distilled without decomposition. The lactone ester is transformed by aniline at 160 — 170° into the *mono-anilide*, $\text{C}_{16}\text{H}_{19}\text{O}_5\text{N}$, lustrous leaflets, m. p. 79 — 80° . Hydrolysis of the lactone ester and subsequent removal of carbon dioxide from the product leads to the formation of the lactone of γ -hydroxypimelic acid, $\begin{array}{c} \text{CO} \text{---} \text{O} \\ | \quad \diagup \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} > \text{CH} \cdot [\text{CH}_2]_2 \cdot \text{CO}_2\text{H}$, four- or six-sided plates, m. p.

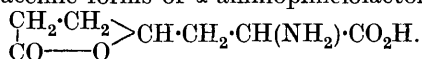
80 — 82.5° . It is converted by methyl alcohol and hydrogen chloride into methyl γ -chloropimelate which could not be isolated in a homogeneous condition, but is characterised by its conversion by ammonia into β -pyrrolidonepropionamide,



colourless needles, m. p. 144 — 145° (decomp.) when slowly heated. Hydroxypimelolactone is brominated by Volhard's method and the product is converted by methyl alcohol into the *methyl* ester

e*

of α -bromo- γ -hydroxypimelolactone which could not be distilled without decomposition; the brominated ester is hydrolysed with boiling hydrobromic acid and the resulting acid, which could not be caused to crystallise, is aminated with aqueous ammonia. The expected products could only be isolated in the form of the copper salts, one of which ($+H_2O$), sky-blue crystals, is the normal salt of γ -hydroxy- α -aminopimelic acid, $OH\cdot CH<\begin{smallmatrix} CH_2\cdot CH(NH_2)\cdot CO_2 \\ CH_2\cdot CH_2\text{---}CO_2 \end{smallmatrix}>Cu$, whereas the remaining two, greyish-blue crystals ($+\frac{1}{2}H_2O$) and paler, greyish-blue needles ($+\frac{1}{2}H_2O$), are considered to be derived from the two racemic forms of α -aminopimelolactone,



The lactone ester is converted by ethyl bromide in the presence of alcoholic sodium ethoxide into the corresponding α -ethyl derivative, $\begin{array}{c} CO\text{---}O \\ | \quad | \\ CH_2\cdot CH_2 \end{array} > CH\cdot CH_2\cdot CEt(CO_2Et)_2$, an odourless liquid, b. p. 206—208°/14 mm., which is hydrolysed to a non-crystalline acid and is converted by methyl alcoholic ammonia into the *di-amide*, $C_{10}H_{16}O_4N_2$, colourless prisms or oblique plates, m. p. 170—171°. The acid is transformed by loss of carbon dioxide into α -ethyl- γ -hydroxypimelolactone, m. p. 89—91°, to which the constitution $\begin{array}{c} CO\text{---}O \\ | \quad | \\ CHEt\cdot CH_2 \end{array} > CH\cdot [CH_2]_2\cdot CO_2H$, is assigned. The latter substance is treated with bromine and a trace of phosphorus at 100° and the product, after being purified through the methyl ester, is treated successively with hydrobromic acid and ammonia. The product is isolated as a homogeneous copper salt, $(C_9H_{14}O_4N_2)Cu\cdot\frac{1}{2}H_2O$, although the constitution of the parent acid indicates the existence of four racemic isomerides; the corresponding free acid could only be obtained as a non-crystalline, very hygroscopic mass.

H. W.

Keto-enolic Tautomerism. I. Desmotropy-isomerism of Ethyl Diacetylsuccinate. H. P. KAUFMANN (*Annalen*, 1922, 429, 247—283).—A general account of this work has already appeared (*A.*, 1922, i, 985). The investigation shows that in 0.1*N*-alcoholic solution at 30° ethyl diacetylsuccinate becomes equilibrated to an approximation of 1 or 2% in twenty-four hours, and that the mixture then contains 10% of the γ -ester (diketo), 30% of the β -ester (diketo), 16% of the $\alpha_2\beta$ -ester (mono-enol), and 44% of the $\alpha_1\beta$ -ester (mono-enol).

C. K. I.

The Amphoteric Nature of the Carbonyl Group. ERICH MÜLLER (*Z. angew. Chem.*, 1922, 35, 689—692, 698—700).—In a lecture delivered before the Dresden Chemical Society, the author gives an extended general account of his work on the electrolysis and catalytic decomposition of solutions of formaldehyde and related compounds and outlines his views on the hydration of formaldehyde to $CH_2(OH)_2$ and the amphoteric nature of the hydrate. The observations are extended to other substances

containing the carbonyl group, such as ketones, carboxylic acids, and carbon monoxide. The assumption of the formation of ions, the existence of which cannot be demonstrated or the quantity measured, is justified by analogy with inorganic compounds such as the complex cyanides, and by the fact that the very involved behaviour of formaldehyde cannot be so clearly and uniformly explained by any other hypothesis. H. W.

The Photolysis of Carbonic Acid. EMIL BAUR and A. REB-MANN (*Helv. Chim. Acta*, 1922, 5, 828—832).—Moore and Webster are stated to have obtained formaldehyde from carbon dioxide solutions by the action of sunlight in presence of colloidal oxides of uranium or ferric iron (A., 1913, i, 1303). The present authors have repeated these experiments and have not succeeded in detecting the formation of oxalic acid, glyoxylic acid, formic acid, or formaldehyde. Failure to confirm the results obtained by the above investigators may be due to their having omitted to describe with sufficient exactitude their experimental conditions.

E. H. R.

Acraldehyde Transformations and Antioxygenisers. CHARLES MOUREU and CHARLES DUFRAISSE (*Bull. Soc. chim.*, 1922, [iv], 31, 1152—1176; cf. Moureu and Dufraisse, A., 1919, i, 574; Moureu and Lepape, A., 1919, i, 574; 1920, i, 10; Moureu, Dufraisse, and Robin, A., 1920, i, 143; Moureu, Dufraisse, Robin, and Pougnet, A., 1920, i, 144; Moureu, Dufraisse, Lepape, Robin, Pougnet, Boutaric, and Boismenu, A., 1921, i, 395; Moureu and Dufraisse, A., 1922, i, 250, 824).—A review of previous publications showing the trend of the work leading to the stabilisation of acraldehyde by addition of pyrocatechol and also by other phenols is followed by development of the subject in the direction of reviewing the chief substances capable of undergoing autoxidation and also of detecting the antioxygenising function in substances other than phenols. The oxidation of the acraldehyde appears to be a necessary preliminary to the formation of disacryl and the addition of a phenol inhibits the change. But on submitting pure acraldehyde to the action of oxygen some disacryl is always formed, the quantity appearing to vary for no definite reason, although the transformation into disacryl was not observed to take place to any considerable extent in the presence of excess of oxygen. These facts appearing to be somewhat contradictory, the action of light on acraldehyde was investigated. The results showed that light effects the condensation into disacryl in absence of oxygen, and, conversely, that acraldehyde undergoes no condensation when prepared and kept in the dark and free from contact with oxygen. In absence of light, extremely small quantities of oxygen bring about the condensation, and the authors regard the phenomenon as one of catalysis, suggesting that a peroxide of acraldehyde is the catalyst. The theory put forward to account for the lack of condensation by excess of oxygen is based on the supposed existence of two types of acraldehyde molecule, one of which is activated. These molecules combine with oxygen but when oxygen is absent they

combine with each other. This is shown by the fact that acetaldehyde in contact with oxygen over mercury remains clear, the mercury meanwhile rising in the tube, but when the mercury ceases to rise oxidation is no longer occurring and the acetaldehyde becomes opaque. The time at which the latter change takes place may be predicted by extrapolating the curve obtained by plotting rise of mercury against time. Reasons are given for continued use of the term "antioxygeniser" (cf. Seyewetz and Sisley, A., 1922, ii, 628).
H. J. E.

The Hydrogenation of Aldehydes and Ketones in Presence of Pure and Impure Platinum Black. FAILLEBIN (*Compt. rend.*, 1922, 175, 1077—1079).—In the reduction of aldehydes and ketones to alcohols in presence of platinum black, considerable experimental difficulties are experienced. The action is slow, the activity of the catalyst is in many cases extremely limited, and the yields obtained are poor owing to the formation of hydrocarbons. If, however, the catalyst is prepared by the reduction of chloroplatinic acid containing 5% of its weight of ferric chloride, good yields are obtained, especially in the case of aromatic aldehydes, and the speed of the reaction is increased. If the ferric chloride is replaced by iridium chloride, similar advantages are obtained, but to a lesser extent. In hydrogenating an ethyl acetate solution of 4-piperonyl-2-butanone in presence of "ferric platinum" to the corresponding secondary alcohol, hitherto unknown, a quantitative yield was obtained. The alcohol is not described.

H. J. E.

Syntheses by means of Sodamide. A. HALLER (*Bull. Soc. chim.*, 1922, [iv], 31, 1073—1144).—A lecture delivered before the Société Chimique de France in which the use of sodamide as a reagent is discussed mainly with regard to the work of the author and his collaborators. The work surveyed comprises substitution reactions of ketones and nitriles, the action of the alkyl derivatives so obtained on various cyclic compounds and also the decomposition and condensation reactions which may be effected by the use of sodamide. The chief papers to which reference is made are those of von Auwers and Krollpfeiffer, A., 1915, i, 818; Bodroux and Taboury, A., 1910, i, 257; Cornubert, A., 1921, i, 730; Haller, A., 1904, i, 600; 1905, i, 214, 602; 1913, i, 629, 984, 1357; 1914, i, 418; Haller and Bauer, A., 1908, i, 987; 1909, i, 108, 654; 1910, i, 219, 300; 1911, i, 299, 726; 1913, i, 488, 829; 1914, i, 418, 549, 724; 1915, i, 411; 1918, i, 24, 428; 1922, i, 258; Haller and Benoist, A., 1912, i, 570; 1922, i, 350; Haller and Cornubert, A., 1914, i, 291, 842, 968; 1920, i, 390, 441; Haller and Louvrier, A., 1918, i, 397; Haller and Ramart-Lucas, A., 1914, i, 1072; 1917, i, 665.

H. J. E.

Diacetone-glucose [Diisopropylidene-glucose]. P. A. LEVENE and G. M. MEYER (*J. Biol. Chem.*, 1922, 54, 805—807).—When oxidised with nitric acid, the monomethyl glucose obtained from diisopropylidene-glucose yields a *methyl saccharolactone*,

$C_7H_{10}O_7$, m. p. 206—207° (after sintering and darkening at 190°), $[\alpha]_D^{20} + 15^\circ$ (cf. Irvine and Hogg, T., 1914, **103**, 1386). The production of this compound indicates that the *isopropylidene* radicals in *diisopropylidene-glucose* are attached to the $\alpha\beta$ and $\epsilon\zeta$ carbon atoms. If *diisopropylidene-glucose* has the structure of a γ -glucose (Irvine and Patterson, T., 1922, **121**, 2146), the methyl group in the saccharolactone will be attached to the γ -carbon atom; otherwise, it will be in the β -position. E. S.

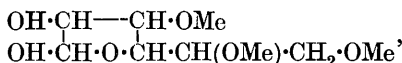
Glucosides. XI. The Glucosides of Glycerol. P. KARRER and O. HURWITZ (*Helv. Chim. Acta*, 1922, **5**, 864—869).—With the object of synthesising a glucoside of glycerol of which the constitution could not be open to doubt, the action of acetobromoglucose on *isopropylidene-glycerol* in presence of silver carbonate was studied. The reaction proceeded smoothly, giving a good yield of α -*tetra-acetyl-d-glucosidoglycerol isopropylidene ether* (annexed formula), white crystals, m. p. 132°, $[\alpha]_D^{20} - 20.77^\circ$. By careful hydrolysis of this compound with dilute sulphuric acid the acetone residue was removed, leaving α -*tetra-acetyl-d-glucosido-glycerol*, an amorphous substance which can be readily reconverted into the *isopropylidene* derivative. By the action of acetic anhydride on the amorphous substance the glycerol residue is acetylated, with formation of α -(*tetra-acetyl-d-glucosido*)-*glycerol* $\beta\gamma$ -*diacetate*, a well-crystallised compound, m. p. 98°, $[\alpha]_D^{18} - 30.96^\circ$. Alkaline hydrolysis of the last gave 1- β -*d-glucosidoglycerol*, $OH \cdot CH_2 \cdot CH(OH) \cdot CH_2 \cdot O \cdot C_6H_{11}O_5$, $[\alpha]_D^{18} - 27.72^\circ$. The β -configuration of the glucoside is proved by its ready hydrolysis by emulsin. It appears to be identical with the glyceryl glucoside synthesised by Bourquelot, Bridel, and Aubry by means of emulsin from glycerol and dextrose (A., 1917, i, 379). E. H. R.

Glucosido-trimethylammonium Salts. P. KARRER and J. TER KUILE (*Helv. Chim. Acta*, 1922, **5**, 870—876).—It was shown by Karrer and Smirnov (A., 1921, i, 766) that when *tetra-acetyl-glucosidotrimethylammonium bromide* is submitted to alkaline hydrolysis, *l-glucosan* is formed. It is now found that by acid hydrolysis only the acetyl groups are removed, and *d-glucosido- α -trimethylammonium bromide* is formed (using hydrobromic acid for the hydrolysis) as hygroscopic crystals, m. p. 161—162°; $[\alpha]_D^{18} + 5.0^\circ$. The *hydroxide*, $C_6H_{11}O_5 \cdot NMe_3 \cdot OH$, was prepared in solution by the action of silver hydroxide on the bromide or chloride; it is a strong base, but decomposes with evolution of trimethylamine when its aqueous solution is warmed. The *chloride* forms very hygroscopic crystals; the *iodide*, transparent, slightly hygroscopic crystals, m. p. 162—163°; the *chloroplatinate*, orange-brown crystals; *chloroaurate*; *picrate*, beautiful yellow needles, m. p. 141°.

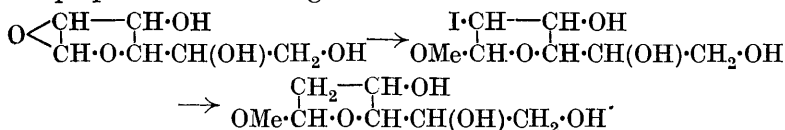
Tetra-acetyl-d-glucosido- α -trimethylammonium bromide forms rhombic crystals ($a : b : c = 0.4520 : 1 : 0.3443$); the *hydroxide* resembles the parent compound in preparation and properties; the *chloride* forms colourless hygroscopic crystals, m. p. 173°; $[\alpha]_D^{18} + 6.26^\circ$; the *perchlorate* forms microscopic needles, m. p. 190°; the *picrate*

crystallises in fine, yellow needles, m. p. 133° ; the *chloroplatinate* in fine orange needles, m. p. $209-210^{\circ}$ (decomp.), and the *chloroaurate* yellow needles which decompose when heated. E. H. R.

The Constitution of Glucosan. MARC CRAMER and EDWARD H. COX (*Helv. Chim. Acta*, 1922, **5**, 884—887).—The structure proposed by Pictet and Castan (A., 1920, i, 594) for glucosan has been confirmed; the objections to this formula raised by Bergmann (A., 1921, i, 648) and Irvine and Oldham (T., 1921, **119**, 1744) are therefore invalid. The attempt was first made to obtain an osazone from tribenzoylglucosan, but this was unsuccessful owing to the difficulty of hydrating the substance without hydrolysing the benzoyl groups at the same time. By the action of methyl sulphate on glucosan in presence of sodium hydroxide at $35-40^{\circ}$, a trimethylglucosan was obtained, b. p. $210-212^{\circ}/9$ mm. This gives a reducing sugar when boiled with water and forms a yellow, crystalline osazone, m. p. $163-164^{\circ}$ (decomp.). This can only be derived from a trimethylglucose of the formula



which confirms the glucosan structure under discussion. A further proof depends on the observation that when glucosan is heated in a sealed tube with methyl iodide at $125-130^{\circ}$ an additive compound is formed which, when reduced with sodium amalgam, gives the β -deoxymethylglucoside described by Fischer, Bergmann, and Schotte (A., 1920, i, 422). This reaction is readily explained by the proposed formula for glucosan thus:



E. H. R.

Cellulose Nitrate. EUGENE C. BINGHAM and WILLIAM L. HYDEN (*J. Franklin Inst.*, 1922, **194**, 731—740).—The mobility of solutions of cellulose nitrate (12.11% nitrogen) in acetone was determined by the viscometer method at various temperatures and concentrations, and with varying shearing stresses, in order to investigate whether the fluidity is a linear function of the concentration only, or whether, as seemed probable, it is influenced by the shearing stress. It was found that there was a steady increase in the mobility with the pressure, and as already known to be the case with many plastic materials, the efflux in ml. per second was a linear function of the shearing stress. When the shearing stress is extrapolated to its value when the efflux is zero, the friction or “yield value” is obtained, which may be defined as the shearing stress at the wall of the tube necessary to start the flow. The “yield value” increased with increasing concentration and with decreasing temperature. On plotting the “yield value” against temperature for a 7.708% nitrocellulose mixture, a sharp transition temperature

was indicated at 43° where the "yield value" became zero, and the material loses its plastic character and becomes a viscous liquid. It seems probable that this transition temperature is independent of the concentration. The mobility of cellulose nitrate dispersions is characterised by the great depression produced by very small percentages of the solid, a 1% solution having a mobility only 20% of that of the pure acetone, whilst that of an 8% solution is 0.1% of that of the solvent. This is one of the most noteworthy distinctions between the polar and the non-polar type of colloid. The mobility increases with the temperature in a nearly linear manner.

G. F. M.

Cellulose Acetate. EMIL KNOEVENAGEL and KARL KÖNIG (*Cellulosechemie*, 1922, 3, 113—122).—Gelatinisation of solutions of cellulose acetate takes place when kept in the presence of small quantities of suitable catalysts such as sulphuric acid or sulphoacetic acid, the gelatinised product becoming insoluble in the usual solvents. If the system is not completely anhydrous, as, for instance, solutions of cellulose acetate in acetone or in glacial acetic acid, this gelatinisation may be accounted for by a large decrease in the acetyl value owing to acid hydrolysis of the ester, and it takes place more rapidly as the concentration of the catalyst is increased. If the system (solution of cellulose acetate in glacial acetic acid) be rendered anhydrous by the addition of acetic anhydride, another set of conditions arises and gelatinisation may be delayed for three months, when an increase of acetyl value and a large increase in copper value, indicative of acetolysis, are recorded. When, however, moisture is totally excluded from the first, a different type of gelatinisation is characterised, which may be described as the result of condensation or polymerisation of the cellulose ester. The purified gelatinised product is then insoluble in the usual media with the exception of tetrachloroethane, the acetyl value is only slightly changed, either slightly increased or lowered, and the copper value is slightly decreased. This type of gelatinisation may be produced by completely drying 3 g. of the cellulose acetate at 105° in a glass tube, dissolving this in 100% acetic acid sufficient to give a 15% solution, and keeping this solution in a desiccator over sulphuric acid. Next day, a small quantity of catalyst, *e.g.*, 47 mg. of sulphuric acid or 96 mg. of sulphoacetic acid, is stirred into the viscous solution, 0.476 g. of acetic anhydride is added to react with any moisture which may have been absorbed during the operations, and the tube is sealed up. Gelatinisation takes place after two to three days, but if the quantity of catalyst is increased it is further delayed. With 115 mg. or more of sulphuric acid the solution does not gelatinise, but considerable acetolysis takes place.

J. F. B.

Hydrocellulose [Preparation of Dimethylhydrocellulose]. EMIL HEUSER and WALTER VON NEUENSTEIN (*Cellulosechemie*, 1922, 3, 101—107).—Chopped viscose fibre, partly dried and containing 6—10% of moisture, was placed in a bottle with a paraffined

cork and the air was displaced by passing dry carbon dioxide through for two hours. A current of dry hydrogen chloride was passed very slowly so that fumes appeared at the outlet after two to three hours. The bottle was then tightly closed and allowed to remain for several hours until a test showed that the hydrocellulose was completely soluble in 10% sodium hydroxide. The fibre was neutralised and washed. For methylation, 5 g. of the hydrocellulose (1 mol.) was dissolved in 50 c.c. of 10% sodium hydroxide solution (4 mols.) and after some hours 10 g. of methyl sulphate (3 mols.) were added in small quantities at a time with continuous agitation. The temperature rose to 60° after ten minutes. Subsequent operations were performed without separating the methylated product, using the same proportions of the reagents but taking the sodium hydroxide in the form of a 25% solution instead of 10%. After the fifth operation the greater portion of the methylated cellulose remained insoluble in the saline liquid. An excess of alkali was added and while hot the cellulose ether was collected. The precipitate was dissolved in cold water, the solution filtered to remove traces of under-methylated residue, and the ether which was precipitated on heating collected while hot and washed with boiling water. When completely methylated, this ether retained its solubility in cold water even after drying. Theoretical yields were obtained when the operations were performed with mechanical stirring and the maximum degree of methylation corresponded with a methoxyl content of 33.76. (See also this vol., i, 17.)

J. F. B.

Complex Magnesium Salts. II. G. SPACU (*Bul. Soc. Stiințe Cluj*, 1922, 1, 247—266; from *Chem. Zentr.*, 1922, iii, 1045—1046; cf. A., 1922, i, 859).—*Magnesium tetrapyridine chloride*, $\text{Mg}(\text{C}_5\text{NH}_5)_4\text{Cl}_2$, prepared from magnesium chloride and anhydrous pyridine at the ordinary temperature, is a white, crystalline powder; it is very hygroscopic, with separation of pyridine. This salt differs from the corresponding bromide and iodide in that it is not co-ordinately saturated. *Magnesium triethylenediamine chloride*, $\text{Mg en}_3\text{Cl}_2$, forms colourless crystals which cannot be resolved into their optically active components. It is highly hygroscopic. The chloride reaction is given with silver nitrate. *Magnesium diaquodiethylenediamine iodide*, $\text{Mg en}_2(\text{H}_2\text{O})_2\text{I}_2$, forms crystals; it is unstable in air. *Magnesium triethylenediamine sulphate*, $\text{Mg en}_3\text{SO}_4\text{aq}$, is a hygroscopic, white powder. *Magnesium tetrapyridine thiocyanate*, $\text{Mg}(\text{C}_5\text{NH}_5)_4(\text{CNS})_2$, from magnesium thiocyanate and anhydrous pyridine, forms small, colourless, highly refractive crystals; it is very hygroscopic. *Magnesium hexapyridine thiocyanate* forms large, colourless, highly refractive crystals. *Magnesium hexamine thiocyanate*, $\text{Mg}(\text{NH}_3)_6(\text{CNS})_2$, prepared by the action of ammonia on solid magnesium tetrapyridine thiocyanate, is a colourless powder. *Magnesium tetra-aquodipyridine chloride dipotassium chloride*, $\text{Mg}(\text{C}_5\text{NH}_5)_2(\text{H}_2\text{O})_4\text{Cl}_2 \cdot 2\text{KCl}$ is obtained by prolonged shaking of powdered carnallite with anhydrous pyridine. It is a white, crystalline powder.

G. W. R.

Preparation of Chloro-substitution Products of Hexamethylenetetramine. ROMOLO BURATTI (Swiss Pat. 90703; from *Chem. Zentr.*, 1922, iv, 891).—An aqueous solution of hexamethylenetetramine is mixed with a solution of a hypochlorite, previously neutralised with an organic or weak mineral acid, and the mixture concentrated to the point of crystallisation. Using neutral sodium hypochlorite containing 10% of active chlorine, the reaction is as follows: $C_6H_{12}N_4 + 4HClO = C_6H_8N_4Cl_4 + 4H_2O$. The *tetrachlorohexamethylenetetramine* thereby formed separates on concentration of the solution as a colourless mass; it forms salts with acids. G. W. R.

A Hydrolysis of Glycine. EMIL BAUR (*Helv. Chim. Acta*, 1922, 5, 825—828).—When a freshly prepared solution of glycine in air-free water is shaken for a long time in absence of air with animal charcoal, gradual decomposition takes place. After 240 hours at 40°, using 10 g. of charcoal to 1 g. of glycine, 17.6% of the nitrogen present is found in solution as ammonia. Since the final solution is always neutral, the reaction is probably a simple hydrolysis according to the equation $NH_2 \cdot CH_2 \cdot CO_2H + H_2O = OH \cdot CH_2 \cdot CO_2 \cdot NH_4$. Attempts to separate calcium glycolate from the solution were unsuccessful, but the salt was recognised microscopically. E. H. R.

A Series of Metallo-cysteine Derivatives. LESLIE JULIUS HARRIS (*Biochem. J.*, 1922, 16, 739—746).—Cysteine forms metallic derivatives much more readily than cystine. The former compound was found to give coloured metallic derivatives with the following ions: Fe^{+++} , Mn^{+++} , Mn^{v+} , Cu^{+} , Co, Ni, Cr, Bi. Cuprous salts give a characteristic white derivative insoluble in neutral solutions. Tin also gives a compound with it. No oxidation takes place on addition of stannic chloride, and it is suggested that owing to the strong affinity of tin for sulphur it protects that atom in cysteine from oxidation. The mercuric ion, but not the mercurous, acts as precipitant of cysteine. The colorimetric ammonia test for cysteine is only effective in the presence of traces of a metallic compound. In alkaline solution and in the presence of oxygen, the reduced metal formed an oxygen acceptor, whilst in the absence of oxygen the oxidised metal can act as an oxygen-donor, the cysteine acting as the oxidisable substance. The system is therefore reversible so long as unoxidised cysteine is present. S. S. Z.

The Decompositions of Mercury Fulminate. A. LANGHANS (*Z. ges. Schiess- u. Sprengstoffw.*, 1922, 17, 122—126, 131—133, 141—143, 150—153, 159—162).—The properties of the brown product produced by drying mercury fulminate for prolonged periods (A., 1922, i, 328), and the action of dilute and concentrated nitric acid, aqua regia, sulphuric acid, chlorosulphonic acid, and hydrofluoric acid on mercury fulminate are described.

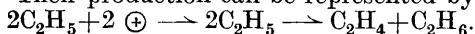
Mercury fulminate dissolves readily in boiling sodium sulphite solution. Two forms of crystals are obtained from the solution, both having the formula $HgSO_3 \cdot Na_2SO_3 \cdot H_2O$. If enough fulminate is added to produce a marked foaming, the salt $Na_2SO_3 \cdot 2HgSO_3 \cdot H_2O$

is obtained. When treated with concentrated sodium sulphide solution, mercury fulminate gives off a little carbon dioxide and is coloured black owing to formation of mercuric sulphide, which dissolves in excess of the sodium sulphide. With yellow ammonium sulphide, the black precipitate at first produced turns red, and cinnabar is produced. Wet mercury fulminate is converted into mercuric sulphide, ammonium thiocyanate, and carbon dioxide by treatment with hydrogen sulphide.

Grey mercury fulminate dissolves in sodium thiosulphate, giving an almost clear solution, but the solution of white fulminate is always opalescent and a greyish-black mass is gradually deposited, which, however, shows no trace of mercury globules under the microscope. The decrease of alkalinity on keeping of a thiosulphate solution in which mercury fulminate has been dissolved is ascribed to the liberation of acid owing to the oxidising action of fulminate on the thiosulphate, the reaction being analogous to that with mercuric chloride ($\text{Na}_2\text{S}_2\text{O}_3 + 2\text{HgCl}_2 + \text{H}_2\text{O} = \text{Na}_2\text{SO}_4 + \text{Hg}_2\text{Cl}_2 + \text{S} + 2\text{HCl}$). The change of thiosulphate into sulphate was followed quantitatively by precipitating the latter with barium chloride after various intervals of time had elapsed, and the amount of sulphate formed was found to be directly proportional to the amount of fulminate added and inversely proportional to the concentration of the thiosulphate. In using Brownsdon's titration method for estimating mercury fulminate, 23% of the thiosulphate was found to be converted into sulphate ten minutes after the addition of the fulminate. A thiosulphate solution stronger than $N/10$ is recommended in this determination.

The electrolytic determination of mercury in mercury fulminate was successfully carried out, using the following solutions: potassium cyanide, ammonia, pyridine, warm 10% sodium chloride, potassium bromide, yellow sodium sulphide (10%), 2% hydrogen peroxide, 5% potassium chlorate, sodium hypochlorite, hypobromite, and hypiodite, and ammonium oxalate. The electrolytic deposition of mercury was not quantitative using sodium thiosulphate, potassium iodide, ammonium thiocyanate, or sodium picrate. H. C. R.

The Salt-like Nature of Sodium Ethyl. Indirect Electrolysis of Zinc Ethyl. FRANZ HEIN (*Z. Electrochem.*, 1922, **28**, 469—471).—A solution of sodium ethyl in zinc ethyl is a good conductor of electricity, and can be readily electrolysed, giving metallic zinc at the cathode and a mixture of hydrocarbons at the anode. The gaseous products consist of 82% of ethane and ethylene in equal proportions, and the remainder contains hydrogen and butane. Their production can be represented by the equation



These experiments prove the salt-like nature of sodium ethyl, and support the view that the solution contains Na^+ and either C_2H_5^- or $\text{Zn}(\text{C}_2\text{H}_5)_2^-$ ions. The specific conductivity of a solution of 2 mols. NaC_2H_5 in 3 mols. $\text{Zn}(\text{C}_2\text{H}_5)_2$ is 0.01082 mho at 25°. Zinc ethyl, on the other hand, does not conduct the electric current appreciably.

W. E. G.

Is Kekulé's Benzene Theory Tenable? C. W. A. LELY (*Chem. Weekblad*, 1922, **19**, 593—598).—A triangular formula is put forward for benzene, in which the six carbon atoms, lying all in one plane, are differentiated into three primary and three secondary. The three primary form a chain of three, each having two valencies saturated by the other two primaries, and two saturated by neighbouring secondaries. The three secondaries have each two valencies saturated by primaries, and two by hydrogen atoms, the latter lying in planes perpendicular to the plane of the six carbon atoms; an additional hypothesis of synchronous rotation of the hydrogen atoms or their substituents accounts for the occurrence of only three isomeric disubstituted benzenes, and the absence of optical isomerism. Numerous reactions are cited to support the new formula, and the idea is extended to put forward formulæ for naphthalene, Willstätter's *cyclooctatetraene*, anthracene, etc.

S. I. L.

Specimens of Cymene and Ethylbenzene of Different Origin. K. VON AUWERS and H. KOLLIGS (*Ber.*, 1922, **55**, [B], 3872—3879).—In a previous communication (*A.*, 1922, ii, 174), it has been pointed out that the physical constants of hydrocarbons of the benzene series, and in particular the refractive indices, are frequently dependent on their mode of production. Since particularly marked differences in the various specimens are noticeable in the case of cymene, the hydrocarbon has been re-examined and the observations have been extended to ethylbenzene as a simple representative of the series.

It is found that the "cymene" prepared from toluene, *isopropyl* bromide, and aluminium chloride is, contrary to the general rule, a meta-derivative, since it gives *isophthalic* acid when oxidised.

Specimens of *p*-cymene obtained from *p*- β -iodo*isopropyl*toluene, cuminol, terpinene, α -terpineol, and *p*- $\alpha\alpha$ -dichloro*isopropyl*toluene, and oil of Ajowan have closely similar physical constants if the preparation first mentioned (the uniformity of which is somewhat doubtful) is not taken into account. It is remarkable, however, that *p*-cymene derived from camphor has a particularly low refractive index; even lower values have been observed by Wheeler (Schimmel and Co., Rep., 1921, 105) for a preparation from spruce oil of turpentine.

Specimens of ethylbenzene have been examined which are obtained by reduction of freshly prepared styrene by sodium and alcohol, of acetophenone by amalgamated zinc and hydrochloric acid, by Fittig's method from bromobenzene and ethyl bromide, by Friedel and Crafts' process from thiophen-free benzene and ethyl bromide, and by the action of concentrated hydrochloric acid at 130° on *p*-ethylbenzenesulphonamide, m. p. 109°, respectively. Although all the preparations are to be regarded as "pure" in the generally accepted sense of the term, they exhibit differences in their physical constants similar to those observed with cymene. The products obtained from styrene or by Clemmensen's method have higher densities and refractive indices, whereas the constants

of all the other specimens agree well among themselves and with the values recorded previously.

Since there can be no question of steric influences in the case of ethylbenzene, it appears to be established that the differences are due to traces of impurity which cling obstinately to the various specimens. These cannot be detected by elementary analysis. Attempts to use the determination of the heat of combustion as a criterion of purity do not appear to be successful. H. W.

Investigations on the Dependence of Rotatory Power on Chemical Constitution. XVII. A New Type of Walden Inversion. HENRY PHILLIPS (T., 1923, **123**, 44—59).

Nitration of 3-Chloroacenaphthene. GLADYS FARNELL (T., 1923, **123**, 60—61).

Studies in the *n*-Butyl Series. II. The Four Stereoisomeric $\beta\gamma$ -Di-*p*-tolylamino-*n*-butanes. GILBERT T. MORGAN and WILFRED JOHN HICKINBOTTOM (T., 1923, **123**, 97—105).

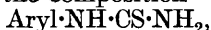
The Reduction of Nitriles with Hydrogen in Presence of Nickel. HANS RUPE and KARL GLENZ (*Helv. Chim. Acta*, 1922, **5**, 937—942).—When optically active valeronitrile was reduced with hydrogen in presence of nickel, instead of the expected hexylamine, the secondary amine, dihexylamine, was obtained. Reduction of the nitrile with sodium and alcohol readily gave optically active hexylamine. The reaction appears to be general, since phenylacetoneitrile and β -phenylpropionitrile likewise gave almost entirely secondary amine when reduced with hydrogen and nickel. α -Cyanocamphor did not give the corresponding secondary amine, but a base which has not been identified. When *o*-tolylcarbylamine was used, it acted as a poison towards the nickel catalyst, and a poor yield of a base was obtained, probably methyl-*o*-toluidine.

The dihexylamine obtained from ordinary amyl alcohol through the cyanide had b. p. 109—115°/12 mm.; its *hydrochloride*, $C_{12}H_{28}NCl$, forms lustrous leaves; the *nitrosoamine* is an oil with an aromatic odour giving Liebermann's nitroso-reaction. Di- β -phenylethylamine, $(C_6H_5 \cdot CH_2 \cdot CH_2)_2NH$, from phenylacetoneitrile, is a viscous oil; its *hydrochloride*, $C_{16}H_{20}NCl$, forms white, lustrous leaflets; the *nitrosoamine* forms white leaflets, m. p. 53—54°. Di- γ -phenylpropylamine, $NH(CH_2 \cdot CH_2 \cdot CH_2Ph)_2$, gives a *hydrochloride*, $C_{18}H_{24}NCl$, white, silky leaflets; the *nitrosoamine* crystallises in white, felted needles, m. p. 55—56°. E. H. R.

Phenyltrimethylammonium Perhalides. HAMILTON MCCOMBIE and THOMAS HAROLD READE (T., 1923, **123**, 141—153).

The Thiocarbimide Reaction. SHINTARO KODAMA (*Japan. J. Chem.*, 1922, **1**, 83—93).—An English version of the paper previously published in Japanese (cf. A., 1921, i, 237). K. K.

Preparation of Complex Silver Compounds of Aromatic Thiocarbamides. F. HOFFMANN-LA ROCHE & Co. (Swiss Pats. 90808, 91780, and 91781; from *Chem. Zentr.*, 1922, iv, 944—945).—Aryl thiocarbamides of the composition



the aryl group being substituted or unsubstituted, in excess are treated with silver salts such as silver chloride or silver nitrate. The complex silver compounds of the *p*-hydroxyphenylthiocarbamide of *p*-thiocarbamidosalicylic acid, $\text{OH}\cdot\text{C}_6\text{H}_3(\text{CO}_2\text{H})\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}_2$, m. p. 221° , are thus prepared. The latter compound is prepared from 4-aminosalicylic acid hydrochloride and ammonium thiocyanate. The complex silver compound of 6-amino-3-thiocarbamido-10-methylacridine (from 3 : 6-diamino-10-methylacridinium chloride) is also mentioned.

G. W. R.

The Two Forms of *o*-Methylcyclohexanol. L. MASCARELLI (*Atti R. Accad. Lincei*, 1922, [v], **31**, ii, 116—118).—Since the molecule of *o*-methylcyclohexanol contains two asymmetric carbon atoms having unequal rotatory values, four optically active and two racemic forms of this compound should exist. The compounds obtained by Godehot and Bédos (A., 1922, i, 334) and by Sabatier and Mailhe (A., 1905, i, 275) probably represent the two racemides. The cycloheptylcycloheptanol prepared by Godehot and Brun (A., 1922, i, 350) should exhibit similar optical isomerism to *o*-methylcyclohexanol. An analogous case is presented by the two modifications of decahydro- β -naphthol (cf. Mascarelli, A., 1911, i, 964; Mascarelli and Recusani, A., 1912, i, 761).

T. H. P.

The Oxide of Methyl- Δ^3 -cyclohexene and the Dimethylcyclohexanols. MARCEL GODCHOT and PIERRE BÉDOS (*Compt. rend.*, 1922, **175**, 1411—1414).—It has previously been shown (A., 1922, i, 334) that the action of organomagnesium complexes on the oxide of cyclohexene gives ortho-substituted homologues of cyclohexanol and that the latter compounds are stereoisomerides of the secondary alcohols obtained by the catalytic hydrogenation of the corresponding phenols. It is now shown that, in a similar manner, methyl- Δ^3 -cyclohexene gives a dimethylcyclohexanol different from those obtained by the catalytic hydrogenation of the xylenols.

Methyl- Δ^3 -cyclohexene oxide, b. p. $141\text{—}142^\circ$ (corr.), d^{14}_4 0.949, n^{14}_D 1.4518, is obtained from methyl- Δ^3 -cyclohexene either by the action of iodine and yellow mercuric oxide followed by the action of solid potassium hydroxide on the product in ethereal solution, or by oxidation with perbenzoic acid. When heated with water at 130° for six hours it is hydrated, giving 1-methylcyclohexan-3 : 4-diol, m. p. 60° , b. p. $112\text{—}115^\circ$, which gives a diphenylurethane, m. p. $176\text{—}177^\circ$. The oxide, described above, reacts with magnesium methyl iodide to yield an alcohol, b. p. $173\text{—}174^\circ$ (corr.), which is probably a 1 : 4-dimethylcyclohexan-2-ol. It has d^{18}_4 0.9106, n^{18}_D 1.452. It does not give a phenylurethane and on oxidation yields a dimethylcyclohexanone, b. p. 171° (corr.), d^{16}_4 0.9044, n^{16}_D 1.4427, which gives a semicarbazone, m. p. 122° . These physical constants are different from those of similar compounds obtained from 1 : 3 : 4- and

1 : 4 : 2-xylenol by catalytic hydrogenation and subsequent oxidation. W. G.

Catalytic Hydrogenation of Liquids by means of the Common Metals. VII. Phenols. ANDRÉ BROCHET (*Bull. Soc. chim.*, 1922, [iv], **31**, 1270—1280).—The effect of temperature and pressure on the catalytic hydrogenation of phenols in presence of a reduced nickel catalyst was studied. With phenol itself, the absorption of hydrogen commences at about 50° at atmospheric pressure, and the velocity of the reaction increases rapidly as the temperature is raised to 150°. To obtain complete hydrogenation to *cyclohexanol* within a reasonable time, it is necessary to use pressure, however, and at 20 atmospheres and temperatures of 200—230° the absorption of 6 atoms of hydrogen per mol. was complete within an hour. For the preparation of pure *cyclohexanol* pressures of 10—20 atmospheres and a temperature of about 150° constitute good practical working conditions, and if an apparatus is employed in which the catalyst can be filtered from the hydrogenised product and used again with fresh phenol it is possible completely to reduce 150 g. of the latter per 1 g. of catalyst without any appreciable loss in activity. The *cyclohexanol* obtained boiled at 160·5°/760 mm., $d_4^{15}=0\cdot950$. The cresols are not hydrogenated appreciably below 100°, but at 150° absorption proceeds with the same facility as with phenol, and by using pressures of 10—20 atmospheres reduction to the corresponding methyl *cyclohexanols* was readily achieved. *o*-Methyl*cyclohexanol* boils at 163—164°, *m*-methyl*cyclohexanol* at 170—171°, and *p*-methyl*cyclohexanol* at 170—171°. G. F. M.

Catalytic Hydrogenation under Pressure in the Presence of Nickel Salts. III. Phenetidine. JULIUS VON BRAUN and ERICH HAHN (*Ber.*, 1922, **55**, [B], 3770—3779).—Under the conditions adopted by the authors, phenetidine can be hydrogenated without loss of the ethoxyl groups; the main product appears to be a mixture of stereoisomeric 4 : 4'-diethoxydicyclohexylamines, $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}_6\text{H}_{10}\cdot\text{OEt}$.

The hydrogenation of phenetidine is effected at 210—230° in the presence of tetrahydronaphthalene; the absorption of the gas occurs somewhat slowly, and the relative amounts of the various products appear to be considerably affected by unknown catalytic influences. About a quarter of the phenetidine used is converted into a product, b. p. 208—216°/16 mm., which can be separated by means of light petroleum into two isomeric 4-ethoxyphenyl-4'-ethoxycyclohexylamines, m. p. 78—79° and 37—38°, respectively. The isomeride of higher melting point is produced in relatively very small amount, so that it has not been possible to make a complete investigation of it. It yields a non-crystalline *hydrochloride*, *picrate*, and *picrolonate*, a crystalline quaternary *methiodide*, m. p. 156°, and an *acetyl* derivative, colourless crystals, m. p. 84°. The variety of lower melting point yields a non-crystalline *hydrochloride*, *picrate*, and *picrolonate*, an *acetyl* compound, m. p. 42—43°.

b. p. 235—240°/18 mm., a *nitroso*-derivative, m. p. 78°, and a very hygroscopic quaternary *methiodide* (the corresponding *methochloride* is hygroscopic, but yields a well-defined *chloroplatinate*, a micro-crystalline, orange-red powder). Fission of the quaternary ammonium hydroxide is effected very readily and gives 4-ethoxy- Δ^1 -cyclohexene, a mobile liquid, b. p. 158—160° (which is converted by fuming hydrobromic acid into *trans*-1 : 4-dibromocyclohexane, m. p. 113°), dimethylphenetidine, m. p. 35—36° (picrate, m. p. 142°), and the tertiary base, $C_{12}H_{27}O_2N$, m. p. 40°, which gives a non-crystalline hydrochloride, picrate, and picrolonate.

4-Ethoxyphenyl-4'-ethoxycyclohexylamine is readily hydrolysed by concentrated hydrochloric acid at the temperature of boiling water, the ethoxyl group attached to the cyclohexyl nucleus being first affected. 4-Ethoxyphenyl-4'-hydroxycyclohexylamine,

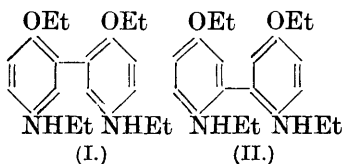


crystallises in colourless leaflets, m. p. 84—85° (*di*-p-nitrobenzoyl derivative, m. p. 192°); it loses water when distilled under diminished pressure, giving p-ethoxyphenylcyclohexenylamine, $OEt \cdot C_6H_4 \cdot NH \cdot C_6H_9$, a viscous, pale yellow liquid which could not be caused to solidify and has not been investigated further. 4-Hydroxyphenyl-4'-hydroxycyclohexylamine has m. p. 136—137°. 4-Ethoxyphenyl-4'-hydroxycyclohexylmethylamine,



m. p. 72°, yields a p-nitrobenzoyl compound, a pale yellow, crystalline powder, m. p. 189°.

The residues left after the distillation of 4 : 4'-diethoxyphenylcyclohexylamine yield a substance, $C_{20}H_{28}O_2N_2$, colourless crystals,



m. p. 169—170°; it yields a *di*-hydrochloride, decomp. 290°, a *di*-nitroso-derivative, $C_{20}H_{26}O_4N_4$, pale yellow crystals, m. p. 190°, and a *di*-acetyl compound, m. p. 240°. One of the annexed formulæ is suggested.

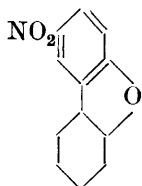
H. W.

Investigations on the Dependence of Rotatory Power on Chemical Constitution. XVIII. The Di-*l*-menthyl Esters of the Saturated Dicarboxylic Acids. LESLIE HALL (T., 1923, 123, 105—113).

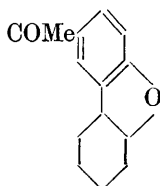
Catalytic Hydrogenation under Pressure in the Presence of Nickel Salts. II. Hexahydrodiphenylene Oxide from 2 : 2'-Dihydroxydiphenyl. JULIUS VON BRAUN (*Ber.*, 1922, 55, [B], 3761—3770).—The catalytic reduction of 2 : 2'-dihydroxydiphenyl follows a somewhat unexpected course which leads to the complete hydrogenation of one nucleus and the formation of the oxide ring. The latter is extraordinarily stable towards further reduction, but readily undergoes fission when treated with oxidising agents.

Hexahydrodiphenylene oxide, $\begin{matrix} C_6H_4 \\ | \\ C_6H_{10} \end{matrix} > O$, a colourless liquid, b. p.

138—141°/100 mm., is conveniently prepared by treating 2:2'-dihydroxydiphenyl at 230° with four atomic proportions of hydrogen and subsequent fractional distillation of the product. It is indifferent towards sodium and alcohol, zinc, and acetic acid, or magnesium phenyl bromide. It reacts slowly with bromine, but does not yield a crystalline product. Warm concentrated sulphuric acid converts it into a *monosulphonic acid*, the *sodium* salt of which is described. It is converted by cautious nitration with nitric acid (d 1.4) and glacial acetic acid at -15° into *nitrohexahydrodiphenylene oxide* (annexed formula), m. p. 126° , which is reduced by stannous chloride and concentrated hydrochloric acid to *aminohexahydrodiphenylene oxide*, pale yellow leaflets, m. p. 56° (*hydrochloride*, colourless needles, decomp. 250° after darkening at 225° and softening at 235° ; *picrate*, m. p. 186° ; *acetyl* derivative, m. p. 123°).

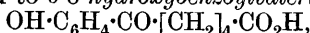


Hexahydrodiphenylene oxide readily becomes resinified under the conditions of the Friedel-Crafts' synthesis, but under definite conditions it can be converted into the corresponding *methyl ketone* (annexed formula), colourless crystals, m. p. $67-68^\circ$.



The *oxime* of the latter, m. p. 167° , is reduced by sodium and alcohol to *aminoethylhexahydrodiphenylene oxide*, a colourless liquid which rapidly absorbs atmospheric carbon dioxide, b. p. $210-213^\circ/16$ mm. (*hydrochloride*, m. p. $267-268^\circ$ after darkening at 264° ; *chloroplatinate*, decomp. 200° after gradual darkening; *picrate*, decomp. 250° after darkening at 240°). It is remarkable that the oxide ring is not ruptured during the reduction. With oxalyl chloride, hexahydrodiphenylene oxide gives the acid, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_3\text{--}\text{O--}\text{C}_6\text{H}_{10}$, colourless crystals, m. p. 250° after softening at 240° , in very poor yield.

Hexahydrodiphenylene oxide is readily oxidised by chromic acid in glacial acetic acid to δ -o-hydroxybenzoylvaleric acid,



long, colourless needles, m. p. 94° , b. p. $240-242^\circ/12$ mm. (*oxime*, m. p. 128° ; *semicarbazone*, m. p. 186° ; phenylhydrazone, yellow leaflets, m. p. 173° ; *benzoyl* derivative, m. p. 82°). The acid is slowly converted by methyl iodide and alkali in methyl-alcoholic solution into the *methoxy-acid*, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot[\text{CH}_2]_4\cdot\text{CO}_2\text{H}$, m. p. 82° (*semicarbazone*, m. p. $175-176^\circ$; *methyl* ester, prismatic needles, m. p. 28°). δ -o-Hydroxybenzoylvaleric acid is smoothly converted by isatin into 2-o-hydroxyphenyl-3-propylquinoline- γ :4-dicarboxylic acid, $\text{C}_6\text{H}_4\text{--}\text{C}(\text{CO}_2\text{H})\text{--}\text{C}[\text{CH}_2]_3\text{--}\text{CO}_2\text{H}$, m. p. 295° (decomp.). Molten sodium hydroxide rapidly transforms δ -o-hydroxybenzoylvaleric acid into phenol and adipic acid.

Nitrohexahydrodiphenylene oxide is oxidised by chromic acid to δ -m-nitro-o-hydroxybenzoylvaleric acid, small, yellow needles, m. p. 116° , which does not appear to be readily obtainable by nitration of the parent acid.

H. W.

Elimination of the Amino-group of Tertiary Amino-alcohols. I. ALEX. MCKENZIE and ANGUS CAMPBELL RICHARDSON (T., 1923, 123, 79—91).

Catalytic Hydrogenation of Liquids by means of the Common Metals. VIII. Naphthols. A. BROCHET and R. CORNUBERT (*Bull. Soc. chim.*, 1922, [iv], 31, 1280—1285).—By the hydrogenation of α - and β -naphthols under pressure, using a reduced nickel catalyst, both the *ac*- and *ar*-tetrahydronaphthols are obtained in each case. The hydrogenation of α -naphthol at 130° gives a mixture of 85% of *ac*-tetrahydro- α -naphthol and 15% *ar*-tetrahydro- α -naphthol, the former boiling at 139—140°/17 mm. (corr.) and having d_4^{17} 1·0896, n_D^{17} 1·5671, R 44·37, showing an exaltation +0·27. It is a thick liquid, becoming brown on prolonged contact with air. The *phenylurethane* melts at 121°. *ar*-Tetrahydro- α -naphthol is a solid, m. p. 68° (corr.). Hydrogenation of β -naphthol at 150° gives 75% of the alicyclic tetrahydro-derivative, and 25% of the phenolic derivative. *ac*-Tetrahydro- β -naphthol is a viscous liquid which darkens on contact with air and on keeping. It boils at 144·5—145·6°/20 mm. (corr.), d_4^{17} 1·0715, n_D^{17} 1·5523, R 44·16, showing exaltation +0·06. The *phenylurethane* melts at 99°. *ar*-Tetrahydro- β -naphthol is a solid, m. p. 57·5°. G. F. M.

Benzo-polymethylene Compounds. II. Hydroxy-bases and β -Ketones of the Tetrahydronaphthalene and Hydrindene Series. JULIUS VON BRAUN, OTTO BRAUNSDORF, and GEORG KIRSCHBAUM (*Ber.*, 1922, 55, [B], 3648—3663).—The bromine atom of *ac*-2-bromo-1-hydroxy(alkyloxy)tetrahydronaphthalenes (A., 1921, i, 407) can be replaced readily by basic residues. The hydroxy-bases formed in this manner differ greatly from *ac*- β -aminotetrahydronaphthalene and its alkyl derivatives, since they are relatively non-toxic and have a more or less marked antipyretic character, whereas the corresponding alkyloxy-compounds are strongly poisonous. The constitution of the latter substances is established by the mode of production, but in the case of the hydroxy-compounds the possibility that the hydroxyl group may occupy position 2 is not definitely excluded (cf. Straus and Rohrbacker, A., 1921, i, 171); comparative experiments on the fission of piperidino-derivatives by cyanogen bromide indicate that this is not the case, and that the striking difference in physiological properties is therefore attributable solely to the replacement of the hydroxyl by the alkyloxy group.

The following alkyloxy-bases are described: 2-Dimethylamino-1-ethoxytetrahydronaphthalene, $C_6H_4 \begin{smallmatrix} \text{CH(OEt)} \cdot \text{CH} \cdot \text{NMe}_2 \\ \text{CH}_2 \text{---} \text{CH}_2 \end{smallmatrix}$, b. p. 152°/13 mm., and its oily hydrochloride, picrate, m. p. 199°, and methiodide, m. p. 166°; β -piperidino-1-ethoxytetrahydronaphthalene, an almost colourless liquid, b. p. 170—172°/10 mm.; 2-diethylamino-1-allyloxytetrahydronaphthalene, b. p. 165°/10 mm.

ac-1-Aminotetrahydronaphthalene is readily prepared by the reduction of 1-oximinotetrahydronaphthalene with sodium and

alcohol and is converted by α -dibromopentane in boiling alcoholic solution into ac-1-piperidinotetrahydronaphthalene, a colourless liquid, b. p. 174—176°/17 mm. The *hydrochloride*, *hydrobromide*, and *methiodide* could not be caused to crystallise; the *chloroplatinate* is amorphous, whereas the *picrate* crystallises in dark yellow needles, m. p. 145—146°, after softening at 140°. ac-2-Piperidinotetrahydronaphthalene is a colourless, odourless liquid, b. p. 186—187°/16 mm. (*hydrochloride*, m. p. 230—231°; *hydrobromide*, m. p. 233—234°; *methiodide*, m. p. 209°; *picrate*, m. p. 203—204°). Both piperidino-compounds suffer fission under the influence of cyanogen bromide, but the production of bromotetrahydronaphthalene is much more marked with the 1- than with the 2-derivative. 2-Piperidino-1-hydroxytetrahydronaphthalene (cf. Straus and Rohrbacker, *loc. cit.*) has b. p. 192—194°/14 mm., m. p. 75—76° (*hydrochloride*, m. p. 185—186°; *picrate*, m. p. 152°; *chloroplatinate*, m. p. 192°). 2-Piperidino-1-benzoyloxytetrahydronaphthalene is acted on by cyanogen bromide, giving cyanopiperidine in a yield which points to the presence of the basic group in the 2- rather than in the 1-position.

ac-2-Amino-1-hydroxytetrahydronaphthalene, m. p. 109°, b. p. 160°/11 mm., is prepared by the action of concentrated ammonia solution on the corresponding bromo-compound. The *hydrochloride*, m. p. 227°; *chloroplatinate*, m. p. 215°; *picrate*, yellow leaflets, m. p. 192°; *phenylthiocarbamide*, m. p. 134°; *benzylidene* derivative, m. p. 115°; *salicylidene* derivative, m. p. 108°; *acetyl* derivative, m. p. 203°; p-nitrobenzoyl derivative, m. p. 228°; p-aminobenzoyl derivative, m. p. 208°, and the *hydrochloride* of the latter, m. p. 239°, are described. When the base is warmed with an equivalent quantity of ethylene oxide in chloroform solution it is converted into 2- β -hydroxyethylamino-1-hydroxytetrahydronaphthalene, $C_6H_4 \begin{matrix} \text{CH(OH)} \cdot \text{CH} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH} \\ \text{CH}_2 \text{---} \text{CH}_2 \end{matrix}$, a very viscous liquid,

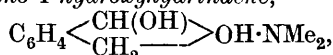
b. p. 190—196°/vacuum; the corresponding *hydrochloride* has m. p. 155°. 2-Benzylamino-1-hydroxytetrahydronaphthalene is a colourless, viscous liquid, b. p. 243—246°/13 mm. (*picrate*, m. p. 192°; *hydrochloride*, m. p. 237°). 2-Nortropyl-1-hydroxytetrahydronaphthalene, b. p. 210—212°/14 mm., yields a *picrate*, m. p. 174°, and an extremely hygroscopic *hydrochloride*. 2-Dimethylamino-1-hydroxytetrahydronaphthalene, m. p. 40° (cf. Straus and Rohrbacker, *loc. cit.*), yields a *picrate*, m. p. 138°, and a *methiodide*, m. p. 138—139°; the *benzoate* and *acetate* and its salts show little tendency towards crystallisation. The p-nitrobenzoate and p-aminobenzoate have m. p. 112° and 137°, respectively. 2-Methylamino-1-hydroxytetrahydronaphthalene *picrate* has m. p. 172°. 2-Diethylamino-1-hydroxytetrahydronaphthalene gives a crystalline *chloroplatinate*, m. p. 192°, and a liquid *acetate*.

If the methiodide of 2-dimethylamino-1-hydroxytetrahydronaphthalene is treated with silver oxide and the solution thus obtained is heated, tetrahydronaphthalene oxide is produced. When the iodide is heated alone at a temperature very slightly above its melting point, it is decomposed into trimethylamine

hydrochloride and 2-ketotetrahydronaphthalene, b. p. 140°/20 mm., 130°/10 mm., $d_4^{16.9}$ 1.1055 (*semicarbazone*, m. p. 190—191°), the yield being 80—85% of that theoretically possible. The behaviour of the ketone does not appear to be well expressed in the formula

$C_6H_4 \begin{smallmatrix} \text{CH}_2 \cdot \text{CO} \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix}$, which does not explain the formation of an intense blue colour under the influence of air and alkali, the difficulty with which it forms additive compounds, and the apparent absence of an activated methylene group. The application of Étard's reaction to tetrahydronaphthalene gives a mixture of the 1- and 2-ketones.

ac-2-Dimethylamino-1-hydroxyhydrindene,



a colourless, crystalline substance which rapidly darkens when exposed to air, b. p. 153—156°/9 mm., m. p. 62°, gives a *hydrochloride*, m. p. 183—184°, a *picrate*, m. p. 145°, and a *methiodide*, m. p. 161—162°. The latter substance is decomposed when distilled under diminished pressure into trimethylamine hydriodide and β -ketohydrindene; the conditions of the change are more drastic and the yield of ketone is smaller than with the corresponding tetrahydronaphthalene derivative. H. W.

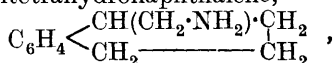
Benzo-polymethylene Compounds. VII. Pharmacological Analogues of *ac*-2-Aminotetrahydronaphthalene.

JULIUS VON BRAUN, HEINRICH GRUBER, and GEORG KIRSCHBAUM (*Ber.*, 1922, 55, [B], 3664—3674).—Substances which contain an aliphatic amino-group in the β -position with respect to an aromatic nucleus have the property of causing an increase in the blood pressure. In addition to this property, *ac*-2-aminotetrahydronaphthalene has also a mydriatic action and causes a marked increase in the body temperature. The effects obviously depend on the simultaneous presence of an aromatic and a hydroaromatic ring. The examination of a number of analogous compounds has shown that similar physiological properties are exhibited by substances which contain an aliphatic amino-group in the β -position to the aromatic portion of the tetrahydronaphthalene complex; if this condition is fulfilled, the further mode of attachment is immaterial.

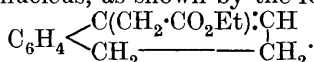
The catalytic reduction of *o*-hydroxydiphenyl with hydrogen under pressure at 210—220° in the presence of nickel salts to 2-phenylcyclohexanol is attended with considerable experimental difficulties, since the completion of the reaction is not marked by any abrupt change in the rate of absorption of the gas. The products obtained when the action is continued to the almost complete cessation of absorption are *dicyclohexyl*, b. p. 103—105°/12 mm., and 2-cyclohexylcyclohexanol, b. p. 134—135°/12 mm., which is probably a mixture of *cis*- and *trans*-isomerides (cf. Wallach, A., 1911, i, 473). The latter substance is oxidised by chromic acid to 2-cyclohexylcyclohexanone, b. p. 128—130°/10 mm. (*benzylidene* compound, m. p. 100°; *semicarbazone*, m. p.

above 200°). Less complete reduction of *o*-hydroxydiphenyl gives a mixture of phenylcyclohexane, dicyclohexyl, 2-phenylcyclohexanol, and 2-cyclohexylcyclohexanol. The alcohols are nearly exclusively produced when only six atomic proportions of hydrogen are used, but they cannot be separated conveniently from one another. Oxidation of the mixture with chromic acid gives the corresponding ketones, from which 2-phenylcyclohexanone is isolated partly in substance and partly as the *oxime*, slender needles, m. p. 174—175°; 2-phenylcyclohexanonesemicarbazone has m. p. 193°. 2-Phenylcyclohexanol, prepared by the reduction of the pure ketone with sodium and alcohol, has b. p. 143—144°/11 mm., m. p. 54—55°, and yields a *phenylurethane*, m. p. 138—139°. 2-Phenylcyclohexanoneoxime is reduced smoothly by sodium and alcohol to 2-phenylcyclohexylamine, b. p. 133—134°/12 mm., m. p. 59—60°. The *hydrochloride*, m. p. 253°, *chloroplatinate*, reddish-yellow needles, decomp. 222°, *acetyl* derivative, m. p. 130°, *phenylthiocarbamide*, m. p. 185°, and *methiodide*, m. p. 235°, are described. The base causes an increase in the blood pressure, but is not otherwise similar to ac-2-aminotetrahydronaphthalene, probably for the reason that the association of the aromatic and hydroaromatic nucleus is not sufficiently close.

ac-1-Aminomethyltetrahydronaphthalene,

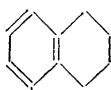


is obtained in 20% yield by the reduction of α -naphthonitrile; the *hydrochloride*, m. p. 230°, *picrate*, m. p. 170°, and *benzoyl* derivative, m. p. 125—126°, are described. The following process does not give the base in better yield. α -Ketotetrahydronaphthalene is condensed with zinc and ethyl bromoacetate to form the unsaturated *ester*, b. p. 183—184°/16 mm., which appears to have the double bond in the nucleus, as shown by the formula,



It is readily hydrolysed to the corresponding *acid*, colourless needles, m. p. 100°, which is slowly hydrogenated in the presence of palladium chloride to 1-tetrahydronaphthylacetic acid, m. p. 35—36°. The latter is convertible through the amide, but in small yield into *ac*-1-aminomethyltetrahydronaphthalene. The physiological properties of the base are similar to, but weaker than, those of *ac*-2-aminotetrahydronaphthalene.

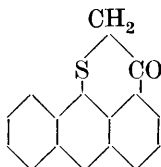
ar-1-Benzoylaminomethyltetrahydronaphthalene is converted by phosphorus pentachloride into *ar*-1-chloromethyltetrahydronaphthalene, b. p. 144—145°/13 mm., m. p. 50—51°. (*ar*-2-Chloromethyltetrahydronaphthalene has b. p. 141—142°/12 mm., but does not solidify when cooled.) It is converted smoothly by potassium cyanide in aqueous alcoholic solution into *ar*-1-cyanomethyltetra-



hydronaphthalene, colourless needles, m. p. 69—70°, b. p. 168—169°/10 mm. The latter is reduced by sodium and alcohol to *ar*-1- β -aminoethyltetrahydronaphthalene (annexed formula), a colourless, somewhat viscous

liquid, b. p. 146—149°/16 mm. The corresponding *hydrochloride*, m. p. 245° (decomp.), *picrate*, small leaflets, m. p. 231°, and *benzoyl* derivative, m. p. 123°, are described. Physiologically the base closely resembles *ac*-2-aminotetrahydronaphthalene. H. W.

The Action of Sulphur Chloride on Anthracene. P. FRIEDLÄNDER and A. SIMON (*Ber.*, 1922, 55, [B], 3969—3980).—Anthracene is readily converted by sulphur chloride into 9-anthryl dithiochloride, $C_{14}H_9 \cdot S_2 \cdot Cl$, yellowish-red, lustrous crystals, m. p. 117—118° (decomp.), when rapidly heated; it reacts readily with ammonia and aromatic bases but only gives resinous products. With dimethylamine, it gives the compound, $C_{14}H_9 \cdot S_2 \cdot NMe_2$, yellow prisms, m. p. 70—71°; the corresponding *piperidide* is described. A solution of anthryl dithiochloride in benzene is converted by a concentrated solution of sodium sulphite at the atmospheric temperature into sodium 9-anthryl thiosulphate, $C_{14}H_9 \cdot S \cdot SO_3Na$, pale yellow leaflets; the corresponding barium salt is intensely yellow, but appears to yield a colourless hydrate. 9-Anthryl hydrogen thiosulphate, $C_{14}H_9 \cdot S \cdot SO_3H$, crystallises in slender, colourless needles; it decomposes slowly in warm aqueous solution, rapidly in the presence of hydrochloric acid, into sulphuric acid and 9-anthryl disulphide, lustrous, orange-yellow octahedra, m. p. 223° (see later); this compound (in addition to thiosulphate) is also produced when a solution of the sodium salt is warmed with sodium hydroxide. 9-Thiolanthracene, orange-yellow octahedra, m. p. 90—91°, is most conveniently prepared by the action of anthryl dithiochloride on a solution of hydrated sodium sulphide in methyl alcohol; the corresponding sodium salt forms orange-yellow leaflets, and the methyl ether, needles, m. p. 153°. The thiol is the sulphur analogue of anthranol (Meyer, A., 1911, i, 193), but, unlike this compound, it exhibits little tendency to pass into a substance of the anthrone type. 9-Anthryl disulphide (see above) is obtained quantitatively by the oxidation of an alkaline solution of the thiol with potassium ferricyanide. 9-Anthrylthiolacetic acid, $C_{14}H_9 \cdot S \cdot CH_2 \cdot CO_2H$, slender, very pale yellow needles, m. p. 164°, is prepared by the addition of the sodium compound of 9-thiolanthracene to an alkaline solution of sodium chloroacetate; the sodium salt, lustrous leaflets, ammonium salt, and the methyl ester, small, yellow needles, m. p. 67°, are described. The acid is converted by phosphorus pentachloride in the presence of light petroleum (but less conveniently by thionyl chloride, which also causes chlorination) into 9-anthrylthiolacetyl chloride, compact, yellow needles, from which the corresponding amide, colourless needles which soften but do not melt at 197°, is prepared. The chloride is converted by aluminium chloride in the presence of light petroleum at 30—40°, into 3-keto-peri-anthracenopenthiophen (annexed formula), small, tile-red crystals, m. p. 150—152°. The substance is transformed by hot nitrobenzene into bis-peri-anthracenopenthiophen, $C_{14}H_8 \langle \overset{S}{\underset{CO}{\parallel}} \rangle C:C \langle \overset{S}{\underset{CO}{\parallel}} \rangle C_{14}H_8$, dark



green needles, and condenses with α -isatinanilide in the presence of pyridine to give 3'-indoxyl-(2:2')-peri-anthracenopenthiophen, $C_{14}H_8 \begin{smallmatrix} \text{S} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{C}:\text{C} \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{NH} \end{smallmatrix} C_6H_4$, dark coloured needles. H. W.

Investigations on the Dependence of Rotatory Power on Chemical Constitution. XV. Some *n*-Alkyl Ethers of *d*-Benzylmethylcarbinol. HENRY PHILLIPS (T., 1923, 123, 22—31).

The Formation and Stability of *spiro*-Compounds. X. *spiro*-Compounds Derived from *cyclo*Heptane. JOHN WILLIAM BAKER and CHRISTOPHER KELK INGOLD (T., 1923, 123, 122—133).

Preparation of Esters. LABORATOIRE-USINE (F.P. 531960; from *Chem. Zentr.*, 1922, iv, 943).—Alkyl carboxylates are heated with aluminium derivatives of alcohols. The reaction takes place according to the equation, $3R \cdot CO_2R' + Al(OR'')_3 = 3R \cdot CO_2R'' + Al(OR')_3$, where R'' has a higher molecular weight than R' . The aluminium alkyl oxides are prepared by heating the corresponding alcohols with aluminium amalgam or other easily decomposed aluminium alloys. For example, aluminium amyl oxide and ethyl acetate give amyl acetate. *Amyl phenylacetate*, α -phenylethyl acetate, β -phenylethyl phenylacetate, and linalyl acetate are similarly prepared. G. W. R.

Some Esters of Anisic Acid. L. G. RADCLIFFE and W. H. BRINDLEY (*Perf. Essent. Oil Rec.*, 1922, 13, 414—415).—Anisic acid was obtained in almost theoretical yield by the oxidation of anisaldehyde with alkaline permanganate. Cannizzaro's method—treatment of the aldehyde with potassium hydroxide—proved unsatisfactory, large amounts of unchanged material being recovered. The following esters were prepared by saturating solutions in the respective alcohols with dry hydrogen chloride. Methyl ester, m. p. 48°, b. p. 256°. Ethyl ester, m. p. 7—8°, b. p. 263°, $d_4^{16.5}$ 1.106, $n_D^{18.5}$ 1.5245. *n*-Propyl ester, b. p. 176°/15 mm., $d_4^{16.5}$ 1.09, $n_D^{18.5}$ 1.5149. *n*-Butyl ester, b. p. 183°/40 mm., $d_4^{16.5}$ 1.054, $n_D^{16.5}$ 1.5141. *iso*Butyl ester, b. p. 170°/46 mm., $d_4^{16.5}$ 1.052, $n_D^{18.5}$ 1.5072. *iso*Amyl ester, b. p. 188°/30 mm., $d_4^{16.5}$ 1.040. Phenylpropyl ester, b. p. 256°/35 mm., $d_4^{16.5}$ 1.111, $n_D^{18.5}$ 1.5623. Only the lower members of the aliphatic series have pronounced odours, the higher members are practically odourless. G. F. M.

Preparation of Alkyl Dihydroxynaphthoylbenzoates. SOCIETY FOR CHEMICAL INDUSTRY IN BASLE (Swiss Pats. 90806, 91106, and 91107; from *Chem. Zentr.*, 1922, iv, 890).—1:5- or 1:6-Dihydroxynaphthoyl-*o*-benzoic acid is esterified in the usual way with aliphatic alcohols. *Allyl* 1:6-dihydroxynaphthoyl-*o*-benzoate forms white, prismatic needles, m. p. 128°. *Ethyl* 1:6-dihydroxynaphthoyl-*o*-benzoate forms slightly yellow crystals, m. p. 156°. *Ethyl* 1:5-dihydroxynaphthoyl-*o*-benzoate forms white needles, m. p. 146°. G. W. R.

The Degradation of Hydroaromatic Acids of the Glutaric Acid Series. A. WINDAUS, F. KLÄNHARDT, and G. REVEREY (*Ber.*, 1922, 55, [B], 3981—3987).—In a previous communication (Windaus and Klänhardt, A., 1921, i, 392), it has been shown that the silver salts of the aliphatic glutaric acids react with iodine in accordance with the schemes $\text{CO}_2\text{Ag}\cdot[\text{CH}_2]_3\cdot\text{CO}_2\text{Ag} + \text{I}_2 = 2\text{AgI} + \text{—O}\cdot\text{CO}\cdot[\text{CH}_2]_3\cdot\text{CO}\cdot\text{O—}$ and $\text{—O}\cdot\text{CO}\cdot[\text{CH}_2]_3\cdot\text{CO}\cdot\text{O—} \rightarrow$ (a) $\text{CO}\cdot[\text{CH}_2]_3\cdot\text{CO} + \text{O}$, or (b) $\text{CO}\cdot[\text{CH}_2]_2\cdot\text{CH}_2 + \text{CO}_2$, or (c) $\text{CH}_2\cdot\text{CHMe} +$

2CO_2 . The observations have now been extended to acids which may be regarded as glutaric acids of which one or more carbon atoms are members of a hydroaromatic ring. The action is found to occur normally in the case of the *cis*-acids unless the glutaric acid substitutes a five-membered ring in the 1 : 3-position.

Silver *cyclohexanediacetate* is converted by iodine into the lactone, $\text{CH}_2\langle\text{CH}_2\cdot\text{CH}_2\rangle\text{C}\langle\text{CH}_2\cdot\text{O}\rangle\text{CH}_2\cdot\text{CO}$, a colourless, viscous liquid, b. p. $273^\circ/759$ mm. (slight decomp.), $154^\circ/16$ mm., $d_{19.7}^{19.7}$ 1.0755, n_D^{20} 1.48386, n_D^{20} 1.48668, n_D^{20} 1.48631. The *barium* and *silver* salts of the corresponding hydroxy-acid have been prepared. The lactone is oxidised by alkaline permanganate or by potassium dichromate and sulphuric acid to *cyclohexane-1-acetic-1-carboxylic acid*, $\text{CH}_2\langle\text{CH}_2\cdot\text{CH}_2\rangle\text{C}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, colourless prisms, m. p. 131° (uncorr.) [cf. Norris and Thorpe, T., 1921, 119, 1206].

Silver *cis*-hexahydrohomophthalate is readily converted by iodine into *hexahydrophthalide*, $\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\langle\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CO}\rangle\text{O}$, a colourless liquid, b. p. $134\text{—}138^\circ/25$ mm., the constitution of which is established by its oxidation with potassium dichromate and sulphuric acid to *cis*-hexahydrophthalic acid; the same lactone is obtained in smaller yield and with greater difficulty from silver *trans*-hexahydrohomophthalate.

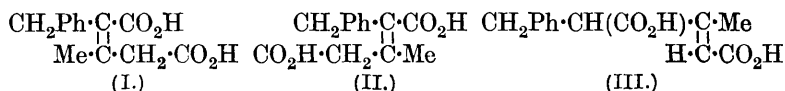
*iso*Phthalic acid is hydrogenated in glacial acetic acid solution to a mixture of *cis*- and *trans*-hexahydroisophthalic acids, in which the former preponderates the more considerably when the reduction proceeds rapidly; the *cis*-acid, however, is not converted into the *trans*-variety if subsequently agitated with glacial acetic acid and platinum black. Silver *cis*-hexahydroisophthalate and iodine give the lactone of *cis*-cyclohexanol-3-carboxylic acid, b. p. $127\text{—}135^\circ/21$ mm. (cf. Perkin and Tattersall, T., 1907, 91, 488) the identity of which is established by converting it into *cis*-cyclohexanol-3-carboxylic acid, m. p. $132\text{—}133^\circ$, and *cis*-3-bromocyclohexanecarboxylic acid, m. p. $61\text{—}63^\circ$.

Silver camphorate is transformed by iodine into camphoric anhydride; a neutral lactone does not appear to be produced.

H. W.

The Chemistry of the Glutaconic Acids. XIII. The Isomerism due to Retarded Mobility. JOCELYN FIELD THORPE and ARTHUR SAMUEL WOOD (T., 1923, 123, 62—64).

α -Benzyl- β -methylglutaconic Acids. FRANZ FEIST and ED. RAUTERBERG (*Ber.*, 1922, **55**, [B], 3697—3705).—In extension of previous investigations (A., 1922, i, 521, 522, 553), the authors have examined the ozonisation of a substituted glutaconic acid which might be expected to yield stable fission products, and for this purpose have selected α -benzyl- β -methylglutaconic acid (cf. Bland and Thorpe, T., 1912, **101**, 1740). It is shown that the (normal) acid of higher melting point and its esters and also the esters of the labile acid are constituted in accordance with the annexed formula (I), whereas the labile acid appears to be a mixture of the two *trans*-forms (II and III). The complex nature of the



latter product explains its low melting point as compared with that of the homogeneous *cis*-acid.

cis- α -Benzyl- β -methylglutaconic acid gives an *ozonide* which is hydrolysed to phenylpyruvic acid, m. p. 153—154° [oxime, m. p. 159°, *phenylhydrazone*, m. p. 187—188° (decomp.)], acetone, and carbon dioxide. The *ozonide* of its ethyl ester similarly yields ethyl benzylglyoxylate and ethyl acetoacetate. *trans*- α -Benzyl- β -methylglutaconic acid is converted successively into its *ozonide* and acetic acid, phenylethyl methyl ketone, and benzoic acid; the formation of oxalic and glyoxylic acids could not be established. The *ozonide* of ethyl *trans*- α -benzyl- β -methylglutaconate is hydrolysed to acetic acid, ethyl acetoacetate, (?) ethyl phenylpyruvate, and benzoic acid.

Ethyl phenylpyruvate is converted into a *diphenylhydrazone*, $\text{CH}_2\text{Ph}\cdot\text{C}(\text{N}\cdot\text{NPh}_2)\cdot\text{CO}_2\text{Et}$, small, yellow crystals, m. p. 105°, and a *p*-nitrophenylhydrazone, pale yellow crystals, m. p. 181°. H. W.

Ring-chain Tautomerism. IV. The Effect of the Methyl Ethyl Grouping on the Carbon Tetrahedral Angle. BALBIR SINGH and JOCELYN FIELD THORPE (T., 1923, **123**, 113—122).

Composition of Erythrosin. M. GOMBERG and D. L. TABERN (*J. Ind. Eng. Chem.*, 1922, **14**, 1115—1117).—Pure tetraiodofluorescein was prepared by direct halogenation of fluorescein in hot dilute acetic acid with excess of iodine, and subsequent purification by washing with dilute sulphuric acid and alcohol and precipitation from solution in dilute sodium hydroxide. This product did not contain free iodine but was amorphous, and the iodine content was low owing to the presence of about 6% of diiodofluorescein, from which it was purified by conversion, by boiling with acetic anhydride, into the diacetate which, after three recrystallisations from bromobenzene alternated with acetone, was obtained analytically pure and melting at 293—294°. Hydrolysis of the acetate gave pure crystalline tetraiodofluorescein. This was converted into erythrosin by neutralisation with sodium carbonate in suspension in absolute alcohol. The salt was deposited in red

crystals after concentration of the solution and addition of ether. It contained both water and alcohol of crystallisation, and the former was not completely expelled even by long drying at 160—170°. The fully hydrated salt contains $4\text{H}_2\text{O}$, and the conclusion seems justified that the true composition of erythrosin is $\text{C}_{20}\text{H}_6\text{O}_5\text{I}_4\text{Na}_2\cdot\text{H}_2\text{O}$ and that it is almost impossible to dehydrate it beyond this point without risk of decomposition. G. F. M.

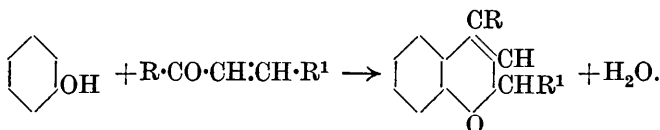
The Semi-pinacolinic Transformation of Alkylhydrobenzoins: Influence of the Alkyl Groups. MARC TIFFENEAU and ALEX. ORÉKHOFF (*Compt. rend.*, 1922, 175, 964—967; cf. Meerwein, A., 1920, i, 2; Orekhoff and Tiffeneau, A., 1922, i, 458).—The transformation of alkylhydrobenzoins under the influence of concentrated sulphuric acid may take place in two different ways, yielding either a phenyl α -alkylbenzyl ketone or a benzhydryl alkyl ketone, and the authors have investigated the influence of the nature of the alkyl group on the relative proportions of the resulting products. The conclusion is drawn that alkyl groups such as methyl, isobutyl, and phenyl, which have a strong "saturation capacity" (Meerwein, *loc. cit.*) yield the former type of product, and conversely. The groups of intermediate "saturation capacity"—ethyl, butyl, propyl, isoamyl—form hydrobenzoins which yield on dehydration mixtures of the two possible products. The results show that the influence of the alkyl group may render the secondary less stable than the tertiary hydroxyl group. This property is evident only in presence of concentrated sulphuric acid, and may result from a temporary linking of the acid with the secondary group. H. J. E.

The Action of Alcohols on Phenyl α -Bromostyryl Ketone. Formation of Various Saturated and Ethylenic Compounds. CH. DUFRASSE and P. GÉRALD (*Bull. Soc. chim.*, 1922, [iv], 31, 1285—1304).—Phenyl α -bromostyryl ketone readily unites with alcohols in presence of small quantities of the corresponding sodium alkoxide, giving α -bromo- β -alkoxybenzylacetophenones of the general formula $\text{COPh}\cdot\text{CHBr}\cdot\text{CHPh}\cdot\text{OR}$, which can be isolated if the reaction is conducted within suitable narrow limits of temperature, but which when warmed with the reaction mixture, lose hydrogen bromide, giving phenyl β -alkoxystyryl ketones, $\text{COPh}\cdot\text{CH}:\text{CPh}\cdot\text{OR}$.

The course of the reaction and the nature of the product initially obtained by Wislicenus (A., 1900, i, 37) by the action of alcoholic potassium hydroxide on phenyl β -bromostyryl ketone, is thus elucidated. The phenyl β -alkoxystyryl ketones are obtained with even greater facility and in purer condition by the addition of alcohol to benzoylphenylacetylene in presence of sodium alkoxide. All attempts to prepare the two stereoisomerides which are theoretically possible in the case of both the saturated and unsaturated compounds, or to prepare derivatives from secondary alcohols or phenols, failed. The preparation and properties of the following compounds are described. *Phenyl α -bromo- β -ethoxystyryl ketone,*

m. p. 60—61°, b. p. 182—183°/3—4 mm., white crystals, readily decomposed by alkalis and hydrolysed to dibromobenzylacetophenone by hydrobromic acid. *α-Bromo-β-methoxybenzylacetophenone*, white crystals, m. p. 76—77°. *α-Bromo-β-propoxybenzylacetophenone*, m. p. 95—96°. *α-Bromo-β-butoxybenzylacetophenone*, m. p. 81—82°. *α-Bromo-β-isobutoxybenzylacetophenone*, m. p. 110—111°. *Phenyl β-ethoxystyryl ketone*, yellowish-white crystals, m. p. 77—78°, b. p. 209°/5 mm., readily hydrolysed to dibenzoylmethane by boiling with 15% alcoholic hydrogen chloride. *Phenyl β-methoxystyryl ketone*, whitish-yellow crystals, m. p. 65—66°. *Phenyl β-propoxystyryl ketone*, m. p. 59—60°. *Phenyl β-butoxystyryl ketone*, a yellow oil, b. p. 204—206°/2 mm. *Phenyl β-isobutoxystyryl ketone*, yellowish crystals, m. p. 55—56°. *Phenyl β-isopropoxystyryl ketone*, crystals, m. p. 49—50°, b. p. 180—183°/2—3 mm. G. F. M.

Preparation of Condensation Products of $\alpha\beta$ -Unsaturated Ketones and Phenols. CHEMISCHE FABRIKEN VORM. WEILERTER MEER (D.R.-P. 357755; from *Chem. Zentr.*, 1922, iv, 890—891).— $\alpha\beta$ -Unsaturated ketones, in the presence of acids, or their acid additive products are condensed with phenols. The reaction in the case of the unsaturated ketones is as follows:



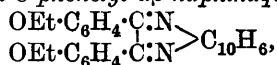
With reactive phenols such as resorcinol or *N*-substituted *m*-aminophenols the reaction is almost quantitative. The compound from the condensation of phenol and styryl methyl ketone is a grey powder. The compound from resorcinol and styryl methyl ketone is a yellow powder. The compound from the hydrogen chloride additive product of phenyl styryl ketone (3-chloro-1-keto-1:3-diphenylpropane) and resorcinol has a red colour; it forms an acetyl derivative (annexed formula). Other condensation products are formed from phenyl *m*-hydroxystyryl ketone and pyrogallol (brown); from phenyl styryl ketone and pyrogallol (bluish-grey); from phenyl *p*-dimethylaminostyryl ketone and *m*-dimethylaminophenol (greyish-blue); from resorcinol and thiodiketobenzylidenethiazolidine (reddish-brown); from styryl methyl ketone and *p*-cresol (light brown); from *p*-acetamidophenyl *o*-chlorostyryl ketone and quinol (reddish-violet). G. W. R.

Crystallographic Study of $\alpha\gamma$ -Diketohydrindene. ANGELO PICCHETTO (*Atti R. Accad. Lincei*, 1922, [v], 31, ii, 143—146).— $\alpha\gamma$ -Diketohydrindene, d^{21}_4 1·37, forms crystals belonging to the bipyramidal tetragonal class of the tetragonal system, $a:c=1:0\cdot9414$. T. H. P.

***o*-Quinones and 1 : 2-Diketones. VI. ψ -Benzils. II. Benzils of the Peroxide Type : 2 : 2'-Diethoxybenzil, a Derivative of Benzil which is Colourless in Solution.** A. SCHÖNBERG and W. MALCHOW (*Ber.*, 1922, 55, [B], 3746—3752).—In a previous communication (Schönberg and Kraemer, A., 1922, i, 663), the isolation of a number of colourless solid benzils has been described which give more or less intensely coloured solutions.

The superoxide structure, $\begin{array}{c} \text{O} \cdot \text{CR} \\ | \\ \text{O} \cdot \text{CR} \end{array}$, has been assigned to the colour-

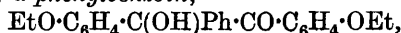
less, and the diketonic structure to the coloured benzils. This conception is strengthened by the observation that the faintly coloured solutions react less readily than those which are intensely coloured with the usual reagents for 1 : 2-diketones. In 2 : 2'-*diethoxybenzil*, colourless, quadratic leaflets, m. p. 157°, the authors have now found a substance which not only is colourless when solid, but also yields colourless solutions in cold alcohol, acetic acid, benzene, and light petroleum (b. p. 100—110°), which become pale yellow when heated. It melts to a dark yellow liquid which re-solidifies to colourless crystals. It is unimolecular in its colourless solutions, so that the absence of colour cannot be attributed to polymerisation. It is an unusually stable compound which is indifferent to concentrated aqueous ammonia under pressure and is not affected by hydrogen peroxide in acid or alkaline solution. It does not react with naphthylenediamine hydrochloride in boiling glacial acetic acid, but in the presence of boiling dimethylaniline it is slowly converted into 2 : 3-di-*o*-phenetyl- $\alpha\beta$ -*naphthaquininoxaline*,



colourless, pointed prisms, m. p. 180°. Similarly, 2 : 2'-dimethoxybenzil is transformed by *o*-phenylenediamine hydrochloride in the presence of boiling dimethylaniline into 2 : 3-di-*o*-anisylquininoxaline, colourless, quadratic prisms, m. p. 183°, by 3 : 4-diaminotoluene hydrochloride into 2 : 3-di-*o*-anisyl-6-methylquininoxaline, colourless prisms, m. p. 135°, and by naphthalene-1 : 2-diamine hydrochloride into 2 : 3-di-*o*-anisyl- $\alpha\beta$ -*naphthaquininoxaline*, colourless prisms, m. p. 180°. The method of condensation appears to be of general applicability.

2 : 2'-Dimethoxybenzil is reduced by amalgamated zinc and concentrated hydrochloric acid to $\alpha\beta$ -di-*o*-anisylethane, m. p. 86° (cf. Späth, A., 1914, i, 1).

4 : 4'-*Diethoxy- α -phenylbenzoin*,



colourless needles, m. p. 111°, is prepared by the addition of an ethereal suspension of 4 : 4'-diethoxybenzoin to an ethereal solution of magnesium phenyl bromide.

3 : 3'-*Dimethoxybenzoin*, colourless prisms, m. p. 55°, obtained by the action of potassium cyanide on *m*-methoxybenzaldehyde, is oxidised by Fehling's solution in boiling aqueous alcohol to 3 : 3'-*dimethoxybenzil*, yellow prisms, m. p. 83°. The latter substance is converted by *o*-phenylenediamine hydrochloride in the

usual manner into 2 : 3-*di-m-anisylquinoxaline*, colourless leaflets, m. p. 110°. H. W.

o-Quinones and 1 : 2-Diketones. VII. ψ -Benzils. III. Separation of a 1 : 2-Diketone into its Coloured Crystalline Ketonic and its Colourless Crystalline Peroxide Form. A. SCHÖNBERG and W. BLEYBERG (*Ber.*, 1922, 55, [B], 3753—3758; cf. A., 1922, i, 163, and preceding abstract).—4 : 4'-Dibenzyl-oxybenzil has been prepared in coloured and colourless forms.

A solution of 4 : 4'-dihydroxybenzil in absolute alcohol is treated with the calculated quantity of potassium ethoxide and a slight excess of benzyl bromide whereby the *diketonic form* of 4 : 4'-*dibenzyl-oxybenzil* is obtained as dark yellow prisms, m. p. 126°. If the hot, concentrated solution of the dibenzyl ether in alcohol, glacial acetic acid, or light petroleum (b. p. 100—110°) is suddenly cooled by immersion in ice-water, the colourless *peroxide* variety, $\text{O} \cdot \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CH}_2\text{Ph}$
 $\text{O} \cdot \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CH}_2\text{Ph}$, m. p. about 124° after becoming distinctly yellow at 121°, separates. The success of the isolation depends greatly on the rapidity with which the cooling is effected, so that it is only possible to work with small quantities at a time. A further essential condition is that the mother-liquor should be removed as rapidly as possible, since, although the colourless form is stable when dry, it rapidly passes into the yellow variety when in contact with solvents; this change occurs with such rapidity that the colourless compound appears to yield immediately coloured solutions.

4 : 4'-Dibenzyl-oxydibenzyl is rapidly converted by hydrogen peroxide in boiling alcoholic solution in the presence of sodium hydroxide into *p*-benzyl-oxybenzoic acid, m. p. 189° (cf. Cohen and Dudley, T., 1910, 97, 1732). It is converted by naphthalene-1 : 2-diamine hydrochloride in the presence of boiling dimethylaniline into the corresponding *naphthaquinoxaline*, $\text{C}_{38}\text{H}_{28}\text{O}_2\text{N}_2$, prisms, m. p. 156°. H. W.

The Acylamidoanthraquinones as Vat Dyes. E. GRANDMOUGIN (*Compt. rend.*, 1922, 175, 970—973).—The introduction of acyl groups into aminoanthraquinones results in the formation of a series of substances the tinctorial characters of which depend on the nature of the substituent entering the amino-group. If a hydroxyl group, which acts as an auxochrome, is present in addition, acetylation or benzylation of this group brightens the colour but usually diminishes the value of the substance as a dye. In the case of α -benzamidoanthraquinone, the colour is changed from bright yellow to deep rose by the introduction of a hydroxyl group in the para position and to scarlet by a methoxyl group. Further addition of benzamido-groups results in a deepening of the colour. Isomerism influences the colour and, in addition, the tinctorial properties; the author states that no adequate explanation of these facts has yet been put forward. The following substances, all crystalline and of high m. p., were prepared; their colours and the tints they impart to vegetable fibres are noted : 4-Benzamido-

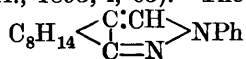
1-hydroxyanthraquinone, red, deep red. 4-Benzamido-1-acetoxyanthraquinone, yellow, rose. 4-Acetamido-1-acetoxyanthraquinone, brownish-red, light brown. 4-Benzamido-1-benzoylanthraquinone, orange-yellow, pale rose. 4-Benzamido-1-methoxyanthraquinone, orange-yellow, scarlet. 4-Acetamido-1-methoxyanthraquinone, orange-yellow, light salmon. 1:4-Diacetamidoanthraquinone, orange-yellow, light brown. 1:4-Dibenzamidoanthraquinone, reddish-yellow, reddish-yellow. 1:5-Dibenzamido-8-hydroxyanthraquinone, red, red. 1:5-Dibenzamido-4:8-dihydroxyanthraquinone, violet-blue, violet-blue. 1:5-Dianisamido-4:8-dihydroxyanthraquinone, violet-blue, violet-blue. 4:5-Dibenzamido-1:8-dihydroxyanthraquinone, violet-blue, light violet. 1:5-Diacetamido-4:8-dihydroxyanthraquinone, orange-brown. 1:5-Diacetamido-4:8-diacetoxyanthraquinone, brownish-yellow. 4:5-Diacetamido-1:8-diacetoxyanthraquinone, reddish-brown. 4:5-Dibenzamido-4:8-diacetoxyanthraquinone, yellowish-brown. The tinctorial colours of the four last-named are not stated. H. J. E.

The Investigation of *meso*-Thioanthracene Derivatives.

I. Observations on the Production of Dithioanthraquinone, Dithiodianthrone, and Other Closely Related Derivatives. ISIDOR MORRIS HEILBRON and JOHN STANLEY HEATON (T., 1923, 123, 173—185).

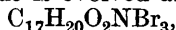
Condensation Products of Phenylhydroxylamine with Hydroxymethylene Compounds and Carbinols. IV. Methylencamphorphenylhydroxylamine. H. RUPE and W. DIEHL (*Helv. Chim. Acta*, 1922, 5, 906—922).—The reduction of methylenecamphorphenylhydroxylamine to anilinomethylene-camphor (cf. A., 1921, i, 426) can be accomplished by means of sodium hydrogen sulphite in aqueous alcoholic solution. When methylenecamphorphenylhydroxylamine is treated with thionyl chloride in ethereal solution, methylenecamphorphenylchloroamine is formed; it crystallises in short, yellowish-white prisms, m. p. 102—103°. The chlorine appears to be firmly attached to the nitrogen atom; that it has not wandered into the phenyl group was shown by condensing hydroxymethylenecamphor with *p*-chloroaniline, when *p*-chloroanilinomethylenecamphor was obtained, which crystallises in small, white prisms, m. p. 167—169°. Methylenecamphorphenylhydroxylamine combines with 1 mol. of hydrobromic acid to form a *hydrobromide*, $C_8H_{14} \begin{smallmatrix} < \text{CH} \cdot \text{CHBr} \cdot \text{NPh} \cdot \text{OH} \\ | \\ \text{CO} \end{smallmatrix}$, yellow needles,

m. p. 121° (decomp.). Similarly, it readily combines with bromine in glacial acetic acid solution to form a *dibromide*, yellow needles, m. p. 117° (decomp.). When the hydroxylamine compound is heated with phenylhydrazine in glacial acetic acid, phenylhydroxylamine is removed and a derivative formed which was found to be identical with the phenylcamphopyrazole described by Bishop, Claisen, and Sinclair (A., 1895, i, 63). The formula



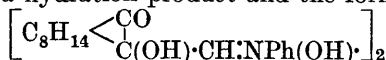
is to be preferred to that given by those authors, in which the phenyl group is attached to the 1-nitrogen atom. By the action of semicarbazide on methylenecamphorphenylhydroxylamine, the simple semicarbazone of hydroxymethylenecamphor is formed. Its m. p. is 205—206°, not 217—218° as given by Wallach (A., 1904, i, 106).

The oxidation product of methylenecamphorphenylhydroxylamine obtained by boiling it with cupric acetate (A., 1921, i, 425) can be obtained in much better yield by oxidising in cold alcohol with potassium ferricyanide. It crystallises in monoclinic needles or prisms, $a : b : c = 0.9971 : 1 : 1.065$; $\beta = 103^\circ 50'$. Its properties agree with the double formula, $\left[\text{C}_8\text{H}_{14} \begin{array}{c} \text{C} \cdot \text{CH} \cdot \text{N} \leq \text{O} \\ \text{CO} \quad | \quad \text{Ph} \end{array} \right]_2$. Its formation requires one atom of oxygen to two molecules of the hydroxylamine. The double molecule takes up four atoms of bromine to form a tetrabromide, $\text{C}_{34}\text{H}_{40}\text{O}_4\text{N}_2\text{Br}_4$, which decomposes when heated. When a solution of the tetrabromide in chloroform is warmed, hydrogen bromide is evolved and a *compound*,



crystallises; white, lustrous aggregates of needles, m. p. 205—208° (decomp.). From the chloroform solution of the tetrabromide a dibromide was also obtained, $\text{C}_{34}\text{H}_{38}\text{O}_4\text{N}_2\text{Br}_2$, m. p. 123—126° (decomp.). All these bromo-derivatives are very unstable.

When the above oxidation product of methylenecamphorphenylhydroxylamine is dissolved in 75% sulphuric acid, and then precipitated by dilution, a new *compound*, $\text{C}_{34}\text{H}_{44}\text{O}_6\text{N}_2$, is obtained. It appears to be a hydration product and the formula



is suggested for it. It has no sharp melting point, but sinters from 170°, decomposing at 190—195°. Molecular-weight determinations in different solvents gave very discordant results. It forms a *methyl* derivative, $\text{C}_{38}\text{H}_{52}\text{O}_6\text{N}_2$, m. p. 226—228°. The above formula expresses the fact that the compound is a stronger acid than the parent substance, dissolving readily in barium hydroxide solution.

There is a possibility that in the condensation of hydroxymethylenecamphor with phenylhydroxylamine, intramolecular change occurs to give a *p*-aminophenol derivative. This has been disproved by condensing *p*-aminophenol with hydroxymethylenecamphor. The product could not be crystallised, but when methylated with methyl sulphate gave *p*-anisidinomethylenecamphor, white leaflets, m. p. 169—172°. It also gave an *acetyl* derivative, white leaflets, m. p. 221—223°. E. H. R.

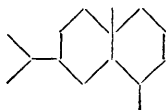
Action of Sulphur and certain Compounds of Sulphur on Terpenes. P. P. BUDNIKOV and E. A. SCHILOV (*Ber.*, 1922, 55, [B], 3848—3853; cf. A., 1922, i, 944).—Pinene or mixtures of limonene and silvestrene are converted by prolonged boiling with sulphur into a viscous, reddish-brown liquid from which a homo-

geneous substance could not be isolated by fractional distillation; the percentage of sulphur in the various fractions increases with increasing boiling point. The products yield unstable precipitates when mixed with the chlorides of mercury, gold, or platinum, lead acetate or arsenic iodide in the presence of acetone or alcohol, but these are not suitable for analysis. The action of methyl iodide on the fractions gives: *methyl terpenesulphinium iodide*, $C_{10}H_{16}S, CH_3I$, a microcrystalline precipitate, m. p. about 121° after previous darkening (the constant is given with reserve by reason of the lack of uniformity of the original material). The substance behaves as a typical sulphinium iodide, and is converted by moist silver oxide into the corresponding base. When treated with the theoretically necessary quantity of mercuric iodide in accordance with Smiles's procedure (T., 1900, 77, 163; 1907, 91, 1394), the iodide gives the compounds $C_{10}H_{16}S, CH_3I, HgI_2$, pale yellow, microscopic prisms, and $C_{10}H_{16}S, CH_3I, 2HgI_2$, lemon-yellow prisms, decomp. about 100° . With arsenic tri-iodide, the compound $C_{10}H_{16}S, CH_3I, AsI_3$, dark orange-coloured crystals, is produced. The yields of the methiodide are not satisfactory, but it was not found possible to effect any improvement in the initial action by the use of aluminium chloride, mercuric chloride, or mercuric iodide as catalysts. Better results are obtained when sulphur is replaced by sulphur chloride, but the course of the change has not yet been elucidated.

The primary action of sulphur on terpenes appears to consist in the formation of a monosulphide which probably combines with a further quantity of sulphur to give polysulphides. Evidence of the formation of thio-ozonides as suggested by Erdmann has not been obtained.

H. W.

Higher Terpene Compounds. VII. The Constitution of Eudalene, Selinene, and α -Santalene. The Carbon Framework of the Sesquiterpenes. L. RUZICKA and M. STOLL (*Helv. Chim. Acta*, 1922, 5, 923—936; cf. A., 1922, i, 560).—On theoretical grounds, it seemed probable that eudalene is formed from sesqui-

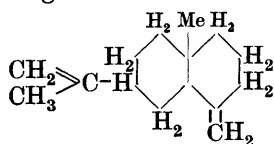
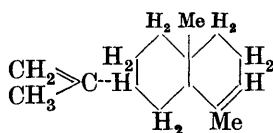


(I.)

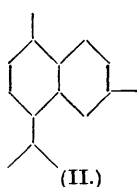
terpene compounds of the type (I) by dehydrogenation and loss of a carbon atom. If this were the case, eudalene should be isomeric with the 2-methyl-8-isopropyl-naphthalene obtained from cadalene (A., 1922, i, 1001) and should give the same naphthalene-1:7-dicarboxylic acid as this when oxidised with dilute nitric acid. This was found to be the case. *Naphthalene-1:7-dicarboxylic acid* forms a nearly white, amorphous precipitate, sinters from 200° , and melts at 265° to a dark brown liquid. There were also obtained in small quantity a *nitro-2-methyl-8-isopropyl-naphthalene*, yellow needles, m. p. 112 — 113° , and a *nitronaphthoic acid*, m. p. 225 — 227° . The identity of eudalene with 1-methyl-7-isopropyl-naphthalene was confirmed by synthesis of the hydrocarbon as follows. Cumol was condensed with ethyl bromoacetate by Reformatzky's method, and from the product ethyl *p*-isopropylcinnamate was obtained.

This was reduced by Bouveault's method giving *p*-isopropylphenyl-propyl alcohol, $C_3H_7 \cdot C_6H_4 \cdot [CH_2]_2 \cdot CH_2 \cdot OH$, b. p. $149^\circ/12$ mm. This was converted through the bromide and cyanide into γ -*p*-cumylbutyric acid, $C_3H_7 \cdot C_6H_4 \cdot [CH_2]_3 \cdot CO_2H$, b. p. $186^\circ/12$ mm., crystallising in leaflets, m. p. $31-32^\circ$. The acid chloride is a mobile oil, b. p. $156^\circ/12$ mm. When this chloride was treated with aluminium chloride, 8-keto-2-isopropyl-5 : 6 : 7 : 8-tetrahydronaphthalene was obtained, b. p. $156^\circ/12$ mm. It forms a semicarbazone, m. p. 195° . This was boiled with magnesium methyl iodide, and 1-methyl-7-isopropyl-3 : 4-dihydronaphthalene was obtained, b. p. $137^\circ/12$ mm. This was dehydrogenated by heating with the theoretical proportion of sulphur and gave 1-methyl-7-isopropyl naphthalene, identical with eudalene.

The constitution of eudalene having been established, it is shown that the two forms of the sesquiterpene selinene, which readily gives eudalene when treated with sulphur, probably have the following constitutions :

 β -Selinene. α -Selinene.

It has now been shown that there are two types of carbon skeleton, in the sesquiterpene series, derived from three isoprene units.



(II.)

These may be called the cadinene type (II) and the eudesmol type (I). The structure of α -santalene was determined by Semmler (A., 1910, i, 574), who, however, considered two formulæ possible, belonging to what he called the camphor-type and the camphene-type. It is shown that these two "types" are but different plane projections of the same three-dimensional structure. The structure is definitely

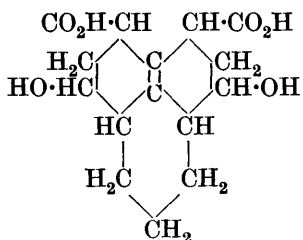
related to the eudesmol type (I). It can now be concluded that all known sesquiterpenes are closely related and are derivable from a regular tri-isoprene chain of the kind present in farnesol.

E. H. R.

The Nature of Shellac. Shellolic Acid. C. HARRIES and W. NAGEL (*Ber.*, 1922, 55, [B], 3833—3848).—A preliminary account of partly completed work on shellac and sticklac.

The lac is freed from wax and colouring matter by successive treatment with light petroleum and water, and the residue is repeatedly agitated with ether, thereby leaving an insoluble "pure resin" which is the subject of investigation and is the vehicle of the characteristic properties of shellac. The "pure resin" is attacked by *N*-potassium hydroxide solution at the atmospheric temperature, which causes the deposition of *potassium aleuritrate*, the amount being 22—24% of the resin taken. The filtrate from the salt is acidified with sulphuric acid and extracted with ether, thus yielding a mixture of shellac resin acids; these are purified

by agitating their ethereal solution with aqueous barium hydroxide and treating the latter with carbon dioxide, when the precipitated barium carbonate adsorbs a portion of the coloured resinous matter. The filtrate contains small amounts of sparingly soluble *barium aleuritate* and the freely soluble barium salts of the shellac resin acids. Attempts to isolate a homogeneous material from the latter by dialysis were not completely successful, but it is shown thereby that the salts are devoid of colour. More rapid but less complete purification can be effected through the zinc salts. The free acids do not crystallise readily. The most satisfactory results are obtained by taking advantage of the observation that the shellac resin acids, unlike other resin acids, are, at any rate in part, esterifiable by methyl-alcoholic hydrogen chloride (3%) at the atmospheric temperature, whereby *methyl shellolate*, $C_{17}H_{24}O_6$, long, prismatic rods, m. p. 149°, b. p. 284—288°/0.1 mm. (slight decomp.), $[\alpha]_D^{20} + 32.61^\circ$ in methyl-alcoholic solution, is obtained, the amount being 8—10% of the weight of the "pure resin" taken. The ester is hydrolysed by boiling aqueous *N*-sodium hydroxide solution to *shellolic acid* (*shellenedioldicarboxylic acid*), colourless leaflets, m. p. 199.5—201°, decomp. 202—203°, which gives the Liebermann cholesterol and the Salkowski-Hesse reactions. It does not reduce Fehling's solution or decolorise a solution of bromine in chloroform; its unsaturated nature is demonstrated by its instability towards alkaline permanganate and the apparent formation of an *ozonide*. The *sodium* and *barium* salts are colourless, amorphous, and freely soluble in water; the *silver*, *copper*, and *lead* salts dissolve more sparingly. The *hydrazide*, $C_{15}H_{24}O_4N_4$, crystallises in well-defined prisms, m. p. 243—244° (decomp.); the non-crystalline *acetyl* derivative and the *diphenylidiurethane*, $C_{31}H_{34}O_8N_2$, m. p. 92—94° (decomp.) according to the rate of heating, are described. The



annexed formula for shellolic acid is suggested tentatively; the positions of the hydroxyl and carboxyl groups cannot yet be definitely assigned. The position of the double bond accounts for the inactivity of the acid towards bromine.

The non-crystalline residue of esters from which methyl shellolate has been separated (*v.s.*) has b. p. 180—210°/0.1 mm., and appears to consist of compounds of hydroxy-acids. The latter are themselves amorphous, but give solid phenylurethanes.

The investigation has rendered it very improbable that shellac resin is the aleuritic ester of a higher alcohol, since no trace of the latter could be detected and it must be present in considerable quantity if it were an actual constituent. Since it is established that the resin does not contain a free acid, it appears probable that the shellac molecule is composed of hydroxy-acids which are united in the form of lactides. For one of the simpler components,

the constitution $\text{CO} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{C}_{13}\text{H}_{16}(\text{OH})\cdot\text{CO}\cdot\text{O}\cdot\text{C}_{15}\text{H}_{28}(\text{OH}) \begin{array}{c} \diagdown \\ \diagup \end{array} \text{CO}$ is suggested.

gested, the composition of which is very similar to that of the "pure resin." H. W.

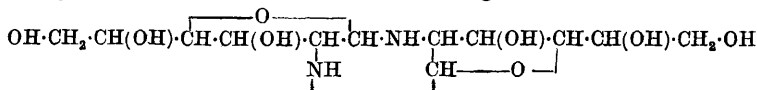
Centaureidin, a Decomposition Product of Centaurein, the Glucoside of Roots of *Centaurea Jacea*. M. BRIDEL and G. CHARAUX (*Compt. rend.*, 1922, **175**, 1168—1170).—Centaureidin, $C_{18}H_{16}O_8$ (this vol., i, 50), crystallises from 50% alcohol in microscopic, yellow needles containing water of crystallisation which is lost at 50°. The crystals melt at 197°, the anhydrous substance at 203°. It is insoluble in water, but dissolves in many organic solvents. With aqueous alkalis or sulphuric acid, it gives a golden-yellow solution. As the result of a general study of its properties, the authors suggest that it may be a flavone derivative, although the evidence on behalf of such a conclusion is mainly negative.

H. J. E.

Polysaccharides. XVII. Chitin. P. KARRER and ALEX. P. SMIRNOV (*Helv. Chim. Acta*, 1922, **5**, 832—852).—To determine how the glucosamine residues are combined in chitin, a study was made of the decomposition products obtained when chitin was distilled with zinc dust. From 300 g. of chitin from lobster shells, 37 g. of a brown oil were obtained which consisted chiefly of pyrrole compounds with a small quantity of pyridine bases, among which α -picoline was identified. From the mixture of pyrrole compounds a fraction was isolated which was identified as 2-methyl-1-*n*-hexylpyrrole. This compound and 2:5-dimethyl-1-*n*-amylpyrrole were synthesised for comparison with the compound from chitin, to which the name chitopyrrole is applied.

2:5-Dimethyl-1-*n*-amylpyrrole was prepared by heating acetonyl-acetone with *n*-amylamine. It is a colourless oil, b. p. 225—227°, with an orange-like odour, and gives a cherry-red, pine-shaving reaction. 2-Methyl-1-*n*-hexylpyrrole was prepared from potassium 2-methylpyrrole and *n*-hexyl iodide. It is a colourless oil, rapidly turning brown, b. p. 200—210°, smelling like old fungus, and gives an intense red, pine-shaving reaction. Chitopyrrole boils over a somewhat wider range than 2-methyl-1-*n*-hexylpyrrole, 190—220°, but essentially the two appear to be identical. Both are oxidised by chromic or nitrous acid to a substituted maleinimide, which when hydrolysed gives maleic acid and *n*-hexylamine. The last was identified by preparation of the *picrolonate*, m. p. 188—189°, which was also prepared from synthetic *n*-hexylamine.

The formation of 2-methyl-1-*n*-hexylpyrrole from chitin indicates the presence in the latter of two glucosamine residues combined through a nitrogen atom as in the following formula:



Neither the position of the acetyl groups nor the number of glucosamine residues present in the molecule can yet be stated. Chitosan, which is formed from chitin by hydrolytic removal of the acetyl groups, is converted by nitrous acid into a reducing sugar with

total loss of its nitrogen in the elementary form. This behaviour is quite in accordance with the above representation of chitin as an aldehyde-ammonia derivative. E. H. R.

Betulin. OTTO DISCHENDORFER (*Ber.*, 1922, 55, [B], 3692—3693).—A preliminary account of the author's observations induced by the recent publication of Schulze and Pieroh (*A.*, 1922, i, 1045).

Monobromobetulin, m. p. 215°, and the corresponding *diacetate*, m. p. 193°, have been prepared. Analyses of the latter indicate the possibility of the formulæ $C_{30}H_{48}O_2$ or $C_{30}H_{50}O_2$ for betulin, whereas Schulze and Pieroh (*loc. cit.*) regard $C_{32}H_{52}O_2$ or $C_{33}H_{54}O_2$ as probable. H. W.

Strophanthin. I. Strophanthidin. WALTER A. JACOBS and MICHAEL HEIDELBERGER (*J. Biol. Chem.*, 1922, 54, 253—261).—When dried in a vacuum at 110° over phosphoric oxide, strophanthidin decreases in weight by an amount corresponding with the loss of $\frac{1}{2}H_2O$. The anhydrous substance therefore has the formula $C_{23}H_{32}O_6$. The loss of $1\frac{1}{2}H_2O$ noted by Windaus and Hermanns (*A.*, 1915, i, 704, 705) was evidently due to partial decomposition. A final decision between the C_{23} formula and the C_{27} formula of Feist is rendered possible by the preparation of the *p-bromobenzoate*, $C_{30}H_{35}O_7Br, H_2O$. In the anhydrous condition this compound has m. p. 222—224° (decomp.), $[\alpha]_D^{25} + 42^\circ$ in acetone. *isoStrophanthidin* (strophanthidinic acid lactone of Feist, *isocymarigenin* of Windaus and Hermans) has the same formula as strophanthidin, crystallises with $\frac{1}{2}H_2O$, and forms a *benzoate*, $C_{30}H_{36}O_7$, rosettes of microscopic leaflets, m. p. about 270° after sintering, $[\alpha]_D^{25} + 38.0^\circ$ in chloroform. When reduced with hydrogen in the presence of colloidal palladium, strophanthidin slowly absorbs two atoms of hydrogen with the formation of *dihydrostrophanthidin*, $C_{23}H_{34}O_6$, which melts at 190—195° when anhydrous and crystallises with one or two molecules of water, according to the method of crystallisation. The dihydrate has $[\alpha]_D^{25} + 34.85^\circ$ in methyl alcohol. Dihydrostrophanthidin forms a *benzoate*, $C_{30}H_{38}O_7$, minute, glistening prisms, m. p. 225—227° (decomp.). The presence of a carbonyl group in strophanthidin is shown by the preparation of the *oxime*, $C_{23}H_{33}O_6N$, glistening prisms, m. p. 270—275° (decomp.), $[\alpha]_D^{25} + 71.3^\circ$ in pyridine, the *phenylhydrazone*,

$C_{29}H_{38}O_5N_2, 2H_2O$,
glistening prisms, m. p. 230—232° after sintering at 175°, $[\alpha]_D^{25} - 5.0^\circ$ in chloroform, and the *p-bromophenylhydrazone*,

$C_{29}H_{37}O_5N_2Br, 1\frac{1}{2}MeOH$,
stout, pointed prisms which soften at 180—185° and become completely molten at 200°, and have $[\alpha]_D^{25} + 105.5^\circ$ in chloroform.

E. S.

[Catechin.] M. NIERENSTEIN (*Ber.*, 1922, 55, [B], 3831—3833).—A reply to Freudenberg (*A.*, 1922, i, 756).

The author maintains that catechincarboxylic acid can be prepared according to his method, and promises further details with regard to Kostanecki's catechone. With respect to the production

of optically active catechin from inactive catechincarboxylic acid, the inactivity of the latter is maintained, but the optical activity of Gambier catechin is not considered to be established. Pure Gambier- and aca-catechins are not precipitated by solutions of gelatin. Freudenberg's observation that tetramethylcatechin cannot be demethylated by the author's method is correct so far as the derivative of Gambier catechin is concerned, but is not true for that of aca-catechin. The identity of the methylated product of the reduction of catechin with pentamethoxy- α - γ -diphenylpropane is not regarded as established. The homogeneity and optical inactivity of aca-catechin, m. p. 204—205°, is maintained.

H. W.

Tannins and Similar Compounds. XII. The Tannin of the Native [German] Oak. KARL FREUDENBERG and ERICH VOLLBRECHT (*Annalen*, 1922, **429**, 284—317).—A more expanded account of work already published (cf. A., 1922, i, 1046).

C. K. I.

Constitution of Thiophen. WILHELM STEINKOPF [with HALVARD AUGESTAD-JENSEN and HANS DONAT] (*Annalen*, 1922, **430**, 78—112).—The lability of the hydrogen atoms in the thiophen nucleus is well illustrated by its behaviour towards cyanogen bromide, with which it reacts analogously to compounds of the type of ethyl acetoacetate and ethyl malonate, which are known to contain labile hydrogen.

Thus ethyl acetoacetate and cyanogen bromide react, giving ethyl γ -bromoacetoacetate. Ethyl malonate yields ethyl bromo-malonate. Acetophenone yields ω -bromoacetophenone, and in a similar way 2-acetothiophenone yields ω -bromo-2-acetothiophenone. Phenol and cyanogen bromide yield *p*-bromophenol, whilst indene and cyanogen bromide give 1-bromo-2-hydroxyhydrindene.

Thiophen reacts with cyanogen bromide, giving bromothiophen, b. p. 151—151.5°, and dibromothiophen, b. p. 195—206°, and with cyanogen iodide, giving 2-iodothiophen (identified as the 5-iodo-2-mercurichloride). Bromothiophen is converted by cyanogen bromide into dibromothiophen, and 2-thiotolen into bromo-thiotolen, b. p. 173—177°.

Alkylthiophens in which both α -positions are substituted are also brominated by cyanogen bromide. 2:5-Dipropylthiophen yields 3-bromo-2:5-dipropylthiophen, b. p. 130—132.5°/10 mm., and 2-ethyl-5-isoamylthiophen yields 3-(or 4-)bromo-2-ethyl-5-isoamylthiophen, b. p. 122—127°/14 mm.

The above 2:5-dialkylthiophens were synthesised by way of the corresponding ketones. 5-Ethyl-2-propiothienone, b. p. 137—138°/19 mm., prepared from 2-ethylthiophen, propionyl chloride, and phosphoric oxide, gives a semicarbazone, m. p. 195—196°, and on reduction with zinc and hydrochloric acid gives 2-ethyl-5-propylthiophen, b. p. 196—197°. 5-Propyl-2-propiothienone, b. p. 137—138.5°/13 mm., prepared from 2-propylthiophen, propionyl chloride, and either phosphorus pentoxide or aluminium chloride, yields a semicarbazone, prisms, m. p. 174—175°, and on reduction

gives 2:5-dipropylthiophen, b. p. 213—214°. 5-isoAmyl-2-acetothienone, b. p. 149—151°/13 mm., prepared from 2-isoamylthiophen, acetyl chloride, and phosphorus pentoxide, gives a semicarbazone, leaflets, m. p. 212°, and on reduction yields 2-ethyl-5-isoamylthiophen, b. p. 103.5—106.5°/12 mm. None of these 2:5-dialkylthiophens gives well characterised mercury compounds on treatment with mercuric chloride. C. K. I.

The Thiophen Series. XV. Cyclic Mercury Compounds, and Experiments on the Formation of Mixed Thiophen-Mercury Compounds. WILHELM STEINKOFF, WILHELM BIELENBERG, and HALVARD AUGESTAD-JENSEN (*Annalen*, 1922, **430**, 40—78).—The experiments carried out with the object of preparing the mixed mercury compound, $C_4H_3S \cdot HgPh$, were based on the reaction between magnesium phenyl bromide and phenyl mercurichloride, the products of which are mercury diphenyl and magnesium chloride and bromide. Pure mercury phenyl thienyl could not be isolated from the product of the action of magnesium phenyl bromide in 2-thienylmercurichloride, although evidence of its formation was obtained. Mercury diphenyl is also formed by the action of mercurous chloride on magnesium phenyl bromide, and by the action of stannous chloride on magnesium phenyl chloride. Similarly, mercury 2:2'-dithienyl is the product of the reduction of thienyl-2-mercurichloride by stannous chloride.

A series of cyclic mercury-thiophen compounds is described of which dimercury 2:2':5:5'-dithienylene, $\begin{array}{c} CH_3C-Hg-C:CH \\ | \quad \quad \quad | \\ >S \quad S< \\ | \quad \quad \quad | \\ CH_3C-Hg-C:CH \end{array}$, is

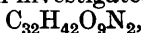
typical. This substance is obtained from 2:5-thienylenedimercurichloride and either sodium iodide or sodium thiocyanate in the presence of pyridine. Pyridine and mercuric chloride convert it into mercury 5:5'-dithienylene-2:2'-dimercurichloride, which may also be obtained by the action of pyridine on thienylene-2:5-dimercurichloride. Dimercury 3:3'-(or 4'-)diethyl-2:2':5:5'-dithienylene, mercury diethyl-5:5'-dithienylene-2:2'-dimercurichloride, and dimercury 3:4:3':4'-tetramethyl-2:2':5:5'-dithienylene are also described; like the unalkylated parent substances, they are all exceedingly insoluble compounds which do not melt at 320°. Dimercury diethyldithienylene, on treatment with mercuric chloride under regulated conditions, yields mercury diethyldithienylene-dimercurichloride, but excess of the reagent effects complete disruption of the molecule, the product being 3-ethylthienylene-2:5-dimercurichloride.

A colorimetric method of estimating the rate of separation of mercuric sulphide when an organic mercury compound is treated with sodium sulphide is described in the original. C. K. I.

Synthesis of Substituted Thianthrens. I. Thianthren and Nitrothianthren. SRI KRISHNA (T., 1923, **123**, 156—160).

Production and Reactions of 2-Dithiobenzoyl. MARY McKIBBEN and ERNEST WILSON McCLELLAND (T., 1923, **123**, 170—173).

The Alkaloids of the Northern Aconite (*Aconitum septentrionale*, Koelle). GUNNAR WEIDEMANN (*Arch. expt. Path. Pharm.*, 1922, **95**, 166—180).—Two alkaloids, isolated from the northern aconite, have been investigated. Lappaconitine,



forms hard, glass clear, six-sided prisms, m. p. 223° , $[\alpha]_D^{25} + 27.0^\circ$ in chloroform. It is a monoacid base, and contains three methoxyl groups. It forms a *chloroplatinate*, $\text{C}_{32}\text{H}_{42}\text{O}_9\text{N}_2 \cdot \text{HPtCl}_5$, and a *chloroaurate*, $\text{C}_{32}\text{H}_{42}\text{O}_9\text{N}_2 \cdot \text{HAuCl}_4$. On hydrolysis with alcoholic potash, it yields lappaconitic acid, $\text{C}_8\text{H}_9\text{O}_3\text{N}$, shown to be acetyl anthranilic acid, and a base *lappaconine*, $\text{C}_{23}\text{H}_{35}\text{O}_7\text{N} \cdot 2\text{H}_2\text{O}$, m. p. 93° , $[\alpha]_D^{25} + 22.41^\circ$. It forms a *hydrochloride*, $\text{C}_{23}\text{H}_{35}\text{O}_7\text{N} \cdot \text{HCl}$, large, colourless crystals. Septentrionaline, $\text{C}_{29}\text{H}_{34}\text{O}_5\text{N}_2 \cdot (\text{OMe})_4$, the other alkaloid investigated, is an amorphous, white powder, m. p. 131° , $[\alpha]_D^{25} + 32.71^\circ$, forming a *chloroplatinate*, $\text{C}_{29}\text{H}_{34}\text{O}_5\text{N}_2 \cdot \text{HPtCl}_5$. On hydrolysis with alcoholic potash, there is obtained (1) an *acid*, $\text{C}_8\text{H}_9\text{O}_3\text{N}$, m. p. $125\text{--}126^\circ$, which when boiled with sodium hydroxide solution yields anthranilic acid, losing CH_2O , and (2) a *base*, $\text{C}_{25}\text{H}_{39}\text{O}_7\text{N}$, m. p. 89° , $[\alpha]_D^{25} + 29.55^\circ$, forming a *hydrochloride*, $\text{C}_{25}\text{H}_{39}\text{O}_7\text{N} \cdot \text{HCl}$.

W. O. K.

Paniculatin, the Alkaloid from *Aconitum paniculatum*, Lam. G. E. BRUNNER (*Schweiz. Apoth. Zig.*, 1922, **60**, 357—358; from *Chem. Zentr.*, 1922, iii, 1007).—*Paniculatin*, $\text{C}_{29}\text{H}_{35}\text{O}_7\text{N}$, the alkaloid from *Aconitum paniculatum*, Lam., is not identical with aconitine. It forms small, rhombic prisms with m. p. 263° .

G. W. R.

Melanins, Arising from Adrenaline. PIETRO SACCARDI (*Biochem. Z.*, 1922, **132**, 439—442).—Melanin-like pigments, obtained by the oxidation of adrenaline with chlorine water, are described.

W. O. K.

Preparation of a Quinine Derivative. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION, JULIUS ALTSCHUL, and MARCELL BACHSTETZ (D.R.-P. 357753; from *Chem. Zentr.*, 1922, iv, 951).—Equimolecular amounts of quinine and 4-ethoxyphenylmalonic acid are fused together and crystallised from hydrolysing solvents or allowed to react as such or in form of their salts in the presence of hydrolysing solvents. *Quinine 4-ethoxyphenylmalonamate* forms long, colourless needles, m. p. $72\text{--}73^\circ$.

G. W. R.

Quiteninone. SIGMUND FRÄNKEL, CHARLOTTE TRITT-ZIRMING, and LILY GOTTESMANN-GRAUER (*Ber.*, 1922, **55**, [B], 3931—3935).—The action of hydrogen peroxide (30%) on a solution of quinine sulphate in dilute sulphuric acid in the presence of copper or ferrous sulphate as catalyst and at the atmospheric temperature leads to the production of *quiteninone*, $\text{C}_{19}\text{H}_{20}\text{O}_4\text{N}_2$, needles, m. p. 156° . The reaction appears to be considerably influenced by external factors and to take place through a number of intermediate products of which quinine oxide (cf. Speyer and Becker, A., 1922,

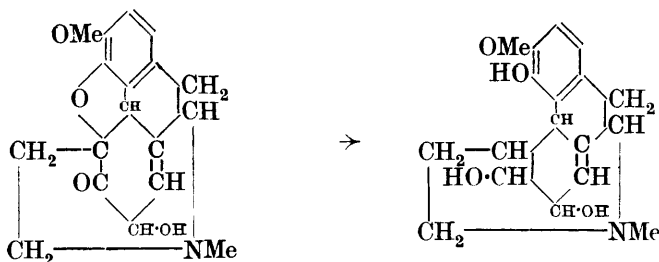
i, 674) is one. Quiteninone is also produced by the oxidation of quitenine (cf. Nierenstein, A., 1920, i, 875). It gives a *picrate*, m. p. 140°. The constitution of quiteninone is partly elucidated by the preparation of the *methyl ester picrate*, $C_{20}H_{22}O_4N_2 \cdot 2C_6H_3O_7N_3$, decomp. 270°, and the *methyl ester dihydrochloride*, m. p. 181°. Quiteninone could not be caused to react with phenylhydrazine, *p*-nitrophenylhydrazine, or semicarbazide hydrochloride; with hydroxylamine in alkaline solution, it gives an oxime which is identified as the corresponding *picrate*, $C_{19}H_{21}O_4N_3 \cdot C_3H_3O_7N_3$, m. p. 126°. H. W.

Esterification of Creatine. ARTHUR W. DOX and LESTER YODER (*J. Biol. Chem.*, 1922, **54**, 671—673).—Saturation of a suspension of creatine in an alcohol with hydrogen chloride results in the formation, not of creatinine, but of an ester of creatine the hydrochloride of which separates on the addition of ether. By this means the author has prepared: *creatine methyl ester hydrochloride*, slender needles, m. p. 139—140°; *creatine ethyl ester hydrochloride*, needles, m. p. 163°; *creatine n-butyl ester hydrochloride*, flat needles, m. p. 138°. Each salt melts with the evolution of gas and leaves a solid residue of creatinine hydrochloride. E. S.

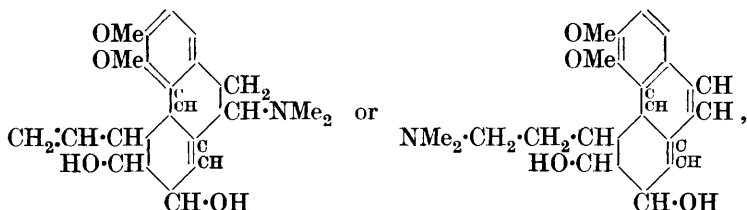
Ergot. A. STOLL (*Schweiz. Apoth. Ztg.*, 1922, **60**, 341—346; from *Chem. Zentr.*, 1922, iii, 1007; cf. Spiro and Stoll, A., 1922, i, 47).—The specific effect of ergot is not considered to be due to the presence of simple amines such as tyramine. After addition of acid reagents such as aluminium sulphate to ergot, extraction of one kg. of the material with ether and benzene removes 350—400 g. of alkaloid-free ergot oil together with soluble acid and neutral substances such as organic acids, phytosterol, and colouring matters. From the acidified cell material a crystalline alkaloid was separated. *Ergotamine*, $C_{33}H_{35}O_5N_5 \cdot 2COMe_2 \cdot 2H_2O$ (from acetone) forms highly refractive rhombic prisms; it has $[\alpha]_D^{20} -155^\circ$ in 0.6% chloroform solution; the monoacid base and its compounds decompose on heating at 140°; at 180° a brown mass is formed with evolution of gas. On keeping an ethyl-alcoholic solution or warming a methyl-alcoholic solution of ergotamine, an isomeride, *ergotaminine*, of weaker basic character, is formed. It crystallises in triangular leaflets and has $[\alpha]_D^{20} +381^\circ$ in 0.6% chloroform solution. Ergotaminine may be reconverted into ergotamine. Both isomerides give a blue coloration with strong sulphuric acid. Ergotamine is unstable in air. G. W. R.

The Hydroxycodeinone Series. EDMUND SPEYER [with S. SELIG and MARTIN HEIL] (*Annalen*, 1922, **430**, 1—40).—A further account (see A., 1915, i, 580; 1916, i, 157, 758; 1921, i, 685) of derivatives of codeine and thebaine including the reduction of hydroxycodeinone to hydroxythebainol and the conversion of the latter into a nitrogen-free substance by exhaustive methylation. All results are interpreted on the basis of Knorr's formula for morphine.

Hydroxycodeinone is converted either by electrolytic reduction or by zinc and formic acid into *hydroxythebainol*, m. p. 234° :



the *formate* of hydroxythebainol, m. p. 227°, and 7-hydroxycodeine being obtained as by-products in the latter case. Hydroxythebainol yields a crystalline *hydrochloride*, *hydrobromide*, m. p. 252—253°, $[\alpha]_D^{20} -157.7^\circ$, *hydriodide*, m. p. 247°, and *picrate*, m. p. 204—206°. On treatment with benzoyl chloride, it gives a *benzoyl* derivative, needles, m. p. 257°; with bromine and acetic acid, a *perbromide*, which on reduction by sulphur dioxide gives a *mono-bromo-derivative*, m. p. 230—231°, reducible to hydroxythebainol, and with hydrogen peroxide an *N-oxide*, which crystallises in prisms, m. p. 237°. On methylation with methyl sulphate and alkali, hydroxythebainol yields the *methyl ether methiodide*, rhombs, decomp. 233°, which with hot alkali hydroxide gives des-*N-methyl-hydroxythebainol methyl ether*,



small needles, m. p. 195—197°. The *hydriodide* forms needles, m. p. 255°, and the *methiodide*, obtained with the aid of methyl iodide, microscopic prisms, decomp. 239—240°. On treating this substance successively with silver oxide and concentrated alkalis, trimethylamine is eliminated and the nitrogen-free substance, 2 : 3-*dihydroxy-5 : 6-dimethoxy-4-vinyl-2 : 3 : 4 : 4a-tetrahydrophenanthrene*, is obtained. This forms stout prisms, m. p. 188—189°, and is insoluble in alkali, which shows that the two hydroxyl groups are in the aliphatic part of the molecule.

An improved method of preparation of hydroxythebainone is described. Its *dibromide*, obtained by the use of bromine and chloroform, decomposes at 258°, and on reduction by hydrogen and palladium black gives hydroxydihydrothebainone, which may be obtained directly from hydroxythebainone by means of the same reducing agent. The *methiodide* of hydroxythebainone forms prisms, m. p. 245°, the *acetyl* derivative, needles, m. p. 197°, and

the *oxime* of the acetyl derivative, prisms, m. p. 216—218°. The *methiodide* of the acetyl derivative decomposes at 212—213°, and gives a non-crystalline *deoxy*-base on decomposition by alkalis. The *methiodide* of the acetyl derivative of 7-hydroxycodeine sinters at 230° and decomposes at 256°.

Reduction of hydroxycodeinone oxime by hydrogen and palladium under various conditions yielded hydroxydihydrocodeinone, and it was not found possible to prevent the elimination of the oximino-group. Parallel experiments with styrylmethylketoxime and distyrylketoxime yielded analogous results, the products being benzylacetone and dibenzylacetone, respectively. C. K. I.

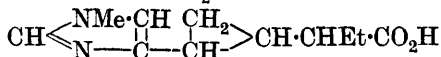
The Pilocarpine Series. II. Pilocarpic Esters and their Derivatives. MAX POLONOVSKI AND MICHEL POLONOVSKI (*Bull. Soc. chim.*, 1922, [iv], **31**, 1185—1201; cf. this vol., i, 52).—Although it is generally accepted that a γ -lactone group is present in pilocarpine and its isomeride, few of the properties of a γ -lactone have been actually shown to be characteristic of these substances. The authors find that the esterification of pilocarpine by means of methyl or ethyl alcohol and hydrogen chloride does not yield the ethyl ester of pilocarpic acid but the ethyl γ -chloro-ester, thus confirming the γ -lactone grouping by the characteristic reaction of simultaneous esterification of acidic and alcoholic groups by alcohol and halogen, respectively. *Methyl γ -chloropilocarpate* forms small, transparent prisms, m. p. 42—44°, $[\alpha]_D + 32.6^\circ$, and is a strong base; the *nitrate* forms lustrous plates, m. p. 157°, $[\alpha]_D + 20^\circ$. *Ethyl γ -chloropilocarpate* was obtained as an oil, $[\alpha]_D + 29.2^\circ$; the *nitrate* forms lustrous plates, m. p. 136°, $[\alpha]_D + 23.4^\circ$. On treatment of the nitrate with concentrated sulphuric acid, it is converted into ethyl γ -chloronitropilocarpate. The γ -chloro-esters of pilocarpine are readily lactonised with loss of the halogen atom and the alkyl group; this is accompanied by the transformation of a portion of the alkaloid into its isomeride. *isoPilocarpine* behaves in a similar manner to pilocarpine on esterification. *Methyl γ -chloroisopilocarpate* is an oil of very alkaline reaction, $[\alpha]_D - 7.5^\circ$, (*nitrate*, hygroscopic crystals, m. p. about 100°, $[\alpha]_D - 5.6^\circ$); the *ethyl* ester is also an oil, $\alpha_D - 5^\circ$ (*nitrate*, crystalline, m. p. 95°, $[\alpha]_D 0$). All these chloro-esters are unstable, even in the solid state at the ordinary temperature, a portion of the substance being transformed into the hydrochloride of a quaternary base. The chloro-esters react readily with sodium ethoxide or methoxide, yielding an oily mixture of the ethyl esters of α - and β -anhydropilocarpic acids, separable by the difference in solubility of their nitrates in water.

α -Anhydropilocarpic acid, $C_{11}H_{16}O_2N_2$, forms lustrous plates, m. p. 243°, $[\alpha]_D - 19^\circ$; the *hydrochloride* has m. p. 187°; the *ethyl* ester is an oil and yields a *nitrate*, colourless needles, m. p. 165°, $[\alpha]_D - 19^\circ$ in alcohol and $+3.4^\circ$ in water.

β -Anhydropilocarpic acid forms prismatic crystals, m. p. 186°, $[\alpha]_D + 42^\circ$; the *hydrochloride* has m. p. 142°; the *ethyl* ester forms large, transparent tablets, m. p. 48°, and gives a *nitrate*, m. p. 95°, $[\alpha]_D - 28^\circ$ in water.

On bromination, ethyl α -anhydropilocarpate gives a *bromo-derivative*, $C_{13}H_{15}O_2N_2Br$, from which on hydrolysis the *bromo-acid*, m. p. 138—139°, is obtained.

The formulæ $CH \begin{smallmatrix} \diagup NMe \cdot CH \\ \diagdown N - C \cdot CH_2 \cdot CH \end{smallmatrix} \begin{smallmatrix} CH_2 \\ \diagup CH \end{smallmatrix} > CEt \cdot CO_2H$ and

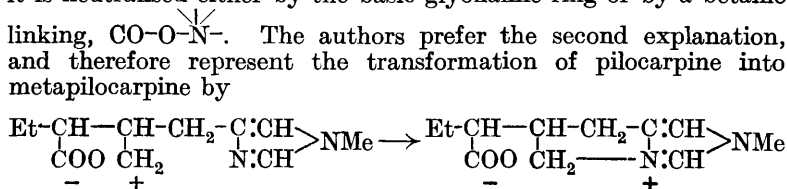


are suggested as possible for the isomeric acids.

H. J. E.

The Pilocarpine Series. III. *iso*Pilocarpinanil or Phenyl-*isopilopyrrolidone*. MAX POLONOVSKI and MICHEL POLONOVSKI (*Bull. Soc. chim.*, 1922, [iv], **31**, 1201—1204; cf. preceding abstract).—Pilocarpine combines with aromatic amines yielding very stable pyrrolidone compounds. This reaction points to the existence of a lactone group in pilocarpine (cf. Emmert and Meyer, A., 1921, i, 268). The same substances may be obtained from the γ -halogen acids derived from the alkaloid. Prolonged heating being necessary, the products are derivatives of *isopilocarpine*. *isoPilocarpinanil* is a hard substance, slightly alkaline in reaction, which gives with mineral acids crystalline salts of acid reaction. The *nitrate*, colourless plates, m. p. 162°, $[\alpha]_D +21.2^\circ$, and the *hydrochloride*, white, hygroscopic prisms, m. p. 135°, were prepared. The base yields on nitration a substance containing a nitro-group in the benzene ring, which was not further investigated. H. J. E.

The Pilocarpine Series. IV. *Metapilocarpine*. MAX POLONOVSKI and MICHEL POLONOVSKI (*Bull. Soc. chim.*, 1922, [iv], **31**, 1204—1208; cf. preceding abstracts).—As substances obtained by the authors from the decomposition of γ -chloro-esters of pilocarpine seemed to be identical with the *metapilocarpine* described by Pinner (A., 1905, i, 658), it appeared that the latter could not be a simple stereoisomeride. An examination of its properties resulted in confirmation of Pinner's observations. The substance is inactive towards polarised light, and, although neutral to litmus and giving with acids salts of acid reaction, does not combine with alkalis. Its reactions lead to the conclusion that in *metapilocarpine* the lactone grouping is absent and the acid group which replaces it is neutralised either by the basic glyoxaline ring or by a betaine linking, $CO-O-\overset{\diagup}{N}$. The authors prefer the second explanation, and therefore represent the transformation of pilocarpine into *metapilocarpine* by



H. J. E.

The Pilocarpine Series. V. Isomerism of Pilocarpine and *iso*Pilocarpine. MAX POLONOVSKI and MICHEL POLONOVSKI (*Bull. Soc. chim.*, 1922, [iv], **31**, 1314—1330).—The authors discuss the evidence for and against the various hypotheses advanced

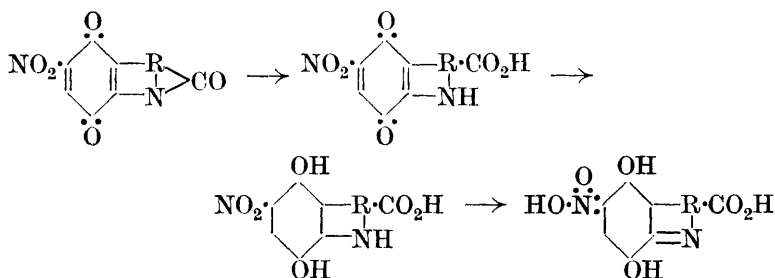
to account for the isomerism of pilocarpine and *isopilocarpine*, and reject as untenable theories based on position isomerism in favour of stereoisomerism arising in or near the lactonic group. Their conclusions are largely based on the isomerisation of pilocarpine and its derivatives to *isopilocarpine* and its corresponding derivatives by action of small quantities of sodium ethoxide on alcoholic solutions of the alkaloid in the cold. It was found that pilocarpine and nitropilocarpine were completely isomerised under these conditions by traces of sodium ethoxide, that molecular quantities of sodium ethoxide gave an isomerised and delactonised product, the de-lactonisation proceeding much more slowly than the isomerisation and requiring twenty-four to forty-eight hours for completion, and that sodium pilocarpate, sodium nitropilocarpate, and ethyl chloropilocarpate were not isomerised to the *iso*-derivatives; in other words, esterification or salt formation causes a stabilisation of the pilocarpine molecule, whence it is concluded that for isomerisation by sodium ethoxide the presence of the unchanged lactone grouping is essential, and this group is probably the seat of the isomerism. Whilst the nature of the stereoisomerism must for the present be left an open question, the authors incline to the view that it may be a case of partial racemisation of one of the two asymmetric C atoms of the lactonic group in view of the similarity between the isomerism of pilocarpine and that of hyoscyamine.

G. F. M.

Strychnos Alkaloids. XXXV. Ethers of Hydroxydihydrobrucinolone and the Violet Colour Reaction of the Nitroquinones obtained therefrom. HERMANN LEUCHS, JOHANNES GRÜSS, and HARRY HEERING (*Ber.*, 1922, **54**, [B], 3729—3738; cf. A., 1921, i, 883).—The action of boiling methyl-alcoholic potassium hydroxide solution on brucinolone or its acetyl derivative leads to the formation of small amounts of *methoxydihydrobrucinolone*, $C_{22}H_{26}O_6N_2 \cdot 3H_2O$, coarse prisms or plates, m. p. 82° , $[\alpha]_D^{25} -50 \cdot 3^\circ$ in glacial acetic acid solution, and (mainly) a product, m. p. $200-202^\circ$ after softening at 190° , which is converted by acetic anhydride into acetylmethoxydihydrobrucinolone, $C_{24}H_{28}O_7N_2$, m. p. $258-270^\circ$, $[\alpha]_D^{25} -92 \cdot 5^\circ$, in glacial acetic acid solution, and acetylcryptobrucinolone. Attempts to separate the mixture, m. p. $200-202^\circ$, into its components by methyl-alcoholic ammonia at 100° were unsuccessful. Under these conditions, cryptobrucinolone is converted into a base, $C_{21}H_{25}O_5N_3$ (isolated as the hydrochloride), identical with that isolated previously, but in much poorer yield, from crude acetylbrucinolone and ammonia (Leuchs, A., 1914, i, 317); its formation in the latter instance appears to depend on the presence of cryptobrucinolone or its ester in the acetylbrucinolone. It unites with phenylcarbimide to give the compound $C_{28}H_{30}O_6N_4$, small prisms, m. p. 200° .

Ethoxydihydrobrucinolone is converted by 5*N*-nitric acid at 0° into the corresponding *quinone*, a yellowish-red resin which yields a *semicarbazone*, slender, orange-coloured needles, m. p. 240° after change at 211° . The free quinone is reduced by sulphur dioxide

to a colourless, amorphous product; the corresponding acetate could not be caused to crystallise. The action of 5*N*-nitric acid on ethoxydihydrobrucinolone at 50–60° leads to the formation of the *nitroquinone hydrate*, $C_{21}H_{23}O_9N_3$, golden-yellow leaflets, which is further transformed into the *semicarbazone*, $C_{22}H_{26}O_9N_6$, slender, pale yellow needles, and the crude *monoethyl ester*. The nitroquinone hydrate is reduced by sulphurous acid to the *nitroquinol hydrate*, $C_{21}H_{25}O_9N_3$, an amorphous, dark violet powder, m. p. (variable) about 185° (decomp.). The latter is converted by hydrogen chloride in methyl and ethyl alcohols into the *methyl* and *ethyl esters*, amorphous, violet substances. The *triacetyl* derivative of the nitroquinol has m. p. 175–180° (decomp.). The relationships of the quinone and quinol compounds are illustrated by the scheme :



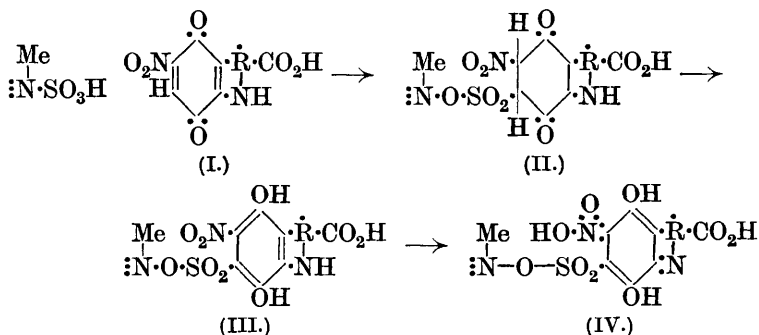
H. W.

Strychnos Alkaloids. XXXVI. The Preparation of Methoxy- and Ethoxy-dihydrostrychninolones and of Strychninolone-c; Oxidation of the Latter. HERMANN LEUCHS and RUDOLF NITSCHKE (*Ber.*, 1922, **55**, [B], 3738–3745; cf. A., 1921, i, 883; Leuchs, Grüss, and Heering, preceding abstract).—Strychninolone-*a* is converted by methyl-alcoholic potassium hydroxide solution initially into the *b*-form, and finally into an inseparable mixture of *methoxydihydrostrychninolone* and strychninolone-*c*. The former has been isolated only as a resin which is converted by sodium acetate and acetic anhydride into a crystalline *acetate*, $C_{22}H_{24}O_5N_2$, colourless, quadratic crystals, m. p. 237–239° after softening at 230°, $[\alpha]_D^{18} -109^\circ$ when dissolved in glacial acetic acid. The course of the change is followed more readily when the methyl- is replaced by ethyl-alcoholic potassium hydroxide solution, since in this instance *ethoxydihydrostrychninolone*, needles, m. p. about 100°, $[\alpha]_D^{18} -51.9^\circ$ in glacial acetic acid solution, m. p. (+MeOH), 65–70°, can be isolated directly.

Strychninolone-*c* is transformed by acetic anhydride and sodium acetate into *acetylstrychninolone-c*, $C_{21}H_{20}O_4N_2$, domatic prisms, m. p. 256–257°, $[\alpha]_D^{18} -229.6^\circ$ in glacial acetic acid solution. The latter substance is oxidised in acetone solution by powdered potassium permanganate to an *acid*, $C_{21}H_{20}O_8N_2 \cdot H_2O$, colourless prisms, m. p. 280–282° (decomp.) after softening at 260°, in which, however, the water of crystallisation appears to be retained with

unusual tenacity. The acid is converted by hydrochloric-acid into acetic and oxalic acids and a non-crystalline, unstable hydrochloride. The behaviour of acetylstrychninone-c is closely analogous to that of cryptobrucinolone; each probably contains the oxidisable group, $\text{CH} \begin{smallmatrix} \text{R}=\text{N} \\ \diagup \quad \diagdown \\ \text{CH} \cdot \text{CO} \end{smallmatrix}$, which is transformed by oxygen into $\text{CO}_2\text{H} \cdot \text{R} \cdot \text{N} \cdot \text{CO} \cdot \text{CO}_2\text{H}$. H. W.

Strychnos Alkaloids. XXXVII. The Degradation of Methylcacotheline and its Violet Colour-reaction with Sodium Sulphite. HERMANN LEUCHS, BERNHARD WINKLER, and W. ROBERT LEUCHS (*Ber.*, 1922, **55**, [B], 3936—3950).—Among the violet products which are formed from cacotheline and analogous substances of the brucine series, methylcacotheline methosulphite (A., 1919, i, 35) occupies a peculiar position, since it becomes isomerised when heated, with the production of a violet isomeride which is therefore not formed in the usual manner by the addition of two atoms of hydrogen. The isomerism cannot be regarded as definitely proved by analytical methods, since the presence of two additional atoms of hydrogen in the molecule does not greatly affect the composition, but it is now placed beyond doubt by the observations that the substance is produced in 50% yield by the action of one molecular proportion of sodium sulphite on two molecular proportions of methylcacotheline, that sulphuric acid is not produced thereby, and that the remainder of the methylcacotheline passes into the yellow methylbetaine (cf. A., 1920, i, 179), which is convertible by further treatment with sodium hydrogen sulphite into the violet methosulphite. The reactions which take place in the production of the violet methosulphite are indicated by the scheme :



The ammonium sulphite becomes added to the quinone nucleus with the formation of a phenylsulphite ester group or a sulphonic acid, whereupon the quinone becomes isomerised to quinol without addition of extraneous hydrogen; the nitro-group subsequently passes into the isonitro-form with production of a new quinonoid arrangement and development of the dark colour.

The so-called violet "methosulphite" (formula IV) is converted

aqueous solution (corresponding *nitrate*, colourless needles or prisms, $[\alpha]_D^{18} -7.4^\circ$ when dissolved in water); it appears to be analogous to the salt, $C_{18}H_{22}O_6N_2 \cdot HBr$, prepared by Hanssen (A., 1887, 505; cf. Leuchs, Millbrand, and Leuchs, A., 1922, i, 1052) by the action of bromine water on cacotheline. The second *compound* is obtained initially in unstable union with sulphurous acid, after the removal of which it has the composition $C_{18}H_{23}O_3N_2Br_3$, $[\alpha]_D^{18} -4.3^\circ$ in aqueous solution; it appears to be a *N*-methyl derivative of a dibrominated bromide.

The methyl ester of the oxime of cacotheline methochloride is converted by methyl alcoholic ammonia at 100° into the *methyl* ester of the *nitrosophenolmethylbetaine*, $C_{23}H_{26}O_7N_4$, apple-green prisms.
H. W.

Nitropyrroles. ANGELO ANGELI (*Atti R. Accad. Lincei*, 1922, [v], 31, ii, 3—5).—Fischer and Zerweck (A., 1922, i, 758) state inaccurately that the nitration of alkylypyrroles may be effected smoothly by means of nitric acid (cf. Angeli, A., 1911, i, 397). The compounds investigated by these authors are not alkylypyrroles, but esters of carboxylic acids derived from keto-, formyl-, etc., derivatives of pyrrole, and the action on them of nitric acid consists, not in true nitration, but in replacement of acetyl, aldehydo-, methyl, etc., groups by nitro-groups.
T. H. P.

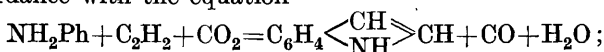
Melanins from Pyrrole Derivatives. PIETRO SACCARDI (*Biochem. Z.*, 1922, 132, 443—456).—A general review of the relations of melanin pigment to the pyrrole group.
W. O. K.

The Tetrachlorodipyridinoiridiates. MARCEL DELÉPINE (*Compt. rend.*, 1922, 175, 1075—1077; cf. A., 1922, i, 859).—Details of the preparation of the red and orange isomerides of potassium tetrachlorodipyridinoiridiate by the action of pyridine on potassium iridichloride or potassium aquapentachloroiridiate are given, together with an account of certain of their properties. The introduction of pyridine into the complex diminishes the number of acid functions and at the same time renders the substance more stable.
H. J. E.

The Reaction between Acetylene and Aniline at High Temperatures. RIKO MAJIMA, TADASHI UNNO, and KASHICHI ONO (*Ber.*, 1922, 55, [B], 3854—3859).—The production of small quantities of indole by subjecting a mixture of acetylene and aniline to a red heat has been observed previously in the presence of aluminium oxide as catalyst. Experiments in which the latter was replaced by the oxides of silicon, iron, chromium, thorium, nickel, cobalt, manganese, molybdenum, tungsten, vanadium, or titanium, or by metallic nickel, iron, cobalt, platinum, palladium, osmium, or copper, did not lead to satisfactory results; nickel is the most powerful catalyst, but speedily loses its activity. Better results are obtained by leading a mixture of aniline vapour, acetylene, and carbon dioxide through a tube heated at 600 — 700° , whereby, under the most favourable conditions, the yield of indole

amounts to 34% of the changed aniline. Benzene, carbazole, and β -naphthylamine are produced in considerably smaller quantity, and still smaller amounts of pyrrole, naphthalene, and quinoline are formed. Glass and porcelain tubes are unsatisfactory on account of frequent breakage, but excellent service is rendered by wide iron tubes which have been subjected to previous protracted heating at 600–650° in a current of acetylene, whereby the inner surface becomes coated with a thin, black, compact layer possibly composed of carbon.

The formation of indole and β -naphthylamine is probably due to the intermediate production of vinylaniline, thus: $\text{NH}_2\text{Ph} + \text{CH}:\text{CH} \rightarrow \text{NHPh}\cdot\text{CH}:\text{CH}_2 \xrightarrow{-\text{H}_2} \text{C}_6\text{H}_4 < \begin{smallmatrix} \text{CH} \\ \text{NH} \end{smallmatrix} > \text{CH}$ and $\text{NHPh}\cdot\text{CH}:\text{CH}_2 \rightarrow \text{CH}_2\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2 \xrightarrow{+\text{C}_6\text{H}_5} \text{C}_{10}\text{H}_7\cdot\text{NH}_2$. Carbazole is probably attributable to intermediate diphenylamine. It is uncertain whether carbon dioxide acts merely as a diluent or takes part in the change in accordance with the equation



other gases, such as ammonia, hydrogen, nitrogen, or water vapour, give less satisfactory results. H. W.

Catalytic Hydrogenation under Pressure in the Presence of Nickel Salts. IV. Quinoline Bases. JULIUS VON BRAUN, ADOLF PETZOLD, and JON SEEMANN (*Ber.*, 1922, 55, [B], 3779–3792).—Under the conditions used by the authors, quinoline is readily and quantitatively hydrogenated at 210–215° into 1:2:3:4-tetrahydroquinoline, which can thus be prepared more readily than by the older methods. At 250°, a portion of the tetrahydro-base is reduced further to decahydroquinoline, and another portion is reduced to tertiary bases of pyridine character which have not been fully examined. Quinoline derivatives which contain a substituent in the benzenoid nucleus or in position 1 behave in the same manner as the parent bases, whereas those which have a substituent in position 3 are also hydrogenated in the benzenoid nucleus to an extent which depends on the particular substituent present.

The reductions are effected with the pure bases or with solutions of them in tetra- or deca-hydronaphthalene. The results are similar in every case, and the rate of absorption of the gas is not appreciably influenced by the diluent.

6-Methylquinoline is converted at 120° into 6-methyl-1:2:3:4-tetrahydroquinoline, b. p. 131–133°/9 mm., m. p. 37–38°, the yield being 90% of that theoretically possible. 6-Chloro-1:2:3:4-tetrahydroquinoline, long, colourless needles, m. p. 43°, b. p. 155°/18 mm., is prepared at 160°; the corresponding *hydrochloride*, m. p. 190°, *picrate*, yellow needles, m. p. 150°, and *nitroso-derivative*, yellow, lustrous prisms, m. p. 67°, are described.

[With A. SCHULTHEISS.]—6:7-Ethylenedioxyquinoline (Sonn and Benirschke, A., 1921, i, 805) is very readily hydrogenated at 180–190° to 6:7-ethylenedioxy-1:2:3:4-tetrahydroquinoline,

b. p. $193^{\circ}/11$ mm., m. p. 101° (*picrate*, m. p. 168° ; hydrochloride, m. p. 199° (Sonn and Benirschke give m. p. 201°); nitroso-derivative, m. p. 110°).

2-Phenyl-1 : 2 : 3 : 4-tetrahydroquinoline, b. p. $196\text{--}197^{\circ}/12$ mm., is obtained from 2-phenylquinoline at 150° .

3-Ethylquinoline, an almost colourless liquid with an odour of quinoline, is prepared in 80% yield by the action of *n*-butyraldehyde on *o*-aminobenzaldehyde at $120\text{--}130^{\circ}$ (cf. Wislicenus and Elvert, A., 1909, i, 420); it has b. p. $135\text{--}138^{\circ}/12$ mm., d_4^{20} 1.0508, n_D^{18} 1.6030 (*hydrochloride*, m. p. 173° ; *picrate*, m. p. 197° ; *methiodide*, m. p. 191°). The base is readily hydrogenated at $180\text{--}190^{\circ}$, yielding thereby a mixture of 3-ethyl-5 : 6 : 7 : 8-tetrahydroquinoline and 3-ethyl-1 : 2 : 3 : 4-tetrahydroquinoline, which are separated from one another with the aid of benzoyl chloride. The former is a colourless liquid, b. p. $125\text{--}128^{\circ}/12$ mm., d_4^{20} 0.99218, n_D^{18} 1.5311 (it gives a *methiodide*, m. p. 120° , and a *picrate*, yellow crystals, m. p. 158°). The latter has b. p. $140^{\circ}/12$ mm., d_4^{20} 1.0041, n_D^{18} 1.5625 (*hydrochloride*, m. p. 210° ; *picrate*, m. p. 142° ; *methiodide*, $C_{13}H_{20}NI$, m. p. 205° ; the benzoyl and nitroso-derivatives are non-crystalline).

3-*n*-Amylquinoline, prepared in almost quantitative yield from *o*-aminobenzaldehyde and heptaldehyde at 180° , is a colourless liquid, b. p. $179^{\circ}/16$ mm., d_4^{17} 1.0048, n_D^{17} 1.5715 (*hydrochloride*, m. p. 174° ; *picrate*, m. p. 153° ; *methiodide*, m. p. 69°). It is hydrogenated at $180\text{--}190^{\circ}$ with the formation of approximately equal amounts of 3-*n*-amyl-1 : 2 : 3 : 4-tetrahydroquinoline, a colourless liquid, b. p. $159\text{--}164^{\circ}/12$ mm., d_4^{17} 0.96625, n_D^{17} 1.5339 (*hydrochloride*, needles, m. p. 124° , *methiodide*, $C_{16}H_{26}NI$, m. p. 145° ; the *picrate*, benzoyl compound, acetyl derivative, and nitroso-compound are non-crystalline) and 3-*n*-amyl-5 : 6 : 7 : 8-tetrahydroquinoline, a colourless, nearly odourless liquid, b. p. $167^{\circ}/12$ mm., d_4^{17} 0.96028, n_D^{17} 1.5188. The latter substance gives a *picrate*, long needles, m. p. 135° , and a *methiodide*, m. p. 105° , whereas the *chloride* and *chloroplatinate* are non-crystalline; it does not react with acetic anhydride or nitrous acid. The base is oxidised by potassium permanganate to oxalic and pyridine-2 : 3 : 5-tricarboxylic acids.

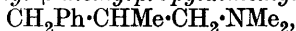
3-Phenylquinoline is hydrogenated with remarkable ease at 160° to a mixture of 3-phenyl-1 : 2 : 3 : 4-tetrahydroquinoline and 3-phenyl-5 : 6 : 7 : 8-tetrahydroquinoline, from which the former is very readily separated by taking advantage of its sparing solubility in alcohol, with which the latter is readily miscible. 3-Phenyl-1 : 2 : 3 : 4-tetrahydroquinoline is a colourless, crystalline substance, m. p. 83° (*hydrochloride*, matted needles, m. p. 229° ; *picrate*, m. p. 181° ; *picrolonate*, a yellow powder, m. p. 205° ; *acetyl derivative*, feathery crystals, m. p. 78° ; *nitroso-compound*, m. p. 147°). 3-Phenyl-5 : 6 : 7 : 8-tetrahydroquinoline is a colourless liquid, b. p. $211\text{--}212^{\circ}/18$ mm. (*hydrochloride*, m. p. 235° after darkening at $225\text{--}230^{\circ}$; *picrolonate*, a yellow powder, m. p. 201° ; *methiodide*, $C_{16}H_{18}NI$, m. p. $240\text{--}243^{\circ}$; the base does not react with nitrous acid or acetic anhydride). 3-Phenyl-5 : 6 : 7 : 8-tetrahydro-

quinoline is reduced by sodium and ethyl alcohol to 3-phenyl-decahydroquinoline, colourless crystals, m. p. 98° after softening at 95° (nitroso-derivative, m. p. 110°; picrate, m. p. 210—212°; the acetyl compound could not be caused to crystallise). H. W.

The Relative Stability of Cyclic Bases. VII. Substituted Tetrahydroquinoline Rings. JULIUS VON BRAUN, JON SEEMANN, and ADAM SCHULTHEISS (*Ber.*, 1922, **55**, [B], 3803—3817).—In previous communications (von Braun and Neumann, A., 1917, i, 282; von Braun, Heider, and Neumann, A., 1917, i, 167), it has been pointed out that whereas the stability of the tetrahydroquinoline ring towards scission during reduction by sodium amalgam is little affected by the introduction of the methyl group in position 2, that of the dihydroindole ring is modified profoundly by 2 or 3 methylation. The presence of a methyl group in position 3 or 4 in the tetrahydroquinoline ring is now shown not to exert a marked effect on the course of the change. On the other hand, the presence of a phenyl group in position 2 causes the almost quantitative rupture of the non-aromatic ring linking, whereas when the group is in position 3 the three possible types of change are realised.

1:3-Dimethyl-1:2:3:4-tetrahydroquinoline, $C_6H_4 \begin{matrix} < CH_2-CHMe \\ NMe \cdot CH_2 \end{matrix}$,

an almost colourless liquid, b. p. 130—132°/17 mm., is obtained by the reduction of 3-methylquinoline methiodide by tin and hydrochloric acid; the very hygroscopic hydrochloride, m. p. about 110°, picrate, m. p. 131°, and methiodide, m. p. 204°, are described. The corresponding quaternary chloride is converted by sodium amalgam into a mixture of 1:3-dimethyl-1:2:3:4-tetrahydroquinoline and γ -phenyl- β -methylpropyldimethylamine,

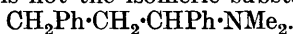


from which the former is removed by treatment with formaldehyde in hydrochloric acid solution. The latter base is a colourless liquid, b. p. 100—105°/7 mm., 221°/atmospheric pressure (hydrochloride, m. p. 90°; picrate, m. p. 87°; methiodide, m. p. 140°).

1:4-Dimethyl-1:2:3:4-tetrahydroquinoline methiodide is converted into the corresponding chloride, which is transformed by sodium amalgam into 1:4-dimethyl-1:2:3:4-tetrahydroquinoline and γ -phenylbutyldimethylamine, $CHMePh \cdot CH_2 \cdot CH_2 \cdot NMe_2$, a liquid, b. p. 112—115°/7 mm. (hydrochloride, m. p. 100°; picrate, m. p. 98°; methiodide, m. p. 125°), which constitutes 60% of the mixture of bases.

2-Phenyl-1:2:3:4-tetrahydroquinoline is converted by methyl iodide and aqueous alkali mainly into 2-phenyl-1-methyl-1:2:3:4-tetrahydroquinoline, colourless crystals, m. p. 101°, b. p. 188—192°/14 mm.; the corresponding hydrochloride, m. p. 157°, chloroplatinate, m. p. 172°, nitroso-compound, a microscopic, green powder, m. p. 75°, and diphenylmethane derivative, $C_{33}H_{34}N_2$, m. p. 60° after slight previous softening, are described. The base unites with difficulty with methyl iodide to give the quaternary iodide, $C_{17}H_{20}NI$, m. p. 185°. The quaternary chloride (chloro-

platinate, orange-coloured crystals, m. p. 203°) is almost quantitatively converted by sodium amalgam into *o*- γ -phenylpropyldimethylaniline, $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2\text{Ph}$, b. p. $175\text{--}178^{\circ}/10\text{ mm.}$ The *picrate*, golden-yellow needles, m. p. 110° , the non-crystalline *hydrochloride*, and the *chloroplatinate*, a yellowish-brown powder, m. p. 170° , are described. The base does not unite readily with methyl iodide, thus proving that the dimethylamino-group is attached to the benzenoid nucleus and is sterically hindered, and that the compound is not the isomeric substance,

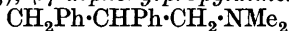


2-Phenyl-1-methyl-1 : 2 : 3 : 4-tetrahydroquinoline suffers fission in accordance with the scheme $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}_2 - \text{CH}_2 \\ \text{NMe} \cdot \text{CHPh} \end{smallmatrix} + \text{BrCN} \rightarrow$

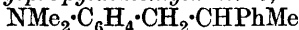
$\text{CN} \cdot \text{NMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CHPhBr}$ to the extent of at least 50% when treated with cyanogen bromide in a gently boiling water-bath. Since cyanoamides cannot be distilled without decomposition and seldom crystallise, the product of the action is treated directly with an excess of piperidine, whereby it is converted into a portion insoluble in acid, b. p. $218^{\circ}/\text{vacuum}$, and a bromine-free, amorphous *base* which readily unites with methyl iodide, giving the *substance* $\text{C}_{33}\text{H}_{30}\text{N}_3\text{I}$, a pale-brown, microcrystalline powder which loses methyl iodide without definitely melting above 60° .

The *hydroxide*, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}_2 - \text{CH}_2 \\ \text{NMe}_2(\text{OH}) \end{smallmatrix} \text{CHPh}$, is mainly decomposed with loss of methyl alcohol when distilled under diminished pressure, giving 2-phenyl-1-methyl-1 : 2 : 3 : 4-tetrahydroquinoline.

In striking contrast to the 2-phenyl derivative, 3-phenyl-1 : 2 : 3 : 4-tetrahydroquinoline is readily converted by methyl iodide into the quaternary *iodide*, $\text{C}_{17}\text{H}_{20}\text{NI}$, m. p. 172° , which loses methyl iodide when distilled under diminished pressure and gives 3-phenyl-1-methyl-1 : 2 : 3 : 4-tetrahydroquinoline, m. p. 42° , b. p. $195\text{--}202^{\circ}/12\text{ mm.}$ The corresponding *picrate*, m. p. 178° , the non-crystalline *hydrochloride*, and *chloroplatinate*, m. p. 192° , the *nitroso*-compound, m. p. about 105° , and the diphenylmethane derivative, $\text{C}_{33}\text{H}_{34}\text{N}_2$, m. p. 92° , are described. The quaternary *chloride* (*chloroplatinate*, m. p. 204°) is converted by sodium amalgam into a mixture of 3-phenyl-1-methyl-1 : 2 : 3 : 4-tetrahydroquinoline (47%), β - γ -diphenylpropyldimethylamine,



(45%), and *o*- β -phenylpropyldimethylaniline,



(8%). The two bases last mentioned are separated by taking advantage of the inability of the *o*-dimethylaniline derivative to unite with methyl iodide in ethereal solution. The quantity of *o*- β -phenylpropyldimethylaniline available was insufficient to permit its isolation in a homogeneous condition, and it is characterised by its *picrate*, m. p. $166\text{--}167^{\circ}$, non-crystalline *hydrochloride*, and *chloroplatinate*, m. p. 181° . β - γ -Diphenylpropyldimethylamine *methyl iodide* is exceedingly hygroscopic; it is converted into the corresponding *chloride* (*chloroaurate*, yellow needles, m. p. 164° ; *chloroplatinate*, a microcrystalline powder, m. p. 236°). The constitution

of the iodide is established by the observation that the corresponding *hydroxide* is decomposed when distilled under diminished pressure into α -benzylstyrene, $\text{CH}_2\text{Ph}\cdot\text{CPh}\cdot\text{CH}_2$, a liquid, b. p. 140—143°/vacuum, d_4^{20} 1.0143, n_D^{20} 1.5903 (corresponding *dibromide*, colourless crystals, m. p. 98°). 3-Phenyl-1-methyl-1:2:3:4-tetrahydroquinoline is converted to a slight extent by cyanogen bromide into the corresponding *methobromide* (identified by its conversion into the chloroplatinate, m. p. 203°) but mainly into 1-cyano-3-phenyl-1:2:3:4-tetrahydroquinoline, m. p. 78°; fission of the ring, as in the case of the 2-phenyl compound, is not observed.

6:7-Ethylenedioxyquinoline *methiodide*, m. p. 270°, is reduced by tin and hydrochloric acid to 6:7-ethylenedioxy-1-methyl-1:2:3:4-tetrahydroquinoline, colourless leaflets, m. p. 53°, b. p. 165—170°/8 mm.; the *hydrochloride*, m. p. 203°, *picrate*, m. p. 170°, and the *methiodide*, m. p. 220°, are described. The latter compound is prepared more advantageously by exhaustive methylation of 6:7-ethylenedioxy-1:2:3:4-tetrahydroquinoline. It is converted into the corresponding chloride which is transformed by sodium amalgam into a mixture of 6:7-ethylenedioxy-1-methyl-1:2:3:4-tetrahydroquinoline (40%) and γ -3:4-ethylenedioxy-phenylpropyldimethylamine, $\text{C}_2\text{H}_4\text{O}_2\cdot\text{C}_6\text{H}_3\cdot[\text{CH}_2]_3\cdot\text{NMe}_2$, b. p. 162—164°/7 mm., which are separated from one another by careful fractional distillation; the *methiodide*, m. p. 165°, *picrate*, m. p. 167°, and *hydrochloride*, m. p. 169°, of the latter base are described.
H. W.

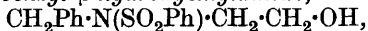
The Mechanism of Syntheses of *iso*Quinoline from Benzylamine Derivatives. PAUL STAUB (*Helv. Chim. Acta*, 1922, 5, 888—894).—Many attempts to synthesise *iso*quinoline derivatives by ring closure in appropriate benzylamine derivatives are recorded in the literature, but few were successful. In an attempt to determine the conditions requisite for success, the following new compounds were prepared for ring closure experiments.

α -Benzylidinediaminoisopropyl alcohol, $\text{CHPh}\cdot\text{N}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{OH}$, was obtained by reducing nitroisopropyl alcohol,
 $\text{NO}_2\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{OH}$,

and condensing the product with benzaldehyde; it crystallises in needles, m. p. 76—76.5°.

Benzylaminoisopropyl alcohol, $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{OH}$, was obtained by the action of benzyl chloride on aminoisopropyl alcohol; b. p. 142°/11 mm.

Benzenesulphonbenzyl- β -hydroxyethylamide,

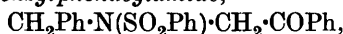


was prepared by heating benzenesulphonbenzylamide with ethylene oxide at 170°; it formed a viscous liquid crystallising slowly, and was not purified.

Benzenesulphonbenzyl- β -bromoethylamide,



was formed by the action of ethylene bromide on sodium benzenesulphonbenzylamide in ether; m. p. 82.5—83°.

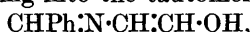
Benzenesulphonbenzylphenacylamide,

was prepared by the action of bromoacetophenone on sodium benzenesulphonbenzylamide in ether. The product was not crystallised.

Acetobenzylphenacylamide, $\text{CH}_2\text{Ph}\cdot\text{N}\cdot\text{Ac}\cdot\text{CH}_2\cdot\text{COPh}$, was obtained as a syrup from the action of bromoacetophenone on sodium benzylacetamide.

In no case could any *isoquinoline* derivative be obtained by the action of any of the usual ring-closing agents on any of the above six compounds.

It is concluded that a benzene derivative containing the chain $\text{Ph}\cdot\text{C}\cdot\text{N}\cdot\text{C}\cdot\text{C}$ — must, if it is to be convertible into an *isoquinoline* base, conform to two rules. In the lateral chain it must have (1) a system of conjugated double bonds, actual or potential; (2) a hydroxyl or alkoxyl group in β -position to the nitrogen atom. The compound $\text{CHPh}\cdot\text{N}\cdot\text{CH}_2\cdot\text{CH}(\text{OEt})_2$ conforms to condition (1) by loss of alcohol, and readily forms *isoquinoline*. Benzylaminoacetaldehyde, $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CHO}$, which is converted by fuming sulphuric acid into *isoquinoline*, may be supposed to undergo oxidation and by passing into the tautomeric form,



satisfies the conditions.

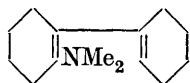
E. H. R.

Catalytic Hydrogenation under Pressure in the Presence of Nickel Salts. V. The Carbazole Complex. JULIUS VON BRAUN and HEINRICH RITTER (*Ber.*, 1922, 55, [B], 3792—3803; cf. Padoa and Chiaves, A., 1908, i, 772).—The process used by the authors does not cause the hydrogenation of pyrazole even at 260° and under a pressure of 30 atmospheres, in spite of the use of a material which has been exhaustively purified in several different manners. Nevertheless, the authors are inclined to the view that pure pyrazole is not unusually resistant to hydrogenation, and that the failure of their experiments is due to some unknown catalytic impurity. The *N*-alkylcarbazoles are readily hydrogenated with initial addition of four hydrogen atoms to one benzene nucleus. Subsequently, the second benzene nucleus is attacked with addition of a further four atoms of hydrogen.

9-Methylcarbazole readily absorbs about seven atomic proportions of hydrogen at 210—215° and 25 atmospheres pressure. About 40% of the initial material remains unchanged whilst a portion is perhydrogenated with production of ammonia. The liquid product of the reaction is a mixture of the octahydro- and tetrahydro-derivatives with 9-methylcarbazole, from which the first-named is readily separated by treatment with hydrochloric acid (20%), in which it alone dissolves. The remaining bases cannot be separated from one another by distillation or crystallisation; the presence of the tetrahydro-compound is established by the formation of the strongly basic hexahydro-derivative when the mixture of bases is treated with tin and hydrochloric acid.

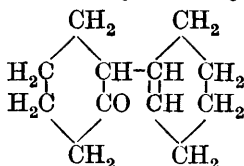
9-Methyloctahydrocarbazole, $\text{MeN} \begin{smallmatrix} \text{C}_6\text{H}_8 \\ \text{C}_6\text{H}_8 \end{smallmatrix}$, lustrous leaflets, m. p. 94°, b. p. 176—178°/16 mm., is somewhat unstable towards air and does not give the pine-shaving or the dimethylaminobenzaldehyde reaction. It does not give a well-defined picrate or methiodide; it is readily oxidised by chromic acid, potassium permanganate, or ferric chloride, but it has not yet been found possible to isolate uniform products of the action. It is conveniently reduced by tin and boiling hydrochloric acid (20%) to 9-methyl-decahydrocarbazole, $\text{MeN} \begin{smallmatrix} \text{C}_6\text{H}_8 \\ \text{C}_6\text{H}_{10} \end{smallmatrix}$, a colourless, mobile liquid, b. p.

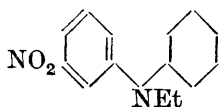
138—139°/12 mm., which is stable towards air; the non-crystalline hydrochloride, hydrobromide, m. p. 202—204°, picrate, m. p. 162°, and methiodide, m. p. 189°, are described. The presence of the double bond in the base is betrayed only by its instability towards permanganate; it yields only the hydrobromide when treated with fuming hydrobromic acid and does not unite with bromine or hydrogen even under widely varied conditions. The methiodide is transformed by successive treatment with silver oxide and distillation into 2-dimethylamino- $\Delta^{1:1'}$ -dicyclohexenyl (annexed formula), an almost colourless liquid, b. p. 148°/15 mm., which is conveniently characterised as the picrate, m. p. 157°. The new base is somewhat unstable and is readily converted by sulphuric acid (10%)



into 2- Δ^1 -cyclohexenylcyclohexanone (annexed formula), b. p. 137—139°/14 mm., d_4^{20} 1.015, n_D^{20} 1.515 (semicarbazone, m. p. 191°). The ketone is certainly not identical with the compound obtained by Wallach (A., 1911, i, 473) by the autocondensation of cyclohexanone, and it would therefore appear that the latter has the alternative constitution, $\text{C}_6\text{H}_8\text{O}:\text{C}_6\text{H}_{10}$, suggested by Wallach. 2- Δ^1 -cyclohexenylcyclohexanone is readily reduced by hydrogen in the presence of palladous chloride to 2-cyclohexylcyclohexanone, b. p. 135°/11 mm., d_4^{20} 0.987, n_D^{20} 1.4915 (cf. Wallach, *loc. cit.*).

The reduction of 9-ethylcarbazole is very similar to that of the methyl compound. 9-Ethyl-octahydrocarbazole, lustrous leaflets, m. p. 43°, b. p. 162—163°/9 mm., is unstable towards air; it does not give a methiodide or a picrate. It is readily reduced to 9-ethyl-decahydrocarbazole, a colourless liquid which is stable towards air, b. p. 140—141°/12 mm.; the non-crystalline hydrochloride, the picrate, m. p. 133°, and the methiodide, m. p. 176—177°, are described. 2-Methylethylamino- $\Delta^{1:1'}$ -dicyclohexenyl is a colourless liquid, b. p. 148—150°/12 mm., which gives a non-crystalline picrate and methiodide. It is readily transformed by dilute sulphuric acid into 2- Δ^1 -cyclohexenylcyclohexanone and methyl-ethylamine. 9-Ethylhexahydrocarbazole is a colourless, odourless liquid, b. p. 155—157°/8 mm., 292—293°/749 mm.; it gives a well-defined methiodide, m. p. 174°. The base is transformed by a mixture of nitric and sulphuric acids at 0° into the nitro-com-

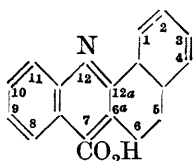




compound (annexed formula), golden-yellow needles, m. p. 142° , which is reduced by stannous chloride to 7-amino-9-ethylhexahydrocarbazole, an almost colourless, very viscous liquid, b. p. $224-225^{\circ}/24$ mm., which shows all the colour reactions characteristic of the simpler meta-diamines of the aromatic series.

It has not been found possible to effect the smooth dehydrogenation of 9-methyl- or 9-ethyl-hexahydrocarbazole; if the substances are passed over lead oxide and pumice the alkyl residues are lost and carbazole is produced. H. W.

Benzo-polymethylene Compounds. VIII. Cyclic Analogues of Atophan. JULIUS VON BRAUN and PAUL WOLFF (*Ber.*, 1922, 55, [B], 3675—3688).—1-Ketotetrahydronaphthalene condenses readily with isatin to give 5:6-dihydro- α -naphthacridine-7-carboxylic acid (annexed formula), which readily undergoes further

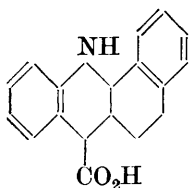


change. Constitutionally the new compound (for which the name tetraphan is proposed) is allied somewhat closely to 2-phenyl-4-cinchoninic acid (atophan), from which, however, it differs entirely in its physiological action, having a characteristic effect on the spinal marrow somewhat resembling that of strychnine. The physiological properties of a number of its derivatives have been examined. Substitution in the benzenoid nuclei of the isatin and tetrahydronaphthalene complexes does not affect the qualitative nature of the action. The presence of the basic nitrogen atom and of the carboxyl group appears essential. A new ring produced by the insertion of more than one carbon atom into the atophan complex must be present, which must not be eccentrically united. The group $-\text{CH}_2\cdot\text{CH}_2-$ need not be so fully hydrogenated.

Since tetrahydroatophan shows close physiological resemblance to tetraphan, it is to be expected that the action of the latter would be considerably enhanced by transforming it into its tetrahydro-derivative; the reverse is, however, found to be the case.

5:6-Dihydro- α -naphthacridine-7-carboxylic acid, slender, pale yellow needles, m. p. 252° (decomp.), is prepared smoothly by heating a mixture of isatin and 1-ketotetrahydronaphthalene with aqueous-alcoholic potassium hydroxide solution. It reacts incompletely with mineral acids, yielding salts which are hydrolysed by water. The sodium, lead, basic copper, and silver salts are described; the ethyl ester, long, coarse needles, m. p. 80° , is prepared from the latter. The acid is decomposed when heated somewhat above its melting point into 5:6-dihydro- α -naphthacridine, b. p. $237-238^{\circ}/10$ mm., m. p. 60° ; the corresponding hydrochloride, long needles, m. p. 226° , picrate, m. p. 206° , and methiodide, a reddish-yellow, crystalline powder, decomp. 191° , are described. The base is readily dehydrogenated by lead oxide at $300-320^{\circ}$ with production of α -naphthacridine, m. p. 108° . It is oxidised by chromic acid in glacial acetic acid solution to 5:6-diketo- α -naphthacridine, an orange-coloured powder, m. p. 242° (a salt with chromic acid is described).

5 : 6-Dihydro- α -naphthacridine-7-carboxylic acid is converted by bromine and glacial acetic acid at 120—130° into α -naphthacridine-7-carboxylic acid, a yellow powder, m. p. 261°; the cobalt, copper, mercuric, and silver salts are described. The methyl ester has m. p. 83°. When heated above its melting point, the acid is converted into α -naphthacridine, m. p. 108°.

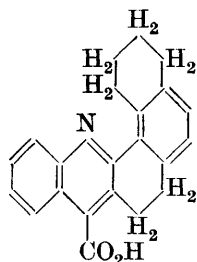


5:6-Dihydro- α -naphthacridine-7-carboxylic acid is reduced by sodium and ethyl or amyl alcohol to 5 : 6 : 6a : 7 : 12 : 12a-hexahydro- α -naphthacridine-7-carboxylic acid (tetrahydrotetraphan) (annexed formula), m. p. 190° (decomp.) after softening at 180°; the corresponding nitroso-compound, m. p. 149°, and acetyl derivative, m. p. 247° after softening at 244°, are described.

5 : 6-Dihydro-11-methyl- α -naphthacridine-7-carboxylic acid, colourless crystals, m. p. 188° (decomp.), is prepared from 1-ketotetrahydronaphthalene and *o*-methylisatin; its metallic salts closely resemble those of the parent acid. 5 : 6-Dihydro-11-methyl- α -naphthacridine has m. p. 93—94°, b. p. 248—253°/16 mm.; it yields a picrate, m. p. 141°, and a hydrochloride, long, pale yellow needles, m. p. 173°, but could not be caused to react with methyl iodide. 11-Methyl- α -naphthacridine, m. p. 107°, gives a picrate, m. p. 155°, and a hydrochloride, m. p. 136°, but does not react with methyl iodide.

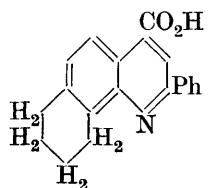
5 : 6-Dihydro-9-methyl- α -naphthacridine-7-carboxylic acid has m. p. 293° (decomp.); the sodium salt dissolves very sparingly in water.

9-Chloro-5 : 6-dihydro- α -naphthacridine-7-carboxylic acid, m. p. 283° (decomp.), is converted when heated above its melting point into 9-chloro-5 : 6-dihydro- α -naphthacridine, m. p. 102°, b. p. 257—262°/14 mm. The hydrochloride of the latter has m. p. 240°. The base loses the chlorine atom when it is treated with lead oxide.



9-Bromo-5 : 6-dihydro- α -naphthacridine-7-carboxylic acid has m. p. 265°; the silver salt and the methyl ester, yellow leaflets, m. p. 128°, are described. 9-Bromo-5 : 6-dihydro- α -naphthacridine crystallises in pale yellow needles, m. p. 168° (hydrochloride, m. p. 211—212°).

5 : 6-Dihydro-1 : 2-tetramethylene- α -naphthacridine-7-carboxylic acid (annexed formula) is prepared from isatin and α -keto-octahydrophenanthrene; it has m. p. 210° (decomp.) after darkening at 180°.



2-Acenaphthylquinoline-4-carboxylic acid, prepared from 4-acetylacenaphthene and isatin, has m. p. 234° after previous softening.

Tetramethyleneatophan (annexed formula), prepared from ar- α -aminotetrahydronaphthylamine, pyruvic acid, and benzaldehyde, forms yellow crystals, m. p. 260° after softening at 255°; its physiological action resembles that of atophan. H. W.

The Relationship between Fluorescence and Chemical Constitution in the Case of Derivatives of Benzoxazole. II.

F. HENRICH [with H. SUNTHEIMER and C. STEINMANN] (*Ber.*, 1922, **55**, [B], 3911—3921).—In a previous communication (A., 1921, i, 886), it has been shown that the development of fluorescence in alkaline solutions of hydroxybenzoxazole derivatives,

$\text{HO}\cdot\text{C}_6\text{H}_3\text{<}\overset{\text{N}}{\text{O}}\text{>C}\cdot\text{R}(\mu)$, is observed only when R in position μ is

an aromatic nucleus directly attached by one of its carbon atoms to the μ carbon atom and when the hydroxyl group is in the para-position to the nitrogen atom. This regularity is now shown to be true of certain derivatives of 2:4-dihydroxytoluene.

2:4-Dihydroxytoluene, m. p. 105—107°, is prepared from 2:4-diaminotoluene through the compounds 2-amino-4-acetamidotoluene, 4-acetamido-2-hydroxytoluene, and 4-amino-2-hydroxytoluene; the necessary conditions for each change are described fully in the original. It is converted by amyl nitrite and potassium hydroxide in absolute alcoholic solution into 5-nitroso-2:4-dihydroxytoluene, decomp. 175—180° according to the rate of heating after darkening and softening at 146°; the potassium salt and the dibenzoyl derivative, m. p. 146—153°, are described.

2:4-Dihydroxytoluene is converted by fuming nitric acid in the presence of ether into a mixture of 3-nitro-2:4-dihydroxytoluene, bright red needles, m. p. 111°, and 5-nitro-2:4-dihydroxytoluene, orange-yellow needles, m. p. 118—119°, which can be separated from one another by taking advantage of the volatility of the former with steam, with which the latter does not volatilise.

5-Amino-2:4-dihydroxytoluene hydrochloride, long, colourless needles, is prepared by the reduction of the corresponding nitroso- or nitro-compound with stannous chloride and concentrated hydrochloric acid. The free amine is obtained by the addition of sodium hydroxide to an aqueous solution of the hydrochloride; it dissolves to a dark blue solution in an excess of the reagent, and readily absorbs oxygen, without, however, becoming converted into dyes of the type of litmus. The hydrochloride is transformed by acetic anhydride into 6-acetoxy-2-methyl-5-methylbenzoxazole (annexed formula), colourless needles, m. p. 94°, which is converted

by alcoholic potassium hydroxide solution into 6-hydroxy-2:5-dimethylbenzoxazole, colourless crystals, m. p. 221°; the latter substance does not fluoresce in aqueous alkaline solution.

6-Benzoxo-2-phenyl-5-methylbenzoxazole, colourless crystals, m. p. 164—165° after softening at 163°, is prepared from 5-amino-2:4-dihydroxytoluene hydrochloride and benzoyl chloride and is hydrolysed by alcoholic potassium hydroxide solution to 6-hydroxy-2-phenyl-5-methylbenzoxazole, colourless crystals, m. p. 242° after softening at 236°, which has a green fluorescence in aqueous sodium hydroxide solution.

3-Nitro-2:4-dihydroxytoluene is reduced by stannous chloride and concentrated hydrochloric acid to 3-amino-2:4-dihydroxytoluene hydrochloride, colourless needles, which is converted by

successive treatment with benzoyl chloride and alcoholic potassium hydroxide solution into 4-hydroxy-2-phenyl-5-methylbenzoxazole, colourless crystals which do not exhibit fluorescence in alkaline solution. H. W.

The Relative Stability of Cyclic Bases. VIII. The Phenmorpholine and Homotetrahydroquinoline Rings. JULIUS VON BRAUN and JON SEEMANN (*Ber.*, 1922, **55**, [B], 3818—3825).—It is shown that the stability of the morpholine ring is increased to an unexpected extent by its association with an aromatic ring, so that it is at least as stable towards cyanogen bromide as 1 : 2 : 3 : 4-tetrahydroquinoline and even more stable towards sodium amalgam. Homo-1 : 2 : 3 : 4-tetrahydroquinoline does not suffer fission under the action of cyanogen bromide.

The nine rings (pyrrolidine, piperidine, morpholine, dihydroindole, dihydroisoindole, 1 : 2 : 3 : 4-tetrahydroquinoline, 1 : 2 : 3 : 4-tetrahydroisoquinoline, phenmorpholine, and homo-1 : 2 : 3 : 4-tetrahydroquinoline) exhibit uniformity in their behaviour towards cyanogen bromide, sodium amalgam, and the Hofmann degradation if the dihydroindole and the phenmorpholine systems are not considered. The peculiarity of the latter rings appears to be caused by the presence in them of the group $-\text{Ar}-\text{N}-\text{CH}_2-\text{CH}_2-$.

N- β -Hydroxyethyl-*o*-anisidine is conveniently prepared in 75—80% yield by heating *o*-anisidine with a considerable excess of ethylene chlorohydrin on a water-bath; the *picrate*, m. p. 140°, and the *hydrochloride*, m. p. 134°, are described. The base is converted by successive treatment with concentrated hydrochloric acid at 160—180° and with dilute aqueous alkali into phenmorpholine, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O}-\text{CH}_2 \\ | \\ \text{NH}\cdot\text{CH}_2 \end{smallmatrix}$, b. p. 127—128°/12 mm. The latter is

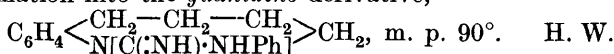
transformed quantitatively by methyl iodide and sodium hydroxide into 1-methylphenmorpholinium methiodide, which is decomposed when distilled under diminished pressure into 1-methylphenmorpholine, b. p. 124°/12.5 mm. (*picrate*, m. p. 144°).

1-Methylphenmorpholine reacts slowly with cyanogen bromide at the temperature of boiling water, giving unchanged material, 4-methylphenmorpholine methobromide, m. p. 213°, and 4-cyano-phenmorpholine, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O}-\text{CH}_2 \\ | \\ \text{N}(\text{CN})\cdot\text{CH}_2 \end{smallmatrix}$, a liquid, b. p. 115—118°/1 mm. ;

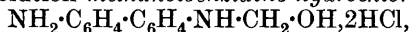
the latter could not be obtained in a perfectly homogeneous condition, and is characterised by converting it into the guanidine derivative, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O}-\text{CH}_2 \\ | \\ \text{N}[\text{C}(\text{NH})\cdot\text{NHPh}]\cdot\text{CH}_2 \end{smallmatrix}$, small, colourless needles,

m. p. 152°, the non-crystalline *hydrochloride* and *chloroplatinate*, m. p. 144°, of which are described. 4-Methylphenmorpholine methochloride is converted by sodium amalgam almost entirely into 4-methylphenmorpholine which is characterised by its conversion into the *diphenylmethane* derivative, $\text{C}_{10}\text{H}_{22}\text{O}_2\text{N}_2$, a very viscous liquid, b. p. about 260°/2 mm. (decomposition occurs before completion of the distillation) (*dimethiodide*, m. p. 157°).

The difficulty of methylating homo-1 : 2 : 3 : 4-tetrahydroquinoline, $C_6H_4 \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{NH} \cdot \text{CH}_2 \end{smallmatrix} > CH_2$, has been indicated previously (von Braun and Bartsch, *A.*, 1913, i, 197); it has now been found possible to isolate the products of the action in a homogeneous form. The quaternary iodide, $C_{12}H_{16}NI$, has m. p. 155° . 1-Methylhomo-1 : 2 : 3 : 4-tetrahydroquinoline has b. p. $108\text{--}110^\circ/10\text{ mm.}$, and gives a *picrate*, m. p. 139° , a non-crystalline *hydrochloride*, and a *chloroplatinate*, m. p. 186° ; it combines very slowly with methyl iodide. It is obtained as the sole basic product when the corresponding quaternary hydroxide is distilled in a vacuum. It is converted by cyanogen bromide into 1-methylhomo-1 : 2 : 3 : 4-tetrahydroquinoline methobromide (identified as the corresponding *chloroplatinate*, m. p. 197°) and 1-cyanohomo-1 : 2 : 3 : 4-tetrahydroquinoline, $C_6H_4 \begin{smallmatrix} [\text{CH}_2]_4 \\ \text{N}(\text{CN}) \end{smallmatrix} >$, b. p. $178\text{--}182^\circ/13\text{ mm.}$, which could not be obtained completely free from bromine and is identified by transformation into the *guanidine* derivative,



Condensation of Benzidine with Formaldehyde. HEISABURO KONDO and SUEZO ISHIDA (*J. Pharm. Soc. Japan*, 1922, 979—985; cf. H. Schiff, *A.*, 1892, 1223).—By adding 30 c.c. of 35% formaldehyde solution to benzidine (10 g.) dissolved in absolute alcohol (200 c.c.), a greyish-white, light, amorphous condensation product, *dimethanolbenzidine*, $C_{12}H_8(\text{NH} \cdot \text{CH}_2 \cdot \text{OH})_2$, is precipitated; it has m. p. $271\text{--}272^\circ$ after sintering at 260° , and is sparingly soluble in alcohol or water, but readily soluble in hydrochloric acid. It is not identical with dimethylenebenzidine, m. p. $140\text{--}141^\circ$, obtained by Schiff by the same method. When dissolved in dilute hydrochloric acid, the odour of formaldehyde is perceptible and from the solution *methanolbenzidine hydrochloride*,



colourless needles, of high melting point, was isolated by adding concentrated hydrochloric acid. When kept for a long time the solution in hydrochloric acid gave a reddish-violet product identical with the compound, $C_{15}H_{12}N_2$, obtained by Schiff. K. K.

The Behaviour of certain Dibenzamidoethylene Derivatives Prepared from Iminazoles towards Acid Anhydrides. A. WINDAUS and W. LANGENBECK (*Ber.*, 1922, 55, [B], 3706—3709; cf. Windaus, Dörries, and Jensen, *A.*, 1922, i, 61).—Dibenzamidoethylene derivatives are converted by the anhydrides of fatty acids into glyoxalines which contain the alkyl group of the fatty acid in position 2.

$\alpha\beta$ -Dibenzamido- Δ^a -propylene is converted by acetic anhydride at 180° into 2 : 4(2 : 5)-dimethylglyoxaline, identified as the *picrate*, m. p. 142° . The action of propionic anhydride under similar conditions leads to the formation of 4(5)-methyl-2-ethylglyoxaline, hygroscopic crystals, m. p. 45° (*oxalate*, colourless leaflets, m. p.

145°; *picrate*, yellow prisms, m. p. 131°; *hydrochloride*, hygroscopic leaflets, m. p. 132°; *nitrate*, m. p. 129°).

4(5)-Ethylglyoxaline (cf. Kolshorn, A., 1904, i, 675) is converted by benzoyl chloride and sodium hydroxide into $\alpha\beta$ -*dibenzamido*- Δ^{α} -*butylene*, NHBz·CH:CET·NHBz, needles, m. p. 146°, which is transformed by acetic anhydride at 140° into 2-methyl-4(5)-ethylglyoxaline (*picrate*, yellow needles, m. p. 90—91°; *oxalate*, m. p. 141°).

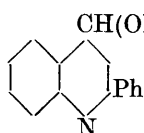
The glyoxaline obtained by Windaus and Ullrich (A., 1914, i, 662) by the action of ammonia on rhamnose is identified as 4(5)-methyl-5(4)-ethylglyoxaline. H. W.

Preparation of Triarylmethane Dyestuffs. BRITISH DYE-STUFFS CORPORATION, LTD., JAMES BADDILEY, and ERNEST HARRY RODD (Brit. Pat. 189295).—New dyes of the triarylmethane series are obtained by condensing a 4 : 4'-dialkyldiamino-3 : 3'-dimethylbenzophenone with a suitable secondary or tertiary amine by warming with phosphoryl chloride with the addition of a neutral diluent if desired. These new basic products dye cotton mordanted with tannin-antimony valuable shades of bright reddish- to bluish-violet. Those containing phenyl, benzyl, or naphthyl residues substituted in the amino-groups can be sulphonated by warming with 20% fuming sulphuric acid, giving new acid dyes which dye wool level shades of violet. The ketones required for the synthesis may be obtained by boiling the corresponding thio-ketones with concentrated hydrochloric acid, and the latter are produced by the condensation of monoalkyl-*o*-toluidines with formaldehyde and converting the resulting diphenylmethane derivatives into thio-ketones by the process of Brit. Pat. 20615/14. 4 : 4'-*Diethyldiamino*-3 : 3'-*dimethylbenzophenone*, m. p. 165°, when condensed with ethyl-*o*-toluidine, gives the triphenylmethane dye in the form of a bronze-coloured paste which dyes mordanted cotton a reddish-violet. Bluer shades are obtained by condensing the ketone with benzylethylaniline or dibenzylaniline. G. F. M.

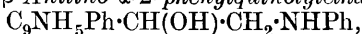
Preparation of Aminopyridines. CHEMISCHE FABRIK AUF ACTIEN (VORM. E. SCHERING) (D.R.-P. 358397; from *Chem. Zentr.*, 1922, iv, 950).—Ammonia is allowed to act on pyridine or its homologues in the presence of alkali metals. For example, anhydrous pyridine at 80° is added to a suspension of finely divided sodium in toluene and anhydrous ammonia is passed in. After the sodium is used up the temperature is raised to 130° and so maintained until no more ammonia is absorbed. From the products of the reaction, by extracting with ether, distilling off the ether and fractionation of the residue, 2-*aminopyridine*, b. p. 103—110°/20 mm., 4 : 4'-*dipyridyl*, b. p. 173—180°/20 mm., and 4-*aminopyridine* are obtained. 6-*Amino*-2-*methylpyridine*, a yellow oil, b. p. 120—130°/20 mm., is similarly prepared from 2-methylpyridine (α -*picoline*). G. W. R.

Preparation of Amino-alcohols of the Quinoline Series. SOCIETY FOR CHEMICAL INDUSTRY IN BASLE (Swiss Pats. 92001, 92607, 92608, and 92609; from *Chem. Zentr.*, 1922, iv, 950—951).—2-Phenyl-4-quinolyl methyl ketone is halogenated on the

methyl group and the halogen derivative allowed to react with primary or secondary amines. The *N*-alkyl-2-phenylquinolyl 4-aminomethyl ketone thus formed is reduced to the amino-alcohol. 2-Phenyl-4-quinolyl methyl ketone, yellow crystals, m. p. 75°, is prepared by condensation of ethyl 2-phenylquinoline-4-carboxylate with ethyl acetate and elimination of carbon dioxide from the intermediate *ethyl 2-phenylquinoline-4-acetate*, m. p. 52—54°, or from 4-cyano-2-phenylquinoline by Grignard's reaction. By the action of bromine on the ketone, 2-phenyl-4-quinolyl bromomethyl ketone hydrobromide is obtained; it forms yellow crystals, m. p. about 225° (decomp.). The free bromomethyl ketone forms light yellow crystals, m. p. 91°. With dimethylamine it gives 2-phenyl-4-quinolyl 4-dimethylaminomethyl ketone, which forms a hydrochloride, light yellow crystals, m. p. 208° (decomp.), and a hydrobromide, m. p. about 206°. Reduction of this compound gives β -dimethyl-



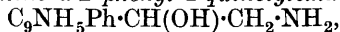
$\text{CH(OH)}\cdot\text{CH}_2\cdot\text{NMe}_2$ amino- α -2-phenylquinolyloethanol (annexed formula), a white, plastic mass. The dihydrochloride forms crystals, m. p. 175° (decomp.). 2-Phenyl-4-quinolyl diethylaminomethyl ketone is similarly prepared; the hydrobromide forms yellow, felted needles, m. p. about 188° (decomp.). 2-Phenyl-4-quinolyl piperidinomethyl ketone gives a hydrochloride, m. p. 235°, and a hydrobromide, m. p. about 241° (decomp.). 2-Phenyl-4-quinolyl anilinomethyl ketone forms yellow crystals, m. p. 123—125°. These ketones may be reduced to the corresponding amino-alcohols. β -Diethylamino- α -2-phenyl-4-quinolyloethanol which forms crystals, m. p. about 185°, with darkening. β -Piperidino- α -2-phenyl-4-quinolyloethanol gives a dihydrochloride, m. p. about 199° (decomp.). β -Anilino- α -2-phenylquinolyloethanol,



has m. p. 146°.

G. W. R.

Preparation of a Primary Amino-alcohol of the Quinoline Series. SOCIETY FOR CHEMICAL INDUSTRY IN BASLE (Swiss Pat. 92301; from *Chem. Zentr.*, 1922, iv, 951; cf. preceding abstract).—2-Phenyl-4-quinolyl methyl ketone is changed into its oximino-derivative and this is submitted to reduction. 2-Phenyl-4-quinolyl oximinomethyl ketone forms yellow crystals, m. p. 182° (decomp.). By reduction, β -amino- α -2-phenyl-4-quinolyloethanol,



is obtained. It forms a dihydrochloride, colourless crystals, m. p. about 190° after softening at about 145°.

G. W. R.

Reduction of 4:4'-Dipyridyl. OTTO DIMROTH and FRITZ FRISTER (*Ber.*, 1922, 55, [B], 3693—3697).—The formation of 1:1'-diacetyldihydro-4:4'-dipyridyl by the action of acetic anhydride on the dark violet solution obtained by the reduction of 4:4'-dipyridyl with nascent hydrogen, has been described previously (Dimroth and Frister, *A.*, 1922, i, 678). It is now shown that the violet solution contains a semiquinonoid compound

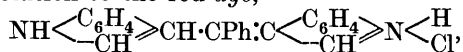
of molar proportions of 4:4'-dipyridyl and 1:1'-dihydro-4:4'-dipyridyl, which has been isolated as the dihydrochloride, for which the name dipyridyl-violet chloride is proposed. The dye differs from other semiquinonoid substances in that the reduced half is quinonoid and the oxidised half has the aromatic constitution.

4:4'-Dipyridyl is obtained conveniently and in 90–95% yield by the action of oxygen on a suspension of 1:1'-diacetyltetrahydro-4:4'-dipyridyl in glacial acetic acid and subsequent addition of sodium hydroxide to the solution. Titration of an aqueous solution of the substance with chromous chloride solution in the absence of air shows that the dye is produced by the action of one equivalent of hydrogen on a molecule of dipyridyl and that further reduction is not caused by chromous chloride. The dye is isolated as a dark green, crystalline powder, $C_{20}H_{20}N_4Cl_2$, by the action of chromous chloride on a solution of dipyridyl in the presence of calcium chloride; the precipitated product is washed successively with water and alcohol in the absence of air, towards which it is unusually sensitive. H. W.

Syntheses in the Indole Group. II. The Influence of the Solvent on the Grignard Reaction. RIKO MAJIMA and MUNIO KOTAKE (*Ber.*, 1922, **55**, [B], 3865–3872).—The unexpected differences observed in the production of indole-3-aldehyde from magnesium indolyl iodide and formic ester according as the reaction is effected in the presence of aliphatic or arylaliphatic ethers (Majima and Kotake, this vol., i, 156) has led the authors to examine possible further cases of this kind. Better yields of the products of the action of magnesium indolyl iodide on carbon dioxide, acetone, or benzaldehyde are obtained in the presence of anisole than in that of ethyl ether, whereas the reverse is the case when ethyl chloroformate, acetyl chloride, or chloroacetyl chloride is used.

Indole-3-carboxylic acid, m. p. 218–220°, is obtained by the action of carbon dioxide on magnesium indolyl iodide in anisole or ethyl ether. The reaction has been examined previously by Oddo (*A.*, 1911, i, 486), who has thus isolated indole-1-carboxylic acid, m. p. 108°; the cause of the discrepancy has not been elucidated. Magnesium indolyl iodide and acetone give di-3-indolyl-dimethylmethane, m. p. 163–165° (cf. Scholtz, *A.*, 1913, i, 520).

Di-3-indolylphenylmethane, $CHPh(CH \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CH} \end{smallmatrix} \text{--} \text{NH})_2$, m. p. 149–152° (+0.5 C_6H_6), m. p. 120–121°, is prepared from magnesium indolyl iodide and benzaldehyde; it is oxidised by ferric chloride in alcoholic solution to the red dye,



m. p. about 245–248°. Ethyl chloroformate and magnesium indolyl iodide give ethyl indole-3-carboxylate, colourless crystals, m. p. 118–119°; Oddo's observation (*loc. cit.*) that ethyl indole-2-carboxylate, m. p. 107°, is produced could not be confirmed. Acetyl chloride and magnesium indolyl iodide yield 3-indolyl

methyl ketone, $\text{NH} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CH} \end{smallmatrix} \gg \text{C} \cdot \text{COMe}$, m. p. 188—189° (oxime, m. p. 143—146°), identical with the products described by Oddo (*loc. cit.*). 3-Indolyl chloromethyl ketone forms small, rhombic crystals, m. p. 212—214°. H. W.

Isomeric Relationships in the Pyrazole Series. K. VON AUWERS and H. BROCHE (*Ber.*, 1922, **55**, [B], 3880—3911).—An examination has been made of the possibility of the existence of isomerides of the types $\text{RN} \begin{smallmatrix} \text{CH} \cdot \text{CH} \\ \text{N} = \text{CH} \end{smallmatrix}$ and $\text{RN} \begin{smallmatrix} \text{N} - \text{CH} \\ \text{CH} \cdot \text{CH} \end{smallmatrix}$, in the pyrazole series analogous to those observed with the closely related

indazoles, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH} \\ \text{NR} \end{smallmatrix} \gg \text{N}$ and $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH} \\ \text{N} - \end{smallmatrix} \gg \text{NR}$. The alkyl and

phenyl derivatives of 3-methyl- and 3:5-dimethyl-pyrazole have been investigated, but evidence of existence of isomerides of the expected type has not been obtained. The observations which have been made throw doubt on the identity of 3- and 5-derivatives of pyrazole as assumed by Knorr and other investigators.

3-Methylpyrazole is converted by an equivalent amount of methyl iodide in ethereal solution at 120° into 1:3-dimethylpyrazole (picrate, m. p. 172.5°; cf. Jowett and Potter, T., 1903, **83**, 467), a portion of the base remaining, however, unchanged. The same substances are obtained by boiling 3-methylpyrazole with methyl iodide and sodium methoxide in methyl alcoholic solution. 1:3-Dimethylpyrazole, b. p. 141—142°, is readily isolated in the homogeneous condition by the dry distillation of its methiodide, m. p. 255—256°. In a similar manner, the ethylation of 3-methylpyrazole with ethyl bromide at 100° or in the presence of alkali gives 3-methyl-1-ethylpyrazole, a colourless liquid, b. p. 152°/atmospheric pressure (picrate, slender yellow needles, m. p. 141°); the formation of quaternary salts in this case is much less pronounced than when methyl iodide is used. The products of the benzylation of 3-methylpyrazole are readily separated by taking advantage of the insolubility of the benzylated compounds in water in which the original material and the pyrazolium salt are soluble; experiments in the presence or absence of alkali yielded 1-benzyl-3-methylpyrazole, a colourless liquid with an odour of hyacinths, b. p. 140—141°/14 mm. (picrate, slender, yellow needles, m. p. 112.5—113.5°). In contrast to the indazoles, 3-methylpyrazole, when alkylated by different methods, gives only one definite substitution product. The proof that this is a 1:3-(and not a 1:5-)derivative is deduced in the following manner. The benzoic ester of hydroxymethyleneacetone, $\text{CH}_3 \cdot \text{CO} \cdot \text{CH} \cdot \text{CH} \cdot \text{OBz}$ (colourless crystals, m. p. 91—92°, prepared by the action of benzoyl chloride on a suspension of the sodium compound of hydroxymethyleneacetone in pyridine and anhydrous ether) is condensed with methylhydrazine and benzylhydrazine, whereby dimethyl- and benzylmethyl-pyrazoles are obtained identical with the products described above; unfortunately, it was not found possible to isolate the immediately formed benzoates, but the mode of formation

leaves practically no doubt that 1:3-derivatives are formed. Under similar conditions, phenylhydrazine gives 1-phenyl-3-methylpyrazole, m. p. 37°. The condensation of hydroxymethyleneacetone with methylhydrazine leads to the production of 1:3-dimethylpyrazole without any isomeric substance, and differs therefore from the action with phenylhydrazine, which yields a mixture of 1:3- and 1:5-compounds.

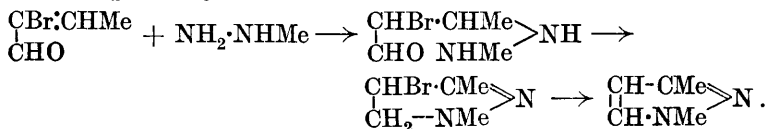
The observations have been extended to 3:5-dimethylpyrazole, $\text{NH} \begin{smallmatrix} \text{CMe} \cdot \text{CH} \\ \text{N} = \text{CMe} \end{smallmatrix}$, the symmetrical structure of which excludes the formation of structurally isomeric 3- and 5-derivatives; any case of isomerism must therefore be due to difference in a ring structure, since the production of 4-derivatives is excluded. It is converted by methyl iodide in the presence of alkali into 1:3:5-trimethylpyrazole, the picrate of which has m. p. 144—145°, whereas Knorr gives 131—133°. Similarly, 3:5-dimethylpyrazole and benzyl chloride at 170° give exclusively 1-benzyl-3:5-dimethylpyrazole, a colourless liquid, b. p. 144—146/10 mm. (picrate, lustrous, greenish-yellow needles, m. p. 126.5—127.5°). The latter compound is also produced by the action of acetylacetone on benzylhydrazine, although in this case the primary production of a three-membered ring might be expected. Finally, 1-phenyl-3:5-dimethylpyrazole has been prepared by the action of phenylhydrazine on acetylacetone and methyl α -bromopropenyl ketone, $\text{CHMe} \cdot \text{CBr} \cdot \text{COMe}$, respectively; the compound obtained in either case gives a picrate, m. p. 101°, and there is no evidence of the production of an isomeric compound.

From the foregoing it appears therefore that cases of isomerism due to the different structure of the ring are not found in the cases of alkylated and arylated pyrazoles. It is, however, still more remarkable that the number of position isomeric alkylpyrazoles is smaller than would be expected from theoretical considerations since 1:3-derivatives are frequently formed exclusively when mixtures of them with 1:5-compounds or when the latter alone would be normally expected. In the hope that the reactions in the pyrazole series would resemble those in the indazole group, an examination of the effect of heat on pyrazolium salts has been made. 1-Phenyl-3-methylpyrazole methiodide, m. p. 144°, and 1-phenyl-5-methylpyrazole methiodide, m. p. 282°, lose methyl iodide when subjected to dry distillation and re-form 1-phenyl-3-methylpyrazole and 1-phenyl-5-methylpyrazole, respectively. Contrary to expectation, however, pure 1:3-dimethylpyrazole and 3-methyl-1-ethylpyrazole are obtained from 1-benzyl-3-methylpyrazole methiodide, m. p. 153—154°, and 1-benzyl-3-methylpyrazole ethiodide, colourless prisms, m. p. 149.5—150.5°. The formation of 1:3- instead of 1:5-compounds discloses a surprising atomic

migration in accordance with the scheme $\begin{smallmatrix} \text{CH} \text{---} \text{CMe} \\ | \\ \text{CH} \cdot \text{N}(\text{C}_7\text{H}_7) \end{smallmatrix} \gg \text{N} \begin{smallmatrix} \text{Me}(\text{Et}) \\ | \\ \text{I} \end{smallmatrix} \rightarrow \left[\begin{smallmatrix} \text{CH} \cdot \text{CMe} \\ | \\ \text{CH} \text{---} \text{N} \end{smallmatrix} \gg \text{N} \begin{smallmatrix} \text{Me}(\text{Et}) \end{smallmatrix} \right] + \text{C}_7\text{H}_7\text{I} \rightarrow \begin{smallmatrix} \text{CH} \text{---} \text{CMe} \\ | \\ \text{CH} \cdot \text{NMe}(\text{Et}) \end{smallmatrix} \gg \text{N}$. The im-

portance of the observation has caused special attention to be directed to the constitution of the pyrazolium salts. The possibility that, contrary to rule, the addition of alkyl iodide occurs at the nitrogen atom which is already attached to an alkyl group is excluded by the observation that 1-benzyl-3-methylpyrazole methiodide differs from 1:3-dimethylpyrazole benzyl iodide, colourless leaflets, m. p. 167° (corresponding *picrate*, flat, yellow needles, m. p. 126°). The further possibility that the difference in the two iodides is due to the different spatial arrangement of the substituents around the same nitrogen atom and not to structural differences is improbable, and is more definitely excluded by the apparent impossibility of effecting their mutual interconversion. The wandering of alkyl groups during the fission of certain pyrazolium salts must therefore be regarded as established. Nevertheless, it does not follow that 1:5-dialkylpyrazoles are incapable of existence, since the high temperature involved in the fission can greatly facilitate the transformation of the primary products of the change into the 1:3-isomerides.

The synthesis of 1:5-dialkylpyrazoles has therefore been attempted under conditions which are less likely to involve transformation. The action of phenylhydrazine on α -bromocrotonaldehyde leads to the formation of 1-phenyl-5-methylpyrazone (cf. Vignier, A., 1913, i, 444), but under precisely similar conditions, methylhydrazine gives 1:5-dimethylpyrazole in good yield. A possible explanation of the difference in the reaction lies in the assumption that the alkylhydrazine, unlike the aryl compound, becomes primarily added at the double bond, thus:



This hypothesis is shown to be improbable in the following manner. β -Keto-*n*-butyl alcohol condenses with methylhydrazine sulphate in aqueous solution in the presence of acetic acid and sodium acetate to yield 1:3-dimethylpyrazoline, $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ | \quad | \\ \text{CMe} = \text{N} \end{array} \text{>NMe}$, a colour-

less liquid, b. p. 127—129° (*picrate*, yellow needles, m. p. 131.5—132.5°) (1-phenyl-3-methylpyrazoline, m. p. 71—72°, is prepared similarly from phenylhydrazine). If crotonaldehyde, which may be assumed to react in the same manner as its bromo-derivative, is similarly condensed with methylhydrazine, it must yield 1:3-dimethylpyrazoline if the hydrazine is added initially at the double bond and 1:5-dimethylpyrazoline if the initial reaction occurs at the aldehyde group. It is found that the compound which is produced is not identical with that derived from β -keto-*n*-butyl alcohol, and hence must be regarded as 1:5-dimethylpyrazoline, $\begin{array}{c} \text{CH}_2 \cdot \text{CHMe} \\ | \quad | \\ \text{CH} = \text{N} \end{array} \text{>NMe}$; it is a colourless, very hygroscopic liquid, b. p. 124—125°, which gives a *picrate*, thin, golden-yellow leaflets,

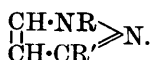
m. p. 113—114°. It must therefore be considered that the production of 1:3-dimethylpyrazole from methylhydrazine and bromocrotonaldehyde instead of the expected 1:5-derivative is actually due to atomic wandering.

Attempts to convert 1:3- and 1:5-dimethylpyrazolines into the corresponding pyrazoles by cautious oxidation with bromine led to remarkable results. The 1:3-compound is transformed smoothly into 1:3-dimethylpyrazole; the 1:5-derivative is largely resinified but is partly converted into 1:3-dimethylpyrazole.

It therefore appears that, under usual conditions, 1:5-dimethylpyrazole (and presumably other 1:5-dialkylpyrazoles) are incapable of existence, whereas 1-phenyl-3-methylpyrazole and 1-phenyl-5-methylpyrazole are stable substances.

Knorr's conception that the pyrazole molecule is symmetrically constituted owing to the oscillation of the double bonds and of the hydrogen atom united to the nitrogen: $\begin{array}{c} \text{CH}\cdot\text{NH} \\ || \\ \text{CH}\cdot\text{CH} \end{array} \gg \text{N} \rightleftharpoons$

$\begin{array}{c} \text{CH}=\text{N} \\ | \\ \text{CH}:\text{CH} \end{array} \gg \text{NH}$, can scarcely be extended to the alkyl derivatives of pyrazole, since a continuous oscillation of an alkyl group between two nitrogen atoms is contrary to all experience of tautomerism and the firmness of attachment of alkyl groups. The authors do not regard the production of 1:3-dialkylpyrazoles in place of the expected 1:5-derivatives as due to the identity of the two series of compounds in consequence of "mobile" double bonds and oscillatory atomic displacements; it is caused by the great instability of the 1:5-derivatives which immediately after formation become isomerised in accordance with the scheme: $\begin{array}{c} \text{CH}=\text{N} \\ | \\ \text{CH}:\text{CR}' \end{array} \gg \text{NR} \rightarrow$

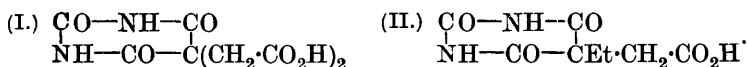


H. W.

The Polymorphism of Antipyrine, Vanillin, and the Erythritols. PAUL GAUBERT (*Compt. rend.*, 1922, **175**, 1414—1417).—In general, a substance which can be superfused, or, better, can pass into the amorphous state, will occur in several crystalline forms depending on the temperature. This appearance may be favoured by the presence of some impurity or sometimes by the more or less prolonged heating of the substance at a temperature above its melting point. In this manner, it is shown that antipyrine melted on a glass plate may occur in three crystalline modifications, vanillin may give four crystalline modifications, and the erythritols two crystalline forms. The conditions for obtaining these modifications and the forms obtained are detailed. W. G.

Preparation of a Derivative of Barbituric Acid Soluble in Water. HERMANN STAUDINGER (Swiss Pat. 91561; from *Chem. Zentr.*, 1922, iv, 840).—Diallylbarbituric acid or ethylallylbarbituric acid is treated with ozone and the ozonide is changed into the corresponding carboxylic acid. Diallylbarbituric acid gives a crystalline ozonide which is decomposed by heating over a water-bath with

formation of a *dicarboxylic acid* (I), colourless crystals, m. p. 280° (decomp.). Ethylallylbarbituric acid gives similarly a *monocarboxylic acid* (II) which forms colourless crystals, m. p. 280—281°:



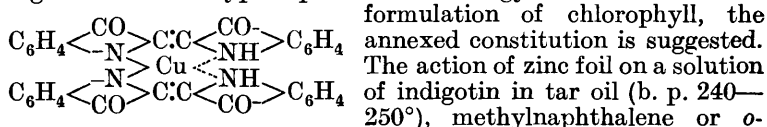
The compounds have therapeutic uses and serve as intermediates for the preparation of other barbituric acid derivatives.

G. W. R.

Preparation of a Compound of 5-isoPropyl-5-allylbarbituric Acid. F. HOFFMANN LA ROCHE & Co. (Brit. Pat. 188251).—5-isoPropyl-5-allylbarbituric acid when fused in approximately molecular proportions with 4-dimethylamino-1-phenyl-2:3-dimethyl-5-pyrazolone form as double compound which is apparently homogeneous, and melts sharply at 92—93°. It is yellow in colour and dissolves in hydrocarbons to a deep yellow solution. Water and other solvents containing hydroxyl give only slightly yellow solutions, indicating that in these solvents the compound is resolved into its colourless components to a considerable extent. The compound is valuable therapeutically, as it combines the soporific action of the barbituric acid with the analgesic action of the pyrazolone, and can therefore partly replace the opiates.

G. F. M.

Complex Metallic Compounds of Indigotin. I. K. KUNZ (*Ber.*, 1922, 55, [B], 3688—3691).—During the course of experiments on the production of 1:1-diphenylindigotin (Friedländer and Kunz, A., 1922, i, 765), it was observed that boiling solutions of indigotin in *o*-nitrochlorobenzene are rapidly decolorized by cuprous chloride and sodium acetate or copper powder. A similar change is now shown to occur in other solvents of high boiling point. It leads to the formation of the *compound*, $\text{C}_{32}\text{H}_{18}\text{O}_4\text{N}_4\text{Cu}$, which is rapidly decomposed by mineral acids and gives a normal indigo vat with hyposulphite. In analogy with Willstätter's

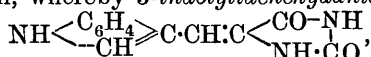


formulation of chlorophyll, the annexed constitution is suggested. The action of zinc foil on a solution of indigotin in tar oil (b. p. 240—250°), methylnaphthalene or *o*-nitrochlorobenzene leads to the formation of a *zinc* compound, $\text{C}_{32}\text{H}_{18}\text{O}_4\text{N}_4\text{Zn}$, black, lustrous prisms, which, unlike the copper compound, is rapidly hydrolysed by warm water with production of indigotin. A crystalline *nickel* derivative has also been prepared by the use of nickel sulphate and sodium acetate, but it has not yet been found possible to prepare a magnesium compound.

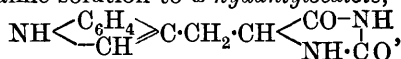
H. W.

Benzbisthiazoles. II. STEPHEN RATHBONE HOLDEN EDGE (*T.*, 1923, 123, 153—156).

Syntheses in the Indole Group. I. A New Synthesis of *r*-Tryptophan. RIKO MAJIMA and MUNIO KOTAKE (*Ber.*, 1922, 55, [B], 3859—3865).—Indole-3-aldehyde, $C_6H_4 \begin{smallmatrix} \text{C(CHO)} \\ \text{NH} \end{smallmatrix} \rangle CH$, m. p. 193—195°, is conveniently prepared in 40% yield by the successive action of indole and formic ester on a solution of magnesium ethyl iodide in anisole which is cooled in a mixture of ice and salt; in ethereal solution only traces of the aldehyde are formed (cf. Alessandri and Florence, A., 1915, i, 452). Phenetole may replace anisole, and ethoxymethylenedianiline may take the place of formic ester, but the yields are thereby somewhat reduced; amyl ether is as unsuitable as ethyl ether. The aldehyde is heated with hydantoin, anhydrous sodium acetate, and acetic anhydride at 106—108°, and the product is treated with aqueous sodium hydroxide solution, whereby 3-indolyldenehydantoin,



m. p. about 320°, decomp. 325°, is formed, the yield being 46.6% of that theoretically possible. 1-Acetylindole-3-aldehyde is obtained as a by-product of the action; it therefore appears probable that it is this derivative which actually undergoes condensation and that acetyl-3-indolyldenehydantoin is hydrolysed by the treatment with sodium hydroxide; the inefficiency of acetic acid and sodium acetate as condensing agents thus receives an explanation. 3-Indolyldenehydantoin is reduced by sodium amalgam in alkaline solution to *ω*-hydantylscatole,



colourless needles, m. p. 220—221°. The latter is hydrolysed by aqueous barium hydroxide solution at 108° to *r*-tryptophan, $NH \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CH} \end{smallmatrix} \rangle C \cdot CH_2 \cdot CH(NH_2) \cdot CO_2H$, hexagonal leaflets, m. p. 283—285° after becoming discoloured at 250°. As by-product, a substance, $C_{12}H_{13}O_3N_3$, leaflets, m. p. 207° (decomp.), is isolated.

H. W.

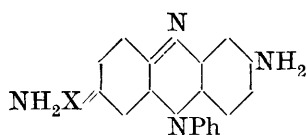
Preparation of a Condensation Product from β -Iminazolyethylamine [4- β -Aminoethylglyoxaline]. SOCIETY FOR CHEMICAL INDUSTRY IN BASLE (Swiss Pat. 92297; from *Chem. Zentr.*, 1922, iv, 890).—When formaldehyde or, preferably, methylal is added slowly to a suspension of 4- β -aminoethylglyoxaline in fuming hydrochloric acid at 100° and the mixture heated for several hours in a reflux apparatus, β -imidazolyisopiperidine [tetrahydro-1:3:6-benzotriazole] (annexed formula) is formed. The hydrochloride is crystalline and has m. p. 249°.

G. W. R.

Determination of the Constitution of Colouring Matters from their Absorption Spectra. IV. F. KEHRMANN and M. SANDOZ (*Helv. Chim. Acta*, 1922, 5, 895—905; cf. A., 1921, i, 276).—In continuation of previous work, the absorption spectra of

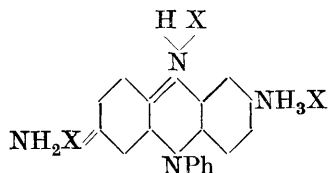
salts of diamino-derivatives of methyl- and phenyl-phenazine have been examined. The introduction of a second symmetrical amino-group into the monoaminomethylphenazine previously described (*loc. cit.*), lightens the colour of the mono-acid salt from cherry-red to orange-red. The absorption maxima are at λ 530 and λ 483. Introduction of a phenyl group into each amino-group deepens the shade to bluish-violet, and there is now only one absorption maximum, at λ 572. The corresponding ditolyl derivative has an absorption maximum at λ 580.

The monoacid salts of the diaminophenylphenazines chosen for examination were the perchlorates, on account of their great stability. The mono-acid salt of 2:7-diaminophenylphenazine (annexed formula) is blue, and to it may be ascribed the same



para-quinonoid structure as to *aposafranine*, which is violet-red. The di-acid salt is red, corresponding very closely with *aposafranine*, from which it is inferred that the second amino-group has been neutralised but that no change in the

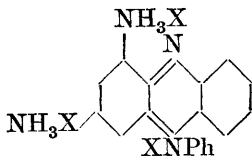
disposition of the double bonds has occurred. When the diaminophenylphenazonium perchlorate is dissolved in concentrated sulphuric acid, the colour of the solution is green. The colour is due



to the tri-acid salt (annexed formula) and is similar to that of the di-acid salt of *aposafranine*. Again there is no change of structure, and it is interesting to note the colour-deepening effect of the fixation of an equivalent of acid by a doubly-linked atom forming part of the chromogen. Finally,

in fuming sulphuric acid the colour is reddish-brown, resembling the di-acid salt of phenylphenazine. This salt must have an ortho-quinonoid structure.

The perchlorate of 1:3-diaminophenylphenazine is green in water, yellowish-green in alcohol, approaching a yellow of the second order. Although the amino-group in position 1 has a considerable colour-deepening effect, the structure is still probably paraquinonoid. The di-acid salt of this compound resembles

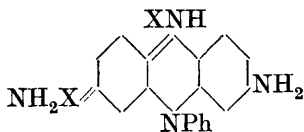


aposafranine, as in the case of the 2:7-isomeride, but the tri-acid salt, obtained by direct solution in concentrated sulphuric acid, is not green, but yellow, resembling the mono-acid salt of phenylphenazine. The structure of this salt must therefore be orthoquinonoid (annexed formula). When

the perchlorate is dissolved in fuming sulphuric acid, the reddish-brown colour of the tetra-acid salt is obtained.

The perchlorate of the third isomeride, *phenosafranine*, is red with an orange fluorescence in solution. Here again, as with methylphenazine, the second symmetrical amino-group brightens the shade whilst the colour intensity is increased. The di-acid

salt is blue, indicating that the second acid equivalent is combined with chromogenic nitrogen (annexed formula). The tri-acid salt is green, resembling, as expected, the di-acid salt of *aposafranine*. The tetra-acid salt is the normal reddish-brown. It is concluded that all the observed facts can be explained if it is granted that two states, ortho- and para-quinonoid, are possible in this series. It is further shown briefly that acetylation of an amino-group in this series has a similar effect on its auxochromic properties to neutralisation of the group with acid.




E. H. R.

The Solubility of the Salts of Uric Acid. GEORG BARKAN (*Z. Biol.*, 1922, **76**, 257—266).—The solubility of freshly precipitated amorphous sodium urate ($C_5H_3O_3N_4Na \cdot H_2O$) at 18° is 2.03 g. or 9.8×10^{-3} gram-molecules per litre. On keeping, or more particularly on stirring in contact with its solution, the solubility decreases, and approaches that of the crystalline form.

W. O. K.

Oxidation of Benzeneazoresorcinol. DINO BIGIAVI and GIULIO GIANNINI (*Atti R. Accad. Lincei*, 1922, [v], **31**, ii, 109—116).—Of the two possible diacetyl derivatives,

(α) $C_6H_5 \cdot NO \cdot N \cdot C_6H_3(OAc)_2$,
and (β) $C_6H_5 \cdot N \cdot NO \cdot C_6H_3(OAc)_2$, obtainable by the oxidation of the diacetyl compound of benzeneazoresorcinol by means of hydrogen peroxide, only the latter is actually obtained, the α -form probably undergoing further oxidation.

β -4-Benzeneazoxyresorcinol, $C_6H_5 \cdot N \cdot NO$ —OH, crystallises in red granules, m. p. 144° , giving a chestnut-yellow powder. The *dibenzoyl* derivative forms pale yellow needles, m. p. 113° , and the *diacetyl* derivative, long, pale yellow, silky needles, m. p. 102° .

4-Benzeneazoxy-2 : 6-dibromoresorcinol, $C_6H_5 \cdot N \cdot NO \cdot C_6HBr_2(OH)_2$, crystallises in transparent, greenish-yellow cubes, m. p. 153° , and yields aniline when reduced by means of zinc and acetic acid.

4-op-Dibromobenzeneazoxy-2 : 6-dibromoresorcinol,
 $C_{12}H_6O_3N_2Br_4$,
forms long, red needles, m. p. 229° (decomp.), and gives 2 : 4-dibromoaniline when reduced by means of tin and hydrochloric acid.

2 : 6-Dibenzeneazo-4-benzeneazoxyresorcinol,
 $C_6H_5 \cdot N_2O \cdot C_6H(OH)_2 \cdot (N_2Ph)_2$,
is a red compound, m. p. 220° .

When treated with alcoholic potassium hydroxide, the diacetyl derivative of β -benzeneazoxyresorcinol yields a dark red compound, m. p. about 190° , which has not yet been characterised.

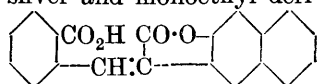
T. H. P.

Oxidation of Benzeneazonaphthols. I. DINO BIGIAVI and RENATO CERCHIAI (*Atti R. Accad. Lincei*, 1922, [v], **31**, ii, 27—30).—Owing to the divergent behaviour towards alkali shown by the three isomeric benzeneazonaphthols, a phenylhydrazonic constitution is attributed to 1-benzeneazo-2-naphthol, whilst 4-benzeneazo-1-naphthol and 2-benzeneazo-1-naphthol are considered to possess the ordinary hydroxylic formulæ (Goldschmidt and Brubacher, A., 1891, 1209; Willstätter and Parnas, A., 1907, i, 425, 1056). Marked differences are found also in the behaviour of these compounds towards 30% hydrogen peroxide solution and acetic acid.

Thus, under these conditions, 1-benzeneazo-2-naphthol and also its acetyl-derivative undergo slow oxidation in the cold to carboxycinnamic acid, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{H}$, m. p. 200° , whilst in the hot they yield the isomeric dihydroisocoumarincarboxylic acid,

$\text{C}_6\text{H}_4\begin{matrix} \text{CO}-\text{O} \\ \diagup \quad \diagdown \\ \text{CH}_2\cdot\text{CH}\cdot\text{CO}_2\text{H} \end{matrix}$, m. p. 153° , which is also obtained when carboxycinnamic acid is fused for a few moments.

Similar oxidation of β -naphthol yields the products obtained by Ehrlich by the action of permanganate (A., 1889, 1001), namely: (1) Carboxycinnamic acid, for which, however, this author gave m. p. 183° instead of 200° ; (2) an acid, $\text{C}_{20}\text{H}_{12}\text{O}_4$, m. p. 281° , which, although regarded by Ehrlich as dibasic, gives only mono-silver and monoethyl derivatives, and has probably the structure



This acid reduces permanganate, but not so rapidly as does carboxycinnamic acid. T. H. P.

Reduction of Ethyl Diazobenzylideneglucuronate. P. A. LEVENE (*J. Biol. Chem.*, 1922, **54**, 809—813).—When reduced with aluminium amalgam in isopropyl-alcoholic solution, ethyl diazobenzylideneglucuronate yields a mixture of ethyl benzylidenedeoxyglucuronate and ethyl benzylidene chitosamate. The former product is identical with that previously obtained (A., 1922, i, 1028) by reduction of ethyl benzylidene- $\alpha\beta$ -anhydromannonate; the latter was not isolated, but was identified by hydrolysis into chitosamic acid. The reduction apparently takes place asymmetrically, for no trace of an epimeride of chitosamic acid can be detected. That the deoxy-compound is not produced through the intermediate formation of an unsaturated compound is shown by the fact that the amide of benzylidene- $\alpha\beta$ -anhydromannonic acid is unchanged when submitted to similar treatment. E. S.

The Formation of Aromatic Thiocyanates by the Diazo-reaction. A. KORCZYNSKI [with J. KNIATOWNA and F. KAMINSKI] (*Bull. Soc. chim.*, 1922, [iv], **31**, 1179—1185).—In the transformation of *o*-nitrodiazobenzene thiocyanate into *o*-nitrophenyl thiocyanate under the catalytic influence of a metallic thiocyanate, the yield obtained depends on the metal of which a salt is used and on the temperature, being greater, in the majority of cases

studied, at 15—20° than at 60—70°. The most effective catalysts of the substances used are the thiocyanates of iron and tungsten.

H. J. E.

The Tryptophan Content of some Proteins. CLARENCE E. MAY and EMBREE R. ROSE (*J. Biol. Chem.*, 1922, **54**, 213—216).—The colour which tryptophan yields with Ehrlich's reagent has been utilised for the estimation. The protein (0.05 to 1 g.) is added to a mixture of concentrated hydrochloric acid (50 c.c.), water (50 c.c.), and a 5% solution of *p*-dimethylaminobenzaldehyde in 10% sulphuric acid (1 c.c.). It is then incubated at 35° for twenty-four hours, left at the ordinary temperature for at least twenty-four hours, and the colour then compared with a casein standard. It is assumed that casein yields 1.5% of tryptophan. Application of the method to a number of proteins yielded the following values: lactalbumin 2.4, gliadin 1.05, glutenin 1.80, edestin 1.5, glycinin 1.65, ovovitellin 1.74, egg-albumin 1.11, phaseolin 0.80, maize gluten 1.08, legumin (vetch) 1.05%. No colour developed in the case of zein and gelatin.

E. S.

The Isoelectric Point of Globin. SHUNGO OSATO (*Biochem. Z.*, 1922, **132**, 485—487).—The isoelectric point of globin from blood-corpuscles is found by the precipitation method to be at P_H 8.1.

W. O. K.

I. The Preparation of Nucleic Acid from the Nucleoprotein of Tubercle Bacilli (Tuberculinic Acid). II. The Pyrimidines contained in Tuberculinic Acid, the Nucleic Acid of Tubercle Bacilli. TREAT B. JOHNSON and ELMER B. BROWN (*J. Biol. Chem.*, 1922, **54**, 721—730, 731—737).—I. A method is described for the preparation of tuberculinic acid from tubercle bacilli (cf. also Ruppel, A., 1899, ii, 237; Levene, A., 1901, i, 299). The protein which remains after removal of this nucleic acid has been analysed for nitrogen distribution with the following results: amide-N 11.83, humin-N 4.11, cystine-N 1.26, arginine-N 10.63, histidine-N 11.48, lysine-N 3.69, monoamino-N 47.39, non-amino-N 9.34%. Tryptophan was also present.

II. Cytosine and thymine have been isolated from the products of hydrolysis of tuberculinic acid; the presence of uracil could not be detected.

E. S.

The Results and Aims of General Enzyme Chemistry. H. VON EULER (*Ber.*, 1922, **55**, [B], 3583—3600).—A lecture delivered at the centenary of the *Versammlung Deutscher Naturforscher und Aerzte*.

H. W.

The Isolation of Enzymes. RICHARD WILLSTÄTTER (*Ber.*, 1922, **55**, [B], 3601—3623).—A lecture delivered at the centenary of the *Versammlung Deutscher Naturforscher und Aerzte*.

H. W.

Saccharase. E. CANALS (*Bull. Soc. chim.*, 1922, [iv], **31**, 1333—1341; cf. A., 1922, i, 1075).—The author traces a relationship between the magnesium and phosphate content of saccharases of various origins, and their respective diastatic powers, which

seems to some extent to support the opinion of Salkowski that invertase is the magnesium salt of a nitrogenous phosphated acid. A direct relationship cannot be traced, however, between the total magnesium and phosphoric acid content and the diastatic power, since, if the preparation is purified by dialysis, the diastatic power is enhanced whilst there is a loss of about 40% of Mg and 58% of P_2O_5 , and all the magnesium and phosphoric acid of the saccharase is therefore not essential for the hydrolysing activity. Purification by precipitation with alcohol results in a similar loss in magnesium and an even greater loss in phosphoric acid, and in this case the diastatic power is greatly diminished, owing probably to a profound modification of the colloidal system of the enzyme by this treatment. Alcoholic precipitation is therefore not suitable for the purification of saccharase. It is observed that the magnesium of the saccharase dialyses less easily, and is less readily separated by alcoholic precipitation than the phosphate, and it would therefore seem to enter to a greater extent into the constitution of the micelle.

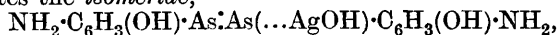
G. F. M.

The Influence of Neutral Alkali-metal Salts on Diastatic Ferment. V. AMANDUS HAHN and HUGO MEYER (*Z. Biol.*, 1922, 76, 227—246).—Purified diastase from commercial pancreatin “Rhenania” is influenced as regards its activity by the presence of neutral salts of the alkali metals similarly to saliva diastase, and to unpurified pancreatin. The optimum P_H depends on the buffer solution used, being 7.2 with a phosphate mixture and 5.6 with an acetate mixture, resembling saliva which has corresponding optimum at P_H 6.6 and P_H 5.6. The influence of neutral salts is much more marked with acetate buffer mixtures than with phosphate buffer mixtures. In both cases the effect is to increase the optimum P_H .

W. O. K.

Arseno-metallic Compounds. II. Isomeric Silver Salvarsans. A. BINZ and W. H. LUDWIG (*Ber.*, 1922, 55, [B], 3826—3831).—The silver complex of silver salvarsan has been considered by Ehrlich and Karrer (A., 1916, i, 95) to be co-ordinatively attached to the arsenic atom and by Binz, Bauer, and Hallstein (A., 1920, i, 401) as united by the residual affinity of the nitrogen atom. The isolation of two isomeric silver salvarsans apparently justifies both formulæ. At present, the allotment of the structure to the isomeride is somewhat arbitrary and is due to the fact that one form is lighter in colour than the other and resembles to this extent the complex compounds containing silver and nitrogen, but not arsenic.

Silver salvarsan I, $NH_2 \cdot C_6H_3(OH) \cdot As : As \cdot C_6H_3(OH) \cdot NH_2 \dots AgOH$, is obtained by adding sodium carbonate solution to salvarsan and silver nitrate dissolved in water; it is insoluble in sodium carbonate and stable towards reduction with hypophosphorous acid. It dissolves in sodium hydroxide solution with the dark brown colour of technical silver salvarsan, and from the solution carbon dioxide precipitates the *isomeride*,



a dark brown substance which dissolves in sodium carbonate solution and is reduced by hypophosphorous acid. Silver salvarsan I is rapidly converted by hydrochloric acid into the *compound* $\text{NH}_2 \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{As} : \text{As} \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{NH}_2 \dots \text{AgCl}$, a pale yellow powder. The dark brown isomeride II appears to be unaffected by similar treatment after several hours, but gradually becomes converted into the chloride just described, the formation of which from the chloride, $\text{NH}_2 \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{As} : \text{As} (\dots \text{AgCl}) \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{NH}_2$, takes place very slowly in comparison with the change in the reverse direction in alkaline solution. The same change occurs when solutions of technical silver salvarsan are treated with hydrochloric acid, the brown colour in this case persisting for a considerable time and gradually giving place to a pale yellow precipitate. H. W.

Physiological Chemistry.

Respiratory Exchange in Fresh-water Fish. IV. Further Comparison of Gold-fish and Trout. JOHN ADDYMAN GARDNER and GEORGE KING (*Biochem. J.*, 1922, **16**, 729—735).—The oxygen tension at the asphyxial point at various temperatures in the case of the gold-fish has been determined. This fish can stand much lower oxygen tensions for any temperature than the trout. The difference is more marked at low temperatures. Trout kept at a low temperature corresponding with a state of hibernation showed a higher glycogen content than control fish kept at higher temperatures, which is consonant with the respiratory coefficients obtained for these fish. Glycogen estimation in the case of the gold-fish yielded results which were in conformity with the low level of their metabolism. S. S. Z.

Respiratory Exchange in Fresh-water Fish. V. Eels. JOHN ADDYMAN GARDNER and GEORGE KING (*Biochem. J.*, 1922, **16**, 736—738).—Eels live at a much lower plane of metabolism than trout. At medium temperatures trout use about four times as much oxygen as eels, and at low temperatures 10—12 times as much. S. S. Z.

Influence of the Introduction of Water on Blood Concentration Induced by Deprivation of Water. FRANK P. UNDERHILL and ROBERT KAPSINOW (*J. Biol. Chem.*, 1922, **54**, 459—464).—The experiments were performed on dogs. Deprivation of water for short intervals produced an increased blood concentration which rapidly returned to approximately the normal on administration of water. E. S.

Gas and Electrolyte Equilibria in the Blood. III. The Alkali-binding and Buffer Values of Oxyhæmoglobin and Reduced Hæmoglobin. DONALD D. VAN SLYKE, A. BAIRD HASTINGS, MICHAEL HEIDELBERGER, and JAMES M. NEILL (*J. Biol. Chem.*, 1922, **54**, 481—506).—The technique previously developed

(A., 1922, i, 1207) has been used to determine the amount of alkali bound both by recrystallised horse oxyhæmoglobin (Heidelberger, A., 1922, i, 962) and by reduced hæmoglobin when under physiological conditions of concentration, carbon dioxide tension, and P_H value. At P_H 7.4 one gram-molecule of oxyhæmoglobin binds 2.15 ± 0.10 equivalents of alkali (sodium) whilst the corresponding figure for reduced hæmoglobin is 1.47 ± 0.08 . The change of one mol. of reduced hæmoglobin to oxyhæmoglobin thus enables it to combine with an additional 0.68 ± 0.10 equivalent of alkali. At intermediate points the increase in base bound is directly proportional to the increase in oxygen content, thus agreeing with Henderson's theory (A., 1921, i, 473) and with the assumption originally made by Christiansen, Douglas, and Haldane (A., 1914, i, 1012). The molecular buffer values (cf. A., 1922, i, 893) of oxyhæmoglobin and reduced hæmoglobin are practically constant over the physiological range of P_H , that for the former being $\beta_o = 2.64$ and for the latter $\beta_R = 2.45$. The authors conclude from these values that the alkali taken up by hæmoglobin is shared between at least five univalent acid groups. The total amount of base bound by hæmoglobin at P_H values varying from 7.2 to 7.5 is given by the equation: $B = 2.64[\text{HbO}_2](P_H - 6.585) + 2.45[\text{Hb}](P_H - 6.80)$.
E. S.

Gas and Electrolyte Equilibria in the Blood. IV. The Effect of Oxygenation and Reduction on the Bicarbonate Content and Buffer Value of Blood. DONALD D. VAN SLYKE, A. BAIRD HASTINGS, and JAMES M. NEILL (*J. Biol. Chem.*, 1922, 54, 507—526).—The experiments recorded in the previous paper have been extended to oxygenated and reduced horse blood (oxalated or defibrinated). Since carbonic acid and hæmoglobin are the only acids present in blood, the assumption has been made, in interpreting the results, that changes in the amount of base present as bicarbonate are accompanied by equal and opposite changes in the amount combined with hæmoglobin. The results show that each specimen of blood, when at the same degree of oxygenation, has a constant buffer value over the P_H range 7.2 to 7.5, the average values of different specimens being 25.3 for oxygenated blood and 24.4 for reduced blood (buffer values are here expressed as millimols. of base per unit change in P_H ; cf. A., 1922, i, 893). The difference between these two values is due to the loss of buffer value which occurs when oxyhæmoglobin is reduced (cf. preceding abstract), a loss which is partly compensated for by an increase in bicarbonate content. Thus, of the total buffer value, hæmoglobin was responsible for 76.0% and bicarbonate for 6.9% in oxygenated blood, the figures for reduced blood being 73.3% and 9.0%, respectively. Each additional molecule of oxygen taken up by hæmoglobin at P_H 7.3 caused decreases in the bicarbonate content varying from 0.50 to 0.59 in different specimens. On the above assumption, a mol. of hæmoglobin when changed from the reduced to the oxygenated state therefore combines with an additional 0.50—0.59 equivalent of alkali. This value differs

from that obtained with solutions of crystallised hæmoglobin and is hence probably influenced by some unknown variable factor in blood. As for solutions of hæmoglobin, the amount of additional base combined with hæmoglobin in blood on oxygenation was directly proportional to the amount of oxygen combined. Over the range P_H 7.2 to 7.5 a rise of P_H 0.1 caused an increase of approximately 0.02 equivalent in the amount of base transferred from bicarbonate to hæmoglobin by one molecule of oxygen. E. S.

Evaluation of Buffers of the Blood. EDWARD A. DOISY, A. P. BRIGGS, EMILY P. EATON, and WILLIAM H. CHAMBERS (*J. Biol. Chem.*, 1922, **54**, 305—329).—The authors have investigated the extent to which the various known buffer systems of the blood participate in binding carbon dioxide during the change of blood from the arterial to the venous state. In the results obtained from three specimens of human blood, from 87—95% of the carbon dioxide has been accounted for. Of the total amount taken up, 75—80% was due to the hæmoglobin, less than 1% to the inorganic phosphates, and less than 5% to the buffers contained in the separated serum. E. S.

Measurement of the Alkalinity of the Blood. CH. O. GUILLAUMIN (*J. Pharm. Chim.*, 1923, [vii], **27**, 5—23).—For the measurement of the P_H of the blood and the alkaline reserve, the methods described by Cullen (*J. Biol. Chem.*, 1922, **52**, 508) with very slight modifications give accurate results with inexpensive apparatus. H. K.

Relations Existing between Arterial and Venous Blood of the Dog with Special Reference to the Plasma Chlorides. EDWARD A. DOISY and J. W. BECKMANN (*J. Biol. Chem.*, 1922, **54**, 683—691).—Analyses were made of arterial and venous blood drawn simultaneously from dogs. The results show that the migration of hydrochloric acid from plasma to corpuscles, which is to a large extent responsible for the buffer action of blood in vitro (cf. A., 1922, i, 963), occurs also in vivo as blood passes from the arterial to the venous state. Evidence was also obtained, although the results were less consistent, that the blood respiratory coefficient has a normal value, that the additional carbon dioxide contained in venous blood is approximately equally distributed between plasma and corpuscles, and that the corpuscles occupy a larger volume in venous than in arterial blood. E. S.

Non-protein Organic Constituents in the Blood of Marine Fish. W. DENIS (*J. Biol. Chem.*, 1922, **54**, 693—700).—Analyses previously made (A., 1914, i, 106) have been repeated using recent methods. The following are the average results, expressed in mg. per 100 c.c. of blood, for different species of elasmobranch and teleost fishes: Elasmobranch blood—non-protein nitrogen, 1000; urea nitrogen 800; amino-nitrogen 28; creatinine 6; creatine 25; uric acid 1.1. Teleost blood—non-protein nitrogen 65; urea nitrogen 9; amino-nitrogen 28; creatinine 1.0; creatine 6; uric acid 4. The blood of invertebrates was found frequently to contain

no amino-nitrogen although considerable amounts were present in the muscle. E. S.

The Neutrality of Blood. J. MELLANBY and C. C. WOOD (*Proc. Physiol. Soc.*, 1922, lii-lij; *J. Physiol.*, 1922, 56; from *Physiol. Abstr.*, 1922, 7, 490).—Corpuscles, partly freed from carbon dioxide and suspended in 0.85% sodium chloride solution, have a slightly acid reaction. When exposed to alveolar air, these corpuscles absorb carbon dioxide and the reaction tends to neutrality. On the other hand, serum from the same blood is alkaline in reaction and on exposure to alveolar air becomes more acidic. This apparently paradoxical effect of carbon dioxide explains the approximate neutrality of the blood under varying tensions of carbon dioxide, and perhaps also the divergence which exists between the calculated reaction of the blood, based on the ratio of the free and combined carbon dioxide contained in it and that actually observed by direct experiment. W. O. K.

Combined Uric Acid in Ox Blood. ALICE ROHDE DAVIS, ELEANOR B. NEWTON, and STANLEY R. BENEDICT (*J. Biol. Chem.*, 1922, 54, 595—599).—The uric acid compound present in the corpuscles of ox blood (cf. A., 1915, i, 612) has been isolated. It forms square plates which do not melt under 300°, and when hydrolysed with sulphuric acid yields equimolecular quantities of uric acid and *d*-ribose. It is apparently a monobasic acid; its sodium salt has $[\alpha]_D^{20} + 20.42^\circ$. E. S.

Distribution of the Combined Uric Acid in the Corpuscles of Ox Blood. ELEANOR B. NEWTON and ALICE ROHDE DAVIS (*J. Biol. Chem.*, 1922, 54, 601—602).—The combined uric acid (cf. preceding abstract) is present entirely in the erythrocytes. E. S.

Combined Uric Acid in Human, Horse, Sheep, Pig, Dog, and Chicken Blood. ELEANOR B. NEWTON and ALICE ROHDE DAVIS (*J. Biol. Chem.*, 1922, 54, 603—605).—The combined uric acid compound (cf. preceding abstracts) seems to be present in the blood of all the above species but in much smaller amounts than in ox blood. E. S.

Influence of Subcutaneous Injections of Indole and Scatole on the Nitrogenous Metabolism of the Rabbit. FRANK P. UNDERHILL and ROBERT KAPSINOW (*J. Biol. Chem.*, 1922, 54, 717—720).—Using doses of 30 mg. per kg., no influence was observed. Indole, but not scatole, apparently increased the excretion of ethereal sulphates. E. S.

Inorganic Metabolism. I. Inter-relations between Calcium and Magnesium Metabolism. L. JEAN BOGERT and ELIZABETH J. MCKITTRICK (*J. Biol. Chem.*, 1922, 54, 363—374).—The addition of magnesium citrate in amounts of 6 g. per day to the diet of four subjects caused an increased excretion of magnesium both in the urine and faeces. There was also an increase in each case in the total calcium excreted, and, in three out of the four

cases, in both urinary and fæcal calcium. The similar addition of calcium lactate caused increase in both urinary and fæcal calcium. There was probably also an increased excretion of magnesium.

E. S.

Inorganic Metabolism. II. Effects of Acid-forming and Base-forming Diets on Calcium Metabolism. L. JEAN BOGERT and ELIZABETH E. KIRKPATRICK (*J. Biol. Chem.*, 1922, **54**, 375—386).—Although certain irregularities occurred, the results, in the main, indicate that acid-forming diets divert calcium from the fæces to the urine and also cause an increased total excretion. Base-forming diets, on the other hand, divert calcium from the urine to the fæces and produce a diminution in the total excretion.

E. S.

Inorganic Metabolism. III. Influence of Yeast and Butter Fat upon Calcium Assimilation. L. JEAN BOGERT and RUTH K. TRAIL (*J. Biol. Chem.*, 1922, **54**, 387—397).—In the case of four women, the addition of either yeast or butter fat to a diet which was otherwise vitamin-free produced an increased retention of calcium. The amount of calcium excreted in the fæces was diminished.

E. S.

Antiketogenesis. IV. The Ketogenic - Antiketogenic Balance in Man and its Significance in Diabetes. PHILIP A. SHAFFER (*J. Biol. Chem.*, 1922, **54**, 399—441).—Further work on the ketolytic reaction in vitro (cf. A., 1921, i, 754) has shown that, under proper conditions, one molecule of dextrose accomplishes the disappearance of two molecules of acetoacetic acid when the latter is in excess. On this basis, the values previously assigned (A., 1922, i, 83) to the antiketogenic factors must be doubled. This conclusion is supported by the results obtained by Wilder and Winter (A., 1922, i, 893), but when applied to cases taken from the literature it leads to a calculated excretion of acetone substances which is considerably smaller than that actually found. The protein ketogenic factor has therefore been arbitrarily increased by 50%. With this modification, moderate agreement between the calculated and actual values has been obtained. In cases of severe ketosis (where the acetoacetic acid is in excess), each molecule of dextrose appears, without doubt, to be equivalent ketolytic substance for two molecules of keto-acid. At the threshold of ketosis, however, the dextrose molecule may have a lower value owing to oxidation taking place without its coming into contact with the keto-acid. The author discusses the bearing of these results on the dietetic problem of diabetes.

E. S.

Colorimetric Researches on Tryptophan. VII. The Tryptophan Requirements of Growing Rats (a Contribution to the Question of Cyclopoiesis). OTTO FÜRTH and FRITZ LIEBEN (*Biochem. Z.*, 1922, **132**, 325—341).—Only a small fraction (3—8%) of the tryptophan consumed by rats is retained in the

body, the rest being destroyed. The miminal tryptophan requirement for rats per kg. of body weight is greater than for man.

W. O. K.

Physical Chemistry of Foodstuffs. Investigation of Acid-taste. THEODOR PAUL (*Z. Elektrochem.*, 1922, **28**, 435—446).—By the employment of the methods of psychophysics, and the introduction of a new terminology, the measurement of acid-taste has been placed on a quantitative basis. Molecular acidity is defined as the number of mols. of hydrochloric acid, dissolved in a fixed volume of water, which tastes as acid as one mol. of the acid substance dissolved in the same volume of water. The molecular acidity is determined, not only by the hydrogen-ion concentration, but also by the capacity of the solute to yield its reserve of hydrogen-ions to the tongue, and, to some extent, by the nature of the anion and the vapour pressure of the acid. The acids investigated have been arranged in a series of increasing molecular acidities, thus: carbonic acid, potassium hydrogen tartrate, acetic acid, lactic acid, α -acetoxypropionic acid, hydrochloric acid, and tartaric acid. In this series, carbonic acid possesses the weakest, and tartaric acid the strongest acid taste. This order is not in agreement with the dissociation constants of these acids. For example, the two acids, α -acetoxypropionic and tartaric acids, although possessing very similar dissociation constants, show very different molecular acidities. The molecular acidity decreases slowly with increase in concentration. The curves obtained by plotting acid taste against concentration show several points of resemblance with the "sweetness" curves of "saccharin" and dulcin. The two properties, acid-taste and sweetness, behave in an analogous manner with increase in concentration, and this suggests that similar relationships may exist between these and the salt and bitter qualities of substances.

W. E. G.

The Course of Oxidative Processes [in the Cell]. HEINRICH WIELAND (*Ber.*, 1922, **55**, [B], 3639—3648).—A lecture delivered at the centenary of the *Versammlung Deutscher Naturforscher und Aerzte*.

H. W.

Glutathione. II. A Thermostable Oxidation-Reduction System. F. GOWLAND HOPKINS and M. DIXON (*J. Biol. Chem.*, 1922, **54**, 527—563).—A continuation of the investigation of the recently discovered glutathione (A., 1921, i, 635) has shown that, in its functions in the cell, this dipeptide is mainly associated with insoluble, thermostable agents which act as hydrogen donors and form with it the thermostable reducing system of the tissues. Thus, tissue which has been extracted with water, treated repeatedly with boiling water or alternatively heated for three hours at 100°, dehydrated with alcohol, and finally dried in a vacuum, all the operations being performed anaerobically, when ground and suspended in a phosphate buffer mixture (P_H 7—8) containing oxidised glutathione is able rapidly to reduce methylene-blue, that portion of its reducing power which depends on the presence of the di-

peptide being practically unaffected by this treatment. The thermostable agents are, however, sensitive to oxidation (for example, by hydrogen peroxide) and are even slowly destroyed by molecular oxygen. The latter effect is enormously accelerated by the presence of glutathione. When suspensions of muscular tissue, prepared as above, are aerated in the presence of the dipeptide oxygen is absorbed to the extent of 400 c.mm. for every gram of dry material used. At the same time carbon dioxide is given off, the "respiratory quotient" of the process being about unity at first and falling off considerably during the later stages. These results suggest that a thermostable mechanism for oxidations and reductions coexists with the specialised enzymic mechanism in living tissue. E. S.

Proportion of Sulphur in the Skin of Children Aged Less than One Year. E. LABORDE (*Bull. Soc. Chim. biol.*, 1922, **4**, 584—586).—In the skin of three children approximately 0.2% of sulphur was found. In the healthy skin of another who had died from poisoning by sulphuric acid, there was 0.15%, whilst the burned areas of the skin contained 0.37%. W. O. K.

Chemistry of the Liver. UBALDO SANMARTINO (*Biochem. Z.*, 1922, **132**, 343—351).—An analysis of the fats in horse liver shows the presence of kephalin, lecithin, myristic acid, butyric acid, and other fatty acids, and certain glycerol and cholesterol esters. W. O. K.

The Proteolytic Enzymes of the Spleen. S. G. HEDIN (*J. Biol. Chem.*, 1922, **54**, 177—202).—At least three enzymes, namely, α -protease, β -protease, and erepsin, are present in the spleen of the ox (cf. A., 1904, ii, 58; Morse, A., 1917, i, 606; Dernby, A., 1918, i, 464). A partial separation of these has been effected by extracting the minced spleen successively with dilute acetic acid, casein, and 5% sodium chloride. The acetic acid extract contains all three enzymes; the casein extract contains mainly β -protease and erepsin; whilst a solution in sodium hydroxide of the globulin obtained from the sodium chloride extract contains mainly α -protease. If the spleen is kept for any length of time in alkaline solution or at an acidity less than P_H 5.2, the enzymes show a loss of activity which cannot be revived by acids. α -Protease, which acts in alkaline solution, converts proteins into peptones more rapidly than peptones into amino-acids; its action is inhibited by serum-albumin (cf. also Bradley, A., 1922, i, 896). E. S.

The Catalytic Destruction of Carnosine in Vitro. WINIFRED MARY CLIFFORD (*Biochem. J.*, 1922, **16**, 792—799).—A catalyst is described which is capable of destroying carnosine in muscle extract. It is present in ox, rat, and cod muscle, but is absent in the muscle of invertebrates such as the oyster and the lobster. It is also present in the liver of the rat and of the ox. The kidney of the rat, ox, or sheep does not contain it. The curve of action of this catalyst is unlike any enzyme curve. The possible mechanism of

its action is discussed. It is also suggested that carnosine may be an intermediate product of metabolism. S. S. Z.

Excretion of Acid and Ammonia. ROGER S. HUBBARD and SAMUEL A. MUNFORD (*J. Biol. Chem.*, 1922, **54**, 465—479).—From a statistical analysis of the results of a series of analyses of human urine the authors conclude that the excretion of ammonia varies with the volume and the reaction of the urine but is not directly affected by the amount of acid excreted. The relation between the reaction of the urine and the excretion of ammonia is concerned rather with the concentration of the ammonia than with the actual amount excreted. The latter fact is interpreted as supporting the theory (Nash and Benedict, A., 1922, i, 191, 483) that the kidney is the seat of formation of ammonia. E. S.

The Influence of Fat and Carbohydrate on the Nitrogen Distribution in the Urine. EDWARD PROVAN CATHCART (*Biochem. J.*, 1922, **16**, 747—753).—The output of total nitrogen, urea, and ammonia rises on a fat diet and falls on the addition of carbohydrate. The output of uric acid is low on the fat diet and increases on the addition of carbohydrate whilst the output of total creatinine is but little affected by the change of diet. Small amounts of creatine are excreted on a carbohydrate-free diet. The output of undetermined nitrogen is greater on diets containing carbohydrate than those from which carbohydrate is absent.

S. S. Z.

Constancy of the Creatine-Creatinine Excretion in Children on a High Protein Diet. VICTOR JOHN HARDING and OLIVER HENRY GAEBLER (*J. Biol. Chem.*, 1922, **54**, 579—587).—The same amount of total creatine (creatine+creatinine) is excreted by normal children of the same age when under the same environment. The amount excreted per kg. of body weight ("total creatine coefficient") is constant for children of all ages and is of the same magnitude as the creatinine coefficient of an adult man. E. S.

Elimination of Cholesterol in Urine. WILHELM GRUNKE (*Biochem. Z.*, 1922, **132**, 543—555).—Cholesterol occurs in normal urine only in traces. In one case of icterus out of nine, 10.1 mg. per day was found, and in one case of diabetes out of five, 12.9 mg.; in other cases there was no more than a normal amount.

W. O. K.

Comparative Toxicity of Ammonium Salts. FRANK P. UNDERHILL and ROBERT KAPSINOW (*J. Biol. Chem.*, 1922, **54**, 451—457).—From experiments on rats it is concluded that, in general, the toxicity of ammonium salts is directly proportional to their content of ammonia. E. S.

Pharmacological Analogues of *ac*-2-Aminotetrahydronaphthalene. JULIUS VON BRAUN, HEINRICH GRUBER, and GEORG KIRSCHBAUM (*Ber.*, 1922, **55**, [B], 3664—3674).—See this vol., i, 107.

Chemistry of Vegetable Physiology and Agriculture.

Some Microbiological Consequences of the Oxidising Properties of Thorium-X. P. LEMAY and L. JALOUSTRE (*Compt. rend.*, 1922, **175**, 1053—1054; cf. A., 1922, ii, 13, 186).—In order to ascertain whether radioactive elements function as oxidation catalysts with regard to the activities of micro-organisms, cultures of anaërobic and aërobic organisms were submitted to the action of thorium-X. In the case of the anaërobic species (*Bacillus butyricus*) the radioactive material exercised an inhibiting effect on development, the number of bacteria being about one-twentieth and the gas evolved about one-third of that in the control experiment, whilst the action of the catalyst on the aërobic species (*B. lacticus*) appeared to be of a favourable nature. H. J. E.

Influence of the Culture Conditions on the Liquefaction of Gelatin and on the Production of Indole by Bacteria. OTTO ARNBECK (*Biochem. Z.*, 1922, **132**, 457—479).—The production of indole and the liquefaction of gelatin by bacteria are inhibited by nitrogen-free foodstuffs such as glucose. Free ammonia, on the other hand, assists the liquefaction. W. O. K.

Ultra-violet Absorption Spectra of some Vitaminic Extracts. HORACIO DAMIANOVICH (*Anal. Asoc. Quím. Argentina*, 1922, **10**, 209—214).—Yeast extracts containing vitamin-B show characteristic absorption spectra in the ultra-violet with general absorption in the extreme portion of the spectrum, and a band between 2478 and 2660 Å. which appears to be due to a pyrimidine or purine group. The absorption spectra of the oils from white and yellow maize, respectively, were also studied and a difference observed corresponding with the presence of vitamin-A in yellow maize oil and its absence from white maize oil. It is uncertain whether there is a causal connexion between presence of pigment and presence of vitamin-A in the yellow maize oil. Photospectrographs of the liquids examined are appended. G. W. R.

Synthesis of Water-soluble [Vitamin]-B by Yeast Grown in Solutions of Purified Nutrients. MARGARET B. MACDONALD (*J. Biol. Chem.*, 1922, **54**, 243—248).—Using five different varieties of yeast, the author confirms the conclusion of Nelson, Fulmer, and Cessna (A., 1921, i, 386) that this organism is able to synthesise vitamin-B. E. S.

Vitamin-D. TREVOR BRABY HEATON (*Biochem. J.*, 1922, **16**, 800—808).—The activating substance of minimal concentrations of yeast (called by Wildiers "bios" and by Funk vitamin-D) is not identical with vitamin-B. Organs of pigeons rendered polyneuritic contain it in the same amount as those of normal pigeons. Its distribution differs from that of antineuric vitamin. Rats subsisting on a diet deficient in the water-soluble vitamin incur also the deficiency of this activating substance. S. S. Z.

Influence of Amines on Fermentation. JULIUS ORIENT (*Biochem. Z.*, 1922, **132**, 352—361).—The various amines used show in general a retarding effect on fermentation by yeast when applied in a concentration of 4.8%. This effect, however, changes into one of acceleration if the concentration of the amine be either higher or lower, except in the cases of methylamine and betaine which inhibit the fermentation even in low concentrations.

W. O. K.

Fermentation of Sugar in Presence of Sodium Sulphite following Neuberg and Reinfurth. Equivalence between Aldehyde and Glycerol. HEINRICH GEHLE (*Biochem. Z.*, 1922, **132**, 566—588).—In the fermentation of sucrose by yeast in the presence of sodium sulphite there is in general rather more than one equivalent of glycerol formed for one equivalent of acetaldehyde. This is particularly the case with small amounts of sulphite, and a short fermentation time. As increased proportions of sulphite are used, the rate of increase in the yields of glycerol and of acetaldehyde gradually decreases until the maximum yield is obtained using 60% of sulphite calculated on the sugar. With increasing percentage of sulphite, the rate of evolution of carbon dioxide is decreased.

W. O. K.

Equivalence in the Production of Acetaldehyde and Glycerol in the Second Form of Fermentation. C. NEUBERG, J. HIRSCH, and E. REINFURTH (*Biochem. Z.*, 1922, **132**, 589—596).—Gehle's results (preceding abstract) are vitiated by a systematic error in the estimation of the acetaldehyde. If this be estimated gravimetrically by the "dimedon" method (A., 1920, i, 914), precise equivalence between glycerol and acetaldehyde is found.

W. O. K.

The Chemistry of Fermentative Phenomena. CARL NEUBERG (*Ber.*, 1922, **55**, [B], 3624—3658).—A lecture delivered at the centenary of the *Versammlung Deutscher Naturforscher und Aerzte*.

H. W.

The Presence of Urease and Urea in Fungi. A. GORIS and P. COSTY (*Compt. rend.*, 1922, **175**, 998—999; cf. A., 1922, i, 1220).—The distribution of urease in the pileus, stipe, and hymenium of twelve species of fungi was investigated. In all cases the hymenium contains the greatest proportion of the ferment. A brief account of the method of extraction and estimation of the urease is given.

H. J. E.

The Action of the Nitrogen of Hexamethylenetetramine on Plant Growth. E. BLANCH, W. GEILMANN, and F. GIESECKE (*J. Landw.*, 1922, **70**, 221—251).—Pot experiments are described, which show that hexamethylenetetramine is as effective a fertiliser as ammonium sulphate. The soil bacteria decompose the substance into ammonia, which is nitrified in the usual way. The presence of hexamethylenetetramine in liquid farmyard manure, preserved by the addition of formaldehyde, brings no unfavourable consequences.

A. G. P.

The Effect of the Kations of Salts on the Destruction and Synthesis of Starch in Plants. W. S. ILJIN (*Biochem. Z.*, 1922, **132**, 494—510).—The rate of disappearance of starch from plant cells immersed in a solution of a salt is influenced by the kation of the salt. Univalent kations and also barium and glucinum effect the solution of the starch and at the same time cause an increase of the osmotic pressure in the cell, whilst magnesium, calcium, and strontium are inactive. If, on the other hand, the cells be immersed in a solution of maltose the synthesis of starch is inhibited by the presence of barium, cæsium, lithium, sodium, calcium, potassium, rubidium, magnesium, and strontium in order of decreasing activity. W. O. K.

Synthesis and Hydrolysis of Starch under the Influence of Anions in Plants. W. S. ILJIN (*Biochem. Z.*, 1922, **132**, 511—525; cf. preceding abstract).—Similar results are obtained with anions, the organic anions being particularly active in raising the osmotic pressure and influencing the synthesis and hydrolysis of starch. W. O. K.

Physiological Protection in Plants against the Harmful Action of Salts. W. S. ILJIN (*Biochem. Z.*, 1922, **132**, 526—542; cf. preceding abstracts).—The salt effects described in the preceding two abstracts would be harmful to plants, but it appears that certain ions act antagonistically to each other. Calcium, for instance, may inhibit the effect of sodium. In this way, the existence of halophytes may be understood. W. O. K.

Pigments of the Mendelian Colour Types in Maize: iso-Quercitrin from Brown-husked Maize. CHARLES E. SANDO and H. H. BARTLETT (*J. Biol. Chem.*, 1922, **54**, 629—645).—*iso*Quercitrin has been isolated from the husks of a brown-husked maize. It forms primrose-yellow, needle-like plates, m. p. 220—222.5°, and is probably identical with the ragweed glucoside obtained by Heyl (A., 1919, i, 615). Aqueous solutions of *iso*-quercitrin give an olive-green coloration with ferric chloride, a yellow precipitate with lead acetate, and a rose-red colour on reduction with magnesium and hydrochloric acid. The yellow colour of the substance is intensified by sodium carbonate and dilute ammonia. The spectral transmission curves of both *iso*-quercitrin and quercetin have been determined. E. S.

Biological Adsorption from Solutions of Metallic Salts. FRIEDRICH PICHLER and ARTUR WÖBER (*Biochem. Z.*, 1922, **132**, 420—438).—An investigation of the adsorption particularly of copper and also of mercury and cerium from solutions of their salts, by the spores of maize rust (?) (Maisbrandsporen). In general there is a connexion between the degree of adsorption and the toxicity of the ion. W. O. K.

Organic Chemistry.

New System for the Linear Representation of the Structure of all Organic Compounds. T. SHERLOCK WHEELER (*Chem. News*, 1923, 126, 33—35, 49—50, 66—67).—A system designed to enable the structure of all organic compounds to be represented linearly by a simple arrangement of letters and figures, from which, with the aid of a few rules, the graphical formula could be deduced easily. The original must be consulted, as the paper does not lend itself to abstraction.

The Solubility of Methane in Water and Organic Solvents under Pressure. F. FISCHER and C. ZERBE (*Brennstoff-Chem.*, 1922, iv, 17—19).—The solubility of mine gases of the composition methane 79·4%, carbon dioxide 0·7%, oxygen 2·8%, and nitrogen 17·1% in a large number of solvents under a pressure of about 20 atm., and also the composition of the gases evolved from the solvent were determined. The latter in most cases differed little from that of the original mixture, so that the figures obtained may be taken as approximately true for pure methane. The figure for the solubility in water (0·09 c.c. per g. for 1 atm.) is, however, too high owing to the higher solubility of carbon dioxide. The highest figure obtained is 1·34 for light petroleum (b. p. below 65°). Others include: for ethyl alcohol 0·60, for chloroform 0·32, for aniline 0·16. If the product of these solubility figures and the surface tension of the solvent are calculated, a series of figures which approximate to a constant is obtained as previously shown by Christoff for carbon monoxide. Water, nitrobenzene, aniline, and chloroform are exceptions. Both surface tension and solubility, however, decrease with a rise in temperature, and it is questionable whether a fair comparison is obtained at a uniform temperature (20°) between liquids of widely differing b. p. C. I.

The Constituents of the Fraction of a Borneo Petroleum which Distills between 37° and 81°. G. CHAVANNE (*Bull. Soc. chim. Belg.*, 1922, 31, 331—364).—An examination of the petrol showed that all the possible isomerides of hexane are present, as are all the hydrocarbons derived from cyclopentane and cyclohexane the boiling points of which are included in the fraction investigated. With the exception of ethylcyclobutane, all the cyclic compounds present are derived from five- or six-membered rings. Of the hexanes present, normal hexane is the most abundant, followed by isohexane and γ -methylpentane, whilst $\beta\beta$ -dimethylbutane and $\beta\gamma$ -dimethylbutane are present in much smaller proportion. The saturated cyclic hydrocarbons present in quantity are cyclohexane and methylcyclopentane. A number of physical constants are given which differ slightly, if at all, from those in the literature, and the author states that the critical

temperature of solution in aniline (cf. Chavanne and Simon, A., 1919, ii, 267, 432, 433) and the density are important factors in the experimental study of complex mixtures of hydrocarbons (cf. Chavanne and Simon, A., 1919, i, 380). H. J. E.

The Mechanism of Thermal Decomposition of the Pentanes G. CALINGAERT (*J. Amer. Chem. Soc.*, 1923, 45, 130—135).—When pentane vapour is passed through a tube at 600°, it is decomposed, giving hydrogen and a mixture of hydrocarbons. Under the experimental conditions, about 30% of the pentane is decomposed and 44% of the product consists of unsaturated hydrocarbons. The product contains hydrogen 5%, methane 12%, ethane 26%, propane 10%, pentane 4%, ethylene 10%, propylene 24%, butylene 3%, and 6% of a C_4H_6 hydrocarbon. These results correspond with a rupture of the pentane molecule at the central carbon atom, giving an ethyl and a propyl group, one of which is then saturated at the expense of the other, which becomes unsaturated, the change going mainly in the direction of forming ethane and propylene. Under similar conditions, isopentane is also decomposed and an analysis of the products shows that in this case the molecule breaks on one side or the other of the tertiary carbon atom. This results in a methyl and an isobutyl group which give methane and Δ^{α} - or Δ^{β} -butylene. A second reaction gives an ethyl and an isopropyl group and ethane results, but never propane. There is also another reaction which occurs to a small extent and results in the formation of amylenes, and, finally, a part of the amylenes and butylenes give, by a secondary reaction, butadiene and pentadiene. W. G.

Constitution of Squalene. RIKO MAJIMA and BENNOSUKÉ KUBOTA (*Japan. J. Chem.*, 1922, i, 19—33).—An English translation of the paper previously published in Japanese (this vol., i, 1). K. K.

Preparation of Methyl Bromide. ARTUR BYGDÉN (*J. pr. Chem.*, 1922, [ii], 104, 285—288).—Steinkopf and Schwen (A., 1921, i, 841) have obtained a 77% yield of methyl bromide, calculated on the bromine taken, if the reagents are employed in the ratio of 1 atom Br+0.5 atom P+2.5 mol. MeOH. It is now shown (cf. A., 1911, i, 43; also Holt, T., 1916, 109, 1) that a 97.3% yield may be obtained by using the following molecular proportions: $1KBr:3H_2SO_4:2MeOH$, the acid being diluted with one-third its weight of water previously to the addition of the other reagents. The most economical preparation, considering the cost of all the materials, is, however, effected by the use of $1KBr:3H_2SO_4:1.25MeOH$, the yield being then 95.9%. W. S. N.

The Spontaneous Decomposition of Unsaturated Aliphatic Iodochlorides. LLOYD B. HOWELL (*J. Amer. Chem. Soc.*, 1923, 45, 182—187; cf. Noyes, A., 1920, i, 469).—When β -chloroethylene iodochloride decomposes spontaneously the products are iodine

monochloride, trichloroiodoethane, $\alpha\alpha\beta\beta$ -tetrachloroethane, and a dichloroiodoethane, and of these the first two are formed in much larger amounts than the last two. Under similar conditions, $\alpha\beta$ -dichloro- β -iodoethylene iodochloride gives no saturated compound except hexachloroethane. The principal products in this case are iodine monochloride and dichlorodi-iodoethylene, together with some α -chloro- $\alpha\beta\beta$ -tri-iodoethylene and some trichloroiodoethylene. The changes consist in several rearrangements involving the splitting off of chlorine and iodine monochloride from the iodochloride group, the addition of one molecule of iodine monochloride or of chlorine to the unsaturated residues, and the replacement of iodine by chlorine or vice versa. If the carbon atoms of the double union in an unsaturated aliphatic α -iodochloride hold hydrogen atoms, the products of its decomposition are saturated halogen derivatives; but if they hold only halogen atoms, the decomposition leads to unsaturated products. Compounds described are: $\alpha\alpha\beta$ -trichloro- α -iodoethane, b. p. $101-102^\circ/31-32$ mm., d_{25}^{25} 2.266, n_D^{25} 1.5884; (?) $\alpha\alpha$ -dichloro- β -iodoethane, b. p. $146-148^\circ/28$ mm., d_{25}^{25} 2.861; $\alpha\beta$ -dichloro- $\alpha\beta$ -di-iodoethylene, b. p. 243.4° , m. p. $2.5-3.0^\circ$, d_{30}^{30} 2.934; and α -chloro- $\alpha\beta\beta$ -tri-iodoethylene. W. G.

Synthesis by Means of Magnesium Allyl Halides. SAMUEL COFFEY (*Rec. trav. chim.*, 1922, **41**, 652-654).—A repetition of Jaworsky's preparation of allyldimethylcarbinol (A., 1909, i, 151) showed that dimethylallylcarbonyl allyl ether, $C_3H_5 \cdot CMe_2 \cdot O \cdot C_3H_5$, is obtained as a by-product, the yield being about 20%, calculated on the basis of the allyl chloride used. It is a pale yellow, mobile oil, b. p. $190-193^\circ$, d_{17}^{17} 0.8765, d_4^{17} 0.8754, n_D^{17} 1.4750. Dimethylallylcarbinol has m. p. -73° , d_{17}^{17} 0.83553, d_4^{17} 0.83452, n_D^{17} 1.430. The acetate, obtained in 40% yield by modifying Houben's method (A., 1906, i, 520), has m. p. -94.5° , b. p. $46-48^\circ/21$ mm., or $136-138^\circ$ /atmospheric pressure (decomp.), d_{15}^{15} 0.88797, d_4^{15} 0.88720, n_D^{15} 1.4230. Neither of these substances reacted with solutions of perbenzoic acid. H. J. E.

The Oxidation of Propylene Glycol with Potassium Permanganate. WILLIAM LLOYD EVANS (*J. Amer. Chem. Soc.*, 1923, **45**, 171-176; cf. A., 1912, i, 743).—A study of the oxidation of propylene glycol by potassium permanganate at 50° and 75° in the presence of various concentrations of alkali. In neutral solutions, the products are acetic acid and carbon dioxide, but above certain minimum concentrations of alkali, oxalic acid is also an oxidation product. Rise in temperature causes an increase in the production of carbon dioxide and a decrease in the acetic acid. Lactic and pyruvic acids are probably two of the intermediate products, the lactic acid arising either from the oxidation of lactaldehyde or from the rearrangement of pyruvaldehyde in the presence of alkalis. The acetic acid is probably obtained either from the oxidation of acetaldehyde, present as a dissociation product, or from the oxidation of pyruvic acid. The oxalic acid is probably formed (a) by the oxidation of glycollic acid obtained

by the oxidation of vinyl alcohol, or (b) by the oxidation of glyoxylic acid, formed from pyruvic acid. Carbon dioxide may arise from the oxidation of formaldehyde, pyruvic acid, or glyoxylic acid. The alkali functions (a) by neutralising the acids formed, (b) by increasing the enolisation of acetaldehyde and pyruvic acid, (c) by causing the rearrangement of pyruvaldehyde to lactic acid. As the concentration of the alkali increases, the dissociation of the three-carbon atom compounds into two other compounds is suppressed in that direction, owing to the increased activity of the alcohol groups in propylene glycol, due to the lower point of dissociation of the alkyl oxides formed in comparison with that of the alcohol itself.

W. G.

The Formation of Geometrical Isomerides by the Reduction of Acetylene Derivatives. JUL. SALKIND (*Ber.*, 1923, 56, [B], 187—192).—It has been shown previously (A., 1907, i, 22) that $\beta\epsilon$ -dihydroxy- $\beta\epsilon$ -dimethyl- $\Delta\gamma$ -hexinene, $\text{OH}\cdot\text{CMe}_2\cdot\text{C}:\text{C}\cdot\text{CMe}_2\cdot\text{OH}$, smoothly adds two atomic proportions of hydrogen in the presence of colloidal palladium and passes thereby into $\beta\epsilon$ -dihydroxy- $\beta\epsilon$ -dimethyl- $\Delta\gamma$ -hexene, $\text{OH}\cdot\text{CMe}_2\cdot\text{CH}:\text{CH}\cdot\text{CMe}_2\cdot\text{OH}$, slender needles, m. p. $76\cdot5$ — 77° (α -form). It has now been found possible to isolate the isomeric β -form, monoclinic prisms, m. p. 69 — $69\cdot5^\circ$, the relationship of which to the α -variety is established by the observation that either compound is smoothly hydrogenated in the presence of spongy platinum to tetramethylbutanediol. The α - and β -forms are soluble to the extent of $0\cdot55$ and $5\cdot14$ parts in 100 parts of light petroleum (d $0\cdot64$ — $0\cdot66$) at 16° . Either variety is transformed by bromine in the presence of carbon tetrachloride, carbon disulphide, or anhydrous ether into a mixture of the solid dibromide, $\text{C}_8\text{H}_{16}\text{O}_2\text{Br}_2$, long, thin prisms, m. p. $98\cdot5$ — 99° , and a liquid dibromide which could not be completely purified (the relative proportions of the solid and liquid products differ according to the isomeride used).

The author has endeavoured to elucidate the configuration of the glycols by a study of their conversion into the γ -oxide, $\begin{smallmatrix} \text{CH}\cdot\text{CMe}_2 \\ | \\ \text{CH}\cdot\text{CMe}_2 \end{smallmatrix} > \text{O}$ (a liquid, b. p. 102 — $102\cdot5^\circ/755$ mm., d_4^{20} $0\cdot8226$, $d_4^{17\cdot5}$ $0\cdot8093$, $n_D^{17\cdot5}$ $1\cdot40926$), which should be obtainable solely from the maleinoid form. Under the action of boiling sulphuric acid (15%), of potassium hydrogen sulphate at 160° , or of a trace of iodine, the oxide is, however, produced in good yield from either glycol, so that interconversion appears to take place under these conditions. Since, however, it is found that the α -isomeride loses water much more readily than the β -form when heated under similar conditions with a little iodine, it is considered to be maleinoid in structure, whereas the fumaroid configuration is assigned to the β -form.

The relative proportion of the α - and β -glycols obtained by hydrogenation of the acetylenic compound appears to depend on the rapidity of the action; the production of the α -variety is favoured by the rapidity of the change.

H. W.

The Cyclic Condensation Products of Acetone with 1 : 3-Diols. J. BÖESEKEN [with G. SCHAEFER and P. HERMANS] (*Rec. trav. chim.*, 1922, 41, 722—723; cf. Böeseken and van Loon, A., 1920, i, 837; Mannich and Brose, A., 1922, i, 1118).—Two condensation products of erythritol with acetone were prepared. *Acetone-erythritol* [*erythritol isopropylidene ether*] has m. p. 135° and is only slightly soluble in benzene. *Diacetone-erythritol* [*erythritol diisopropylidene diether*], m. p. 116°, is soluble in benzene. The solubility difference affords a means of separating the substances from each other. H. J. E.

A New Preparation of Monochloroacetic Acid. L. J. SIMON and G. CHAVANNE (*Compt. rend.*, 1923, 176, 309—311).—Monochloroacetic acid may readily be prepared with a yield of 90% by heating trichloroethylene with 90—93% sulphuric acid at 160—180°. The concentration of the acid and the temperature are regulated so as to give the best yield and the greatest reaction velocity. Part of the chloroacetic acid passes over with the hydrochloric acid and unchanged trichloroethylene and a certain amount remains dissolved in the sulphuric acid. The latter may be recovered by distillation under reduced pressure or by diluting the acid and extracting it with ether. Its presence dissolved in the sulphuric acid does not prevent the further use of the acid as a hydrating agent after the addition of the necessary amount of water to replace that used in the first hydration. W. G.

Hydroxystearic Acid and some of its Derivatives. L. GUY RADCLIFFE and W. GIBSON (*J. Soc. Dyers and Col.*, 1923, 39, 4—10).—*i*-Hydroxystearic acid prepared by the action of sulphuric acid on oleic acid (*ibid.*, 1920, 36, 65) and purified by repeated crystallisation from alcohol, melted sharply at 85°. The acid was further characterised by the preparation of the following derivatives: *Methyl hydroxystearate*, small, white flakes, m. p. 46°; *ethyl hydroxystearate*, white flakes, m. p. 48·5°; *acetoxystearic acid*, a white powder, m. p. 31—32°; and *ethyl benzoxystearate*, a yellow oil. As an attempt to introduce the NO_3 group into the stearic acid molecule, α -bromostearic acid was prepared by Volhard's method. It is a white substance, m. p. 58°, and gives with silver nitrate, in alcoholic solution, a product free from nitrogen which seemed to be a mixture of α -hydroxy- and α -ethoxy-stearic acids. By the direct action of fuming nitric acid in acetic acid solution on the original *i*-hydroxystearic acid, three substances were obtained, a greenish-yellow, crystalline compound, m. p. 83—83·5°, a yellow oil, and a white solid, m. p. 100—120°. Only the first of these was further investigated. It was free from nitrogen, and had a molecular formula approximating to $\text{C}_{18}\text{H}_{34}\text{O}_4$. No confirmation of this could, however, be obtained by a molecular-weight determination. Titration with alcoholic potassium hydroxide in the cold and the analysis of the silver salt gave values of 291—293, but on warming with the alkali a further half molecule was neutralised, suggesting a lactonic structure. Still no confirmation

of this was forthcoming, neither was it in accord with the number of oxygen atoms found by the combustion. G. F. M.

$\alpha\beta$ -Dihydroxynonoic Acid. WALTER KROHS (*Ber. Deut. pharm. Ges.*, 1922, 32, 336—338; cf. Thoms and Deckert, A., 1921, i, 219; Reinger, A., 1922, i, 623).— $\alpha\beta$ -Dihydroxynonoic acid, $\text{CH}_2\text{Me}\cdot[\text{CH}_2]_4\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$, was obtained by the action of 2% potassium permanganate on the corresponding nonenoic acid (Harding and Weizmann, T., 1910, 97, 299) and has m. p. 123° (sinters at 119°). Dehydrating agents, such as 60% sulphuric acid, do not convert it into an unsaturated substance, and with 60% sulphuric acid and 40% acetic acid a *monoacetyl* compound is formed. It is considered that the stability of the hydroxyl group to dehydrating agents is due to the proximity of the carboxyl group. The acid was resolved into its optical antipodes by means of cinchonine. The *l*-acid has $[\alpha]_D^{25} -17.44^\circ$; the *dextro*-acid was not obtained quite pure. On further oxidation the acid easily decomposes, but a well characterised *dinitrate*,

$\text{CH}_2\text{Me}\cdot[\text{CH}_2]_4\cdot\text{CH}(\text{O}\cdot\text{NO}_2)\cdot\text{CH}(\text{O}\cdot\text{NO}_2)\cdot\text{CO}_2\text{H}$, and $\alpha\beta$ -diketononoic acid, $\text{CH}_2\text{Me}\cdot[\text{CH}_2]_4\cdot\text{CO}\cdot\text{CO}\cdot\text{CO}_2\text{H}$, were obtained. The latter has m. p. 95—96°, and its *dihydrazone*, and *disemicarbazide*, m. p. 160°, were prepared. P. M.

Crystalline Structure and Properties of Tartaric Acid. W. T. ASTBURY (*Proc. Roy. Soc.*, 1923, [A], 102, 506—528).—By X-ray analysis, employing a Coolidge bulb with molybdenum anticathode, the unit cell in the crystal structure of active tartaric acid has been shown to be monoclinic, to contain two molecules, and to have the following dimensions: $a = 7.693 \text{ \AA}$, $b = 6.037 \text{ \AA}$, and $c = 6.195 \text{ \AA}$. Molecules at the corners of the cell point in one direction, whilst those lying along the central line of the cell parallel to the a axis point in a diametrically opposite direction. Intensity measurements of the reflections from various planes in the crystal enable the manner in which the unit cell is incorporated in the crystal structure to be ascertained, and hence the structure itself to be determined. This shows only one plane of perfect cleavage, viz., the plane about which lie the junctions of the hydroxyl groups, i.e., the plane (100). The junctions in the —OH— linkings are of a different type from the junctions between the hydrogens of the hydroxyl groups. In the main, the ascertained crystal structure is in accordance with known chemical and physical facts. The theory of stereoisomerism of Le Bel and van't Hoff is in its essentials confirmed, and the link between crystallographic enantiomorphs and the chemical stereoisomerides revealed. The rotatory properties of the acid are discussed with reference to the symmetry of the crystal and the spiral arrangement within the molecule, and it is shown that the assumption by Lowry of the existence of dynamic isomerides within the structure to explain these properties is unnecessary, the crystal structure itself affording a simple explanation of all the facts. Thus the fundamental crystal cell is constructed of molecules exhibiting

two spiral arrangements, one associated with the four carbon atoms forming the nucleus of each molecule, and one, oppositely directed, associated with the four hydroxyl groups. In these spiral formations are located the two opposing rotatory systems adequate to explain the anomalous rotatory properties of the acid and some of its derivatives. Most probably the dextro-rotatory property of ordinary tartaric acid is associated with the carbon nucleus of the molecule. It is shown to be impossible by the diffraction of X-rays to discriminate between the dextro- and lævo-forms of an optically active substance. J. S. G. T.

Some Complex Organic Compounds of Bismuth. E. MOLES and R. PORTILLO (*Anal. Fis. Quím.*, 1922, **20**, 571—576).—Preliminary data are given on the preparation and properties of bismuthotartaric acid, bismutholactic acid, and bismuthocitric acid. G. W. R.

A Synthesis of Derivatives of Muconic Acid. ERICH BENARY and RUDOLF SCHINKOPF (*Ber.*, 1923, **56**, [B], 354—362).—The synthesis depends on the action of $\alpha\beta$ -dichloroethyl ether, $\text{CH}_2\text{Cl}\cdot\text{CHCl}\cdot\text{OEt}$, on ethyl sodiomalonate.

$\alpha\beta$ -Dichloroethyl ether is added gradually to a suspension of ethyl sodiomalonate in boiling ether; after removal of a fraction containing chloroacetaldehyde, chloroacetal, unchanged dichloroethyl ether, and malonic ester, *ethyl* Δ^a -butene- $\alpha\alpha\delta\delta$ -tetracarboxylate, $\text{C}(\text{CO}_2\text{Et})_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{Et})_2$, is isolated as a colourless, viscous liquid, b. p. 223—225°/13 mm. (some decomp.). It is reduced by zinc dust and boiling glacial acetic acid to ethyl butane- $\alpha\alpha\delta\delta$ -tetracarboxylate (cf. Perkin, T., 1894, **65**, 579). It is converted by cold saturated alcoholic ammonia at the atmospheric temperature into the corresponding *triamide*, $\text{C}_{10}\text{H}_{15}\text{O}_5\text{N}_3$, small needles, m. p. 230° (decomp.), and by concentrated aqueous ammonia into the *tetra-amide*, $\text{C}_8\text{H}_{12}\text{O}_4\text{N}_4$, small, colourless needles, m. p. 257° (decomp.) after incipient change at 238°. Hydrolysis of the ester with alcoholic potassium hydroxide solution and subsequent addition of lead acetate leads to the production of the *salt*, $\text{C}_{16}\text{H}_{10}\text{O}_{16}\text{Pb}_3$, which seems to be derived from a tribasic acid; the *latter* is an amorphous, brittle, colourless mass. The unsaturated ester is converted by bromine in the presence of chloroform in *ethyl* $\alpha\beta\delta$ -tribromobutane- $\alpha\alpha\delta\delta$ -tetracarboxylate,

$\text{CBr}(\text{CO}_2\text{Et})_2\cdot\text{CHBr}\cdot\text{CH}_2\cdot\text{CBr}(\text{CO}_2\text{Et})_2$, hexagonal pyramids, m. p. 61—63°, which, when distilled under diminished pressure or warmed with pyridine, passes into *ethyl* Δ^{γ} -butadiene- $\alpha\alpha\delta\delta$ -tetracarboxylate, $\text{C}(\text{CO}_2\text{Et})_2\cdot\text{CH}\cdot\text{CH}\cdot\text{C}(\text{CO}_2\text{Et})_2$, colourless, matted needles, m. p. 56—57°. The latter substance is reduced by zinc dust and glacial acetic acid to ethyl butane- $\alpha\alpha\delta\delta$ -tetracarboxylate. The ester is converted by fuming hydrochloric acid into a mixture of $\beta\gamma$ -diethoxy-*n*-butane- $\alpha\alpha\delta\delta$ -tetracarboxylic acid, colourless needles, m. p. 132°, which evolve carbon dioxide at about 140°, and $\beta\gamma$ -diethoxy-*n*-butane- $\alpha\delta$ -dicarboxylic acid, crystalline scales, m. p. 19·5°, b. p. 149°/13 mm. The latter

acid is converted by bromine in the presence of chloroform into *αδ-dibromo-βγ-di(α'β'-dibromoethoxy)adipic acid*,
 $\text{CO}_2\text{H}\cdot\text{CHBr}\cdot\text{CH}(\text{O}\cdot\text{CHBr}\cdot\text{CH}_2\text{Br})\cdot\text{CH}(\text{O}\cdot\text{CHBr}\cdot\text{CH}_2\text{Br})\cdot\text{CHBr}\cdot\text{CO}_2\text{H}$,
 small, colourless needles, m. p. 77—78°.

The condensation of an excess of $\alpha\beta$ -dichloroethyl ether with an ethereal suspension of ethyl sodiomalonate at a low temperature leads to the production of *ethyl β-chloro-α-ethoxyethylmalonate*, $\text{CH}_3\text{Cl}\cdot\text{CH}(\text{OEt})\cdot\text{CH}(\text{CO}_2\text{Et})_2$, a colourless, mobile liquid, b. p. 149—152°/13 mm. H. W.

Selective Hydrogenation. THOMAS PERCY HILDITCH and CHARLES WATSON MOORE (*J. Soc. Chem. Ind.*, 1923, 42, 15—17T).—Conclusive proof of the preferential saturation of one or more double bonds in the catalytic hydrogenation of compounds containing several unsaturated linkings is furnished by a study of the hydrogenation of a number of natural oils and of the esters prepared from their fatty acids. Samples were withdrawn at intervals corresponding with a drop of 10—20 in the iodine value, and the proportion of saturated and unsaturated fatty acids and of oleic to linoleic acid was calculated from the iodine values obtained. It was found that the amount of saturated derivatives present did not increase until the amount of linoleic derivatives had fallen to 10%, or even less, of the mixture. It is clear, therefore, that linolein and linolenin are almost completely hydrogenated to olein before the unsaturated centre in olein is affected. In the case of the free acids, the strong attraction between the free carboxyl group and the metal dwarfs to some extent the relative activities of the different unsaturated systems. G. F. M.

Perilla Oil. K. H. BAUER (*Chem. Umschau*, 1923, 30, 9—11; cf. A., 1922, i, 983).—The unsaturated acids obtained by debrominating the bromides soluble in a mixture of ether and glacial acetic acid were oxidised by Hazura's method with alkaline permanganate. The resulting mixture of hydroxy-acids was extracted successively with light petroleum, ether, and water. The light petroleum extract was a viscid, yellow oil, which slowly deposited a crystalline mass and was similar to the corresponding extract of the oxidation products of the total fatty acids from perilla oil. The crystalline deposit consisted of palmitic acid, and was due to the imperfect separation of saturated and unsaturated acids given by the lead salt-benzene method. The ethereal extract consisted of a white, crystalline mass of dihydroxystearic acid, m. p. 131°, and comprised 5·7% of the debrominated acids originally oxidised. Glycerides of oleic acid are therefore present in perilla oil. The aqueous extract comprised only 1·5% of the original acids oxidised, and its nature was not determined. Very small quantities of linusic and isolinusic acids were isolated from the insoluble residue. It appears from this that the linolenic acid from perilla oil gives the same hexabromostearic acid as that from linseed oil, but on oxidation of the former with alkaline permanganate, in addition to linusic and isolinusic acids, an isomeric hexahydroxystearic acid is obtained, which is not obtained from the linolenic acid from linseed oil.

The linolenic acid obtained by the debromination of hexabromostearic acid is, however, different from that originally brominated, and only yields 14% of its weight of insoluble bromides. It therefore appears that conclusions as to the presence or absence of isomeric linolenic acids cannot be based only on the behaviour on bromination.

H. C. R.

The Equilibrium between Formaldehyde and Amino-acids in Aqueous Solution. JULIUS SVEHLA (*Ber.*, 1923, 56, [B], 331—337).—The reaction between amino-acids and formaldehyde in dilute aqueous solution has been examined, and the corresponding equilibrium constants are calculated in accordance with the equation: $C_{\text{Ald}} \times C_{\text{acid}} / C_{\text{Ald-acid}} = K$. The following values are observed: glycine, 1.73; alanine, 14.1; valine, 28.9; leucine, 36.8; aspartic acid, 25.7; glutamic acid, 30.7. Leucylglycine appears to react with two molecular proportions of formaldehyde in dilute aqueous solution.

In the cases of the simpler amino-acids, the measurements are effected by determining the freezing points of solutions of the acid and formaldehyde singly and when mixed. With the more complex acids, the results are deduced from determinations of their solubility in pure water and in formaldehyde solutions of various concentrations at 25°.

H. W.

Action of Aldehydes on Mixtures of Sulphites and Hydrogen Sulphites. J. ESTALELLA (*Anal. Fis. Quím.*, 1922, 20, 437—441).—When formaldehyde is added to a solution containing potassium sulphite and potassium hydrogen sulphite, the following reactions take place successively: (1) $\text{H}\cdot\text{CHO} + \text{KHSO}_3 = \text{OH}\cdot\text{CH}_2\cdot\text{SO}_3\text{K}$ and (2) $\text{H}\cdot\text{CHO} + \text{K}_2\text{SO}_3 + \text{H}_2\text{O} = \text{OH}\cdot\text{CH}_2\cdot\text{SO}_3\text{K} + \text{KOH}$. The gradual liberation of potassium hydroxide is demonstrated by the reddening of added phenolphthalein. A similar reaction is given by a solution of potassium sulphite alone in the presence of carbon dioxide, but the red colour with phenolphthalein is then non-persistent. It is suggested that the presence of carbon dioxide in the distillate may interfere with the estimation of volatile acid in wines.

G. W. R.

Density and the Refractive Index of Mixtures of Acetaldehyde and Water or Ethyl Alcohol. E. VAN AUBEL (*Bull. Acad. roy. Belg.*, 1921, 160—162).—Mainly a question of priority. Attention is also directed to some values for the coefficient of thermal expansion of certain mixtures of acetaldehyde and water.

E. E. T.

Syntheses by Means of Mixed Organo-zinc Derivatives: Propylglyoxal. E. E. BLAISE (*Compt. rend.*, 1922, 175, 1216—1218).—The action of oxalyl chloride on α -hydroxyisobutyric acid yields oxalylbisoxoisobutyric acid. The dichloride of this acid on treatment with zinc propyl iodide forms a mixture of the biscycloacetaloxoisobutyrate of dibutyl and of propylglyoxal. Alcoholysis of the mixture leaves the former substance unchanged, and decomposes the latter into ethyl hydroxyisobutyrate and the

h*

acetal of propylglyoxal. The action of methyl alcohol on the mixture of acetals yields the *dimethylacetal* of *propylglyoxal*, $C_3H_7 \cdot CO \cdot CH(OMe)_2$. This is a mobile, colourless liquid, b. p. 65—66°/14 mm., which forms a *disemicarbazone* crystallising from acetic acid with one molecule of the solvent, m. p. above 250°, and a *osazone*, yellow needles, m. p. 105°. On boiling with 3% sulphuric acid, hydrolysis takes place with liberation of *propylglyoxal*, a yellowish-green liquid, b. p. 36°/16 mm.; the vapour is of the same colour as the liquid. On being kept in a sealed tube, it becomes viscous and of paler colour; in air it is rapidly oxidised. It has a powerful reducing action and rapidly restores the colour of Schiff's reagent. H. J. E.

The Nomenclature of Steric Series. A. WOHL and K. FREUDENBERG (*Ber.*, 1923, 56, [B], 309—313).—In two almost simultaneous communications (Wohl, A., 1922, i, 626; Freudenberg, A., 1922, i, 623) systems of nomenclature of steric series have been proposed which differ from one another in certain details; in order to avoid confusion, the following system is advocated.

The direction of the rotation of a compound is indicated by prefixing the sign + or — to the name, thus (+)-glucose, or (+)-tartaric acid. This is the only possible system in the case of many substances, such as tannins and alkaloids, which cannot at present be brought into line with the stereochemical structure of the sugars. It is, however, open to the objection that it is not distinctive in cases in which the sign of rotation varies with the concentration (malic acid), or in which inversion occurs when the acid is converted into its salt (*e.g.*, glyceric acid).

The genetic relationship to glyceraldehyde is adopted as the determining factor in the nomenclature of hydroxy-acids and sugars. The *d*-form of the aldehyde is written as shown in the annexed formulæ I and II. All compounds containing one asymmetric carbon atom which are genetically related to glyceraldehyde and in which the hydroxyl group is to the right of or below the asymmetric carbon atom belong to the *d*-series.

In the cases of compounds with several carbon atoms, each of the latter is indicated in the same manner; the system is distinctive for the sugars themselves and their unsymmetrical derivatives. If the carbonyl group is written at the top of or to the right of the formula, the position of the steric model is established, and also the configurative formula. The order of the single carbon atoms is from below to above or from left to right, because this sequence corresponds with the relation of the sugars to glyceraldehyde; (+)-glucose is thus designated *ddld*. [This necessitates an inversion of Fischer's symbols in the cases of gulose, idose, xylose, and threose, as proposed previously by Rosanoff (*A.*, 1906, ii, 320).]

The mode of formulating symmetrical derivatives of the sugars according to this system is somewhat indefinite. Thus, sacchario

acid is lettered *dddd* if regarded as derived from glucose and *ldll* if considered as formed from gulose. In such cases, it is recommended that the relationship to the more important sugar should be expressed, or, as this is arbitrary, that merely the sign of rotation should be given, (+)-saccharic acid. H. W.

Optical Rotatory Power of Sugars in Hydrochloric Acid. LÁSZLÓ ZECHMEISTER (*Z. physikal. Chem.*, 1922, 103, 316—336).—The optical rotation and its change with time has been determined at 0° and 10° in concentrated hydrochloric acid (40.6%) solutions for various concentrations of the following sugars: dextrose, galactose, mannose, arabinose, xylose, rhamnose, and lævulose. The results show that aldo-hexoses and aldo-pentoses in cold fuming hydrochloric acid solution undergo a measurable reversible change which is evidenced by a large increase of the specific rotation to a constant end-value. The position of the end-value is determined by the concentration of the hydrochloric acid, and in highly concentrated acid exceeds the value of $[\alpha]_D$ for the α -form of the sugar in water solution. In the case of dextrose, in 46.7% hydrochloric acid the value of $[\alpha]_D^{25}$ is +202°. Lævulose shows a somewhat irregular behaviour. Possibilities for the explanation of this phenomenon are considered. J. F. S.

The Biochemical Synthesis of an α -D-Mannoside Starting from Manna. H. HÉRISSEY (*Compt. rend.*, 1922, 175, 1110—1112; cf. A., 1921, i, 628).—The action of dried and powdered lucerne seeds [as a source of α -D-mannosidase] on manna in presence of methyl alcohol results in the formation of α -methyl-D-mannoside. The manna was not present in pure condition, but as carob seed (*Ceratonia siliqua*), which contains a considerable amount of the carbohydrate. The author suggests that in such a reaction the sugar may have at the moment of formation a different structure from that which it possesses in the crystalline form, and indicates the possibility of preparing glucosides directly from starch by a suitable choice of enzymes. H. J. E.

The Constitution of the Disaccharides. VII. Sucrose. WALTER NORMAN HAWORTH and WILFRED HERBERT LINNELL (T., 1923, 123, 294—301).

The Constitution of the Disaccharides. VIII. Sucrose. WALTER NORMAN HAWORTH and JAMES GIBB MITCHELL (T., 1923, 123, 301—310).

Pentosans. III. Purity of Xylan from Straw Cellulose. EMIL HEUSER and MARIA BRADEN (*J. pr. Chem.*, 1922, [ii], 104, 259—264).—It is shown that the lignin content of crude xylan, even if it contains methylxylan, may be estimated by Zeisel's method, but the method is a rough one only, since it depends on a knowledge of the methoxyl content of lignin, in the isolation of which loss of methoxyl occurs (cf. Heuser and Wenzel, A., 1921, ii, 715). A sample of xylan prepared by the modified method of Salkowski (cf. A., 1903, i, 206) is in this way shown not to contain

lignin; the absence of methyl pentosan is demonstrated by the method of Tollens and Ellet (A., 1905, ii, 210).

By a modification of Schulze's process (*Z. physiol. Chem.*, 1892, 16, 403) xylan is prepared from bleached straw cellulose, in 19% yield, containing 93·8% of pure xylan and 0·94% of ash. Precipitation of xylan by calcium chloride solution from a nearly neutralised alkaline solution, and further purification by dialysis, gives a product containing 12·2% of ash, corresponding with a yield of 22% of ash-free xylan. Further purification by solution in sodium hydroxide solution and reprecipitation with acid reduces the ash content to 0·6%, but the yield is then only 15%. These results compare unfavourably with those obtained by the more expensive Salkowski method.
W. S. N.

Pentosans. IV. Hydrolysis of Xylan by Dilute Acids. EMIL HEUSER and LUDWIG BRUNNER (*J. pr. Chem.*, 1922, [ii], 104, 264—281).—It is shown that when xylan is hydrolysed by means of hot hydrochloric acid solution (5% or 12%) or by hot dilute sulphuric acid (12%), the xylose produced is partly converted into humin-like substances before the parallel conversion into furfuraldehyde commences; if, however, the hydrolysis is continued, the formation of furfuraldehyde is mainly accountable for the loss of xylose. The course of the hydrolysis is followed by a method already described (Heuser and Kürschner, A., 1922, i, 113).

W. S. N.

Acetyl Derivatives of Xylan. EMIL HEUSER and PAUL SCHLOSSER (*Ber.*, 1923, 56, [B], 392—395).—The presence of two free hydroxyl groups in xylan, established previously by the production of a dimethyl derivative (Heuser and Ruppel, A., 1922, i, 810) is confirmed by the isolation of a diacetate.

The treatment of xylan with boiling acetic anhydride or with acetyl chloride at the atmospheric temperature does not yield a completely acetylated product, since the acetates are to some extent hydrolysed by the acetic or hydrochloric acid produced simultaneously. This action can be limited by the addition of pyridine, and under these conditions the diacetate, a colourless powder, is obtained in 90% yield. Unlike cellulose, therefore, xylan may be acetylated in the absence of a catalyst, but the experimental conditions can be made less drastic if such an agent is present. The most suitable substance for this purpose is concentrated nitric acid; sulphuric acid is objectionable on account of its tendency to yield charred products. Dry, powdered xylan reacts with difficulty, but can be brought into a more suitable condition by allowing it to swell in water and removing the latter by treating the product successively with acetic acid and acetic anhydride.
H. W.

Cellulose Chemistry. II. The Action of Dry Hydrogen Bromide on Carbohydrates and Polysaccharides. HAROLD HIBBERT and HAROLD S. HILL (*J. Amer. Chem. Soc.*, 1923, 45, 176—182; cf. *J. Ind. Eng. Chem.*, 1921, 13, 256, 334).—The authors have repeated the work of Fenton and Gostling (T., 1898,

73, 554; 1899, 75, 423; 1901, 79, 361; 1909, 95, 1334) on the action of dry hydrogen bromide on carbohydrates and polysaccharides. Contrary to the results of these workers, a yield of 12% of ω -bromomethylfurfuraldehyde was obtained from pure dextrose, from α -methylglucoside the yield was 15%, and from cellobiose 27%. In one case, from a dry cotton cellulose, a 56% yield was obtained. The formation of ω -bromomethylfurfuraldehyde under these conditions is not, therefore, alone characteristic of ketoses and ketose derivatives, but also takes place with aldoses and related compounds. Its formation from cellulose is thus no criterion as to the presence of ketone groupings in this product (cf. Cross and Bevan, "Cellulose," 1918). W. G.

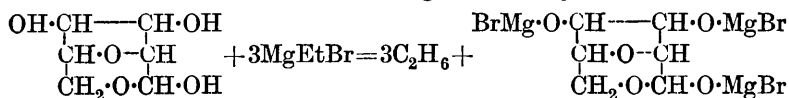
Chemical Decomposition of Cellulose by Oxidation under Pressure. FRANZ FISCHER, HANS SCHRADER, and WILHELM TREIBS (*Ges. Abh. Kennt. Kohle*, 1921, 5, 211—220; from *Chem. Zentr.*, 1922, iii, 1185).—By oxidation of cellulose in sodium carbonate solution under pressure at 200°, 42% of the material used is obtained as acids. Of these, about 11% consists of oxalic acid, and more than 50% of acetic acid. About 25% (9% of the original cellulose) consists of non-volatile acids extractable with ether: these include fumaric acid and succinic acid. Small amounts of formaldehyde are also obtained. On heating cellulose under pressure, both hydrolysis and oxidation take place. Sugars may be formed which undergo oxidation. G. W. R.

[Effect of] Heating under Pressure of Alkaline Solutions obtained from the Oxidation under Pressure of Cellulose and Lignin. FRANZ FISCHER, HANS SCHRADER, and WILHELM TREIBS (*Ges. Abh. Kennt. Kohle*, 1921, 5, 311—318; from *Chem. Zentr.*, 1922, iii, 1186).—By heating the solution of sodium salts, obtained by heating 100 g. of dry cellulose at 200° in the presence of sodium carbonate solution, at 400° under pressure, the following were obtained: gases, 6.5 litres; oils, 1.5 g.; tarry substances, 2.7 g.; volatile acids (acetic and formic acids), 0.28 equivalent; other acids, 1.2 g. (0.014 equivalent). Similarly treated, 100 g. of lignin gave: gases, 3.4 litres; oil, 1.6 g.; volatile acids, 0.17 equivalent (including benzoic acid, 0.7 g.); humic acids, 2.0 g.; isophthalic acid, 1.8 g.; acids extractable by ether, 1.1 g. G. W. R.

[Effect of] Heating Cellulose and Lignin under Pressure in the Presence of Water and Aqueous Alkalis. FRANZ FISCHER and HANS SCHRADER (*Ges. Abh. Kennt. Kohle*, 1921, 5, 332—359; from *Chem. Zentr.*, 1922, iii, 1184—1185).—Cellulose is increasingly decomposed with rising temperature when heated under pressure in the presence of water, giving compounds, including acids, soluble in water, and gaseous products, principally carbon dioxide, and some hydrogen; comparatively little solid residue remains. Decomposition takes place slowly at 200°, but more completely at 300°. Lignin also gives carbon dioxide, but the principal product is black carbonaceous material. Sulphite liquors, heated at 300°,

give insoluble substances which are precipitated as a black powder. Probably association to larger molecules takes place. Cellulose in the presence of alkalis is more resistant than lignin when heated under pressure at 200°. At 300°, strong decomposition takes place with evolution of carbon dioxide and formation of small amounts of an oil of powerful odour together with formic acid, acetic acid, and other decomposition products. Lignin, heated under pressure with aqueous alkalis, goes completely into solution at 200°, with formation of humic substances. On heating the dark brown solution at 300°, the humic acids associate and separate as dark brown or black masses. Wood, peat, bituminous coal, and anthracite heated under pressure with potassium hydroxide solution behave according to their composition. G. W. R.

MagnesyI Derivative of Cellulose. D. COSTA (*Gazzetta*, 1922, 52, ii, 362—365).—On the basis of Green's formula for cellulose, the latter, in virtue of its three hydroxyl groups, might be expected to react with three molecules of magnesium ethyl bromide :



The author finds that, at a temperature not exceeding 35°, an ethereal solution of magnesium ethyl bromide acts on cellulose, yielding ethane and a greenish-grey compound which shows the fibrous structure of the original cellulose and has the composition of a *magnesium cellulosyl bromide*, $\text{C}_6\text{H}_9\text{O}_5\cdot\text{MgBr}\cdot\text{Et}_2\text{O}$. This compound reacts with avidity with water, giving cellulose and magnesium bromohydroxide. It was not found possible to introduce more than the one bromomagnesium residue into the cellulose molecule. T. H. P.

[Cellulose Copper Compounds.] WILHELM TRAUBE (*Ber.*, 1923, 56, [B], 268—274).—Hess and Messmer's conception (*A.*, 1921, i, 401; 1922, i, 988) of the constitution of the compounds formed by the solution of cellulose in copper oxide-ammine solutions is identical in its essential features with that previously put forward by Traube (*A.*, 1922, i, 115, 718). In the author's opinion, the electrolytic observations of Hess and Messmer (*loc. cit.*) do not justify the conclusions which they have based on them and an alternative interpretation of the results is given. H. W.

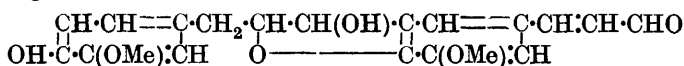
Physico-chemical Studies of Cellulose Nitrates in Organic Media. I and II. I. NEWTON KUGELMASS (*Rec. trav. chim.*, 1922, 41, 751—754, 755—763).—A study of the physical properties of solutions of cellulose nitrate (nitrogen content 11.9%) in ether and in alcohol prepared at a low temperature. Estimation of the nitrogen content of the solute in each case (11.20% and 14.02% respectively) showed that the ethereal solution apparently contains cellulose dinitrate, whilst the constituent soluble in alcohol is the trinitrate. The viscosity of the ethereal solution compared with that of the pure solvent is greater at temperatures

below -20° but identical above this point, the maximum difference observed being in the neighbourhood of -90° . Other properties of the ethereal solution are similar to those of aqueous solutions of colloids.

H. J. E.

Constitution of Pine Lignin. III. PETER KLASON (*Ber.*, 1923, 56, [B], 300—308; cf. A., 1920, i, 822; 1922, i, 324).—The preparation of β -lignosulphonic acid and of its β -naphthylamine and calcium salts is described. New analyses lead to the formula $C_{19}H_{18}O_7$ for β -lignin in place of $C_{19}H_{18}O_9$ proposed previously (A., 1920, i, 822). The calcium salt is converted by molten potassium hydroxide into protocatechuic acid.

α -Lignin is regarded as formed by the condensation of two molecules of coniferyl aldehyde in such a manner that two hydrogen atoms have undergone change in position and the annexed formula is assigned to it:



In this formula, the skeletons of guaiacol, pyrocatechol, *m*- and *p*-cresols, and methyl-, ethyl-, and *n*-propyl-cresols are present, and all these substances are present in pine tar. The formation of methyl alcohol, allyl alcohol, and 2-methylfuran is also explained.

Attempts are described to effect the synthesis of coniferyl aldehyde by the condensation of vanillin with acetaldehyde in dilute aqueous solution in the presence of sodium hydroxide. In place of the desired compound, however, its dimeric form is obtained, which, in virtue of the aldehyde group, can react with one molecular proportion of sulphite, but is distinguished from acraldehyde-lignin by its inability to combine with a second molecular proportion of sulphite as a consequence of the presence of the double bond. α -Lignin, however, after very mild treatment with calcium hydroxide, loses the ability to become converted into α -lignosulphonic acid. It is considered that the synthetic dimeric coniferyl alcohol is identical with hemi- α -lignin.

Further attempts to prepare coniferyl aldehyde by the regulated oxidation of coniferin did not lead to the desired result, the dimeric form being again obtained.

A condensation product, $C_{30}H_{27}O_5N$, from vanillin and β -naphthylamine is incidentally described.

H. W.

Chemical Decomposition of Lignin by Oxidation under Pressure. FRANZ FISCHER, HANS SCHRADER, and WILHELM TREIBS (*Ges. Abh. Kennt. Kohle*, 1921, 5, 221—229; from *Chem. Zentr.*, 1922, iii, 1185).—Lignin, prepared by treatment of wood with concentrated hydrochloric acid (Willstätter and Zechmeister), contains 60.6% of carbon, 4.5% of hydrogen, 12.6% of water, and 3.3% of ash. When shaken with 2.5*N*-sodium carbonate solution in the presence of air at 200° , a dark coloured solution is obtained, 44% of the lignin remaining undissolved, a total of 0.101 equivalent of acid being obtained of which 0.0185 is volatile in steam. Carbon

dioxide, equivalent to 8.4% carbon, 0.60% of a neutral oil, 9.6% of humic acids, and 4.2% of ether-soluble non-volatile acids are also obtained. By oxidation for forty hours, 0.55 equivalent of acids (including 0.18 equivalent volatile in steam, and 0.16 equivalent of oxalic acid), 18.9% of non-volatile acids (by extraction with ether), 0.31% of mellitic acid, and 4.2% of water soluble calcium salts were formed.

G. W. R.

[Effect of] Oxidation and Heating under Pressure of Humic Substances from Sucrose. FRANZ FISCHER, HANS SCHRADER, and WILHELM TREIBS (*Ges. Abh. Kennt. Kohle*, 1921, 5, 230—234; from *Chem. Zentr.*, 1922, iii, 1186).—Humic substances obtained by the method of Conrad and Guthzeit were submitted to oxidation under pressure at 200° for eight and three-quarter hours. 2.2 Equivalents of acid were thus formed: the solution obtained was clear and reddish-brown. After acidifying, 0.27 equivalent of volatile acid (acetic acid) was obtained by steam distillation. The residue, by extraction with ether, yielded a comparatively small amount of a viscid oil. After evaporation to dryness, the residue was heated with water at 400° for three hours. The gases formed included carbon dioxide and the vapour of a substance, most probably furan. The solid products were light coloured and slightly tarry. By steam distillation an oil of basic odour was obtained. The volatile acids included the lower fatty acids and benzoic acid. *iso*Phthalic acid and terephthalic acid were also obtained.

G. W. R.

Thermal Decomposition of Tetramethylammonium Fluoride. F. GONZÁLEZ NÚÑEZ (*Anal. Fís. Quím.*, 1922, 20, 539—549).—Tetramethylammonium fluoride is obtained in 89% yield by exact neutralisation of the hydroxide with hydrofluoric acid. When decomposed by heating in the presence of water catalysed by metals (silver, platinum, or copper) the products are nitrous oxide, methyl fluoride, trimethylamine, and methane.

G. W. R.

Mercuric Compounds with Hexamethylenetetramine. R. DOURIS and G. BEYTOUT (*Compt. rend.*, 1923, 176, 107—109).—When mercuric sulphate is dissolved in water to which is added drop by drop just sufficient sulphuric acid to prevent the formation of the basic sulphate and the solution is added to an equimolecular solution of hexamethylenetetramine the double *mercuric hexamethylenetetramine sulphate*, $C_6H_{12}N_4 \cdot SO_4 \cdot Hg \cdot H_2O$, m. p. 177° (decomp.), is obtained. The double *cyanide* decomposing at 216° and the double *acetate* decomposing at 120° are similarly prepared. In these salts the corrosive action of the ordinary mercuric salt is considerably diminished and the therapeutic action increased.

W. G.

Hexamethylaminetetramine-betaine. F. BOEDECKER and J. SEPP (*Ber. Deut. pharm. Ges.*, 1922, 32, 339—344).—The reaction between hexamethylenetetramine and chloroacetic acid is so violent that profound decomposition ensues. The hydrochloride of the

betaine is formed in good yield, however, when these substances react in chloroform solution. The well-characterised compounds of hexamethylenetetramine-betaine with metallic halides are obtained in good yield by the action of hexamethylenetetramine on aqueous solutions of salts of chloroacetic acid. The *hydrochloride of hexamethylenetetramine-betaine*, $C_6H_{12}N_4Cl \cdot CH_2 \cdot CO_2H$, obtained as indicated above in chloroform solution, forms large crystals which by treatment with moist silver oxide give the hydrated form of *hexamethylenetetramine-betaine*, $OH \cdot C_6H_{12}N_4 \cdot CH_2 \cdot CO_2H$, lustrous plates, easily soluble in water with neutral reaction and slightly sweet taste. By the action of hexamethylenetetramine on aqueous sodium chloroacetate, the *sodium salt*, $C_6H_{12}N_4Cl \cdot CH_2 \cdot CO_2Na \cdot H_2O$, was obtained. Addition of aqueous cadmium chloride to its aqueous solution causes the *double salt*, $(C_6H_{12}N_4Cl \cdot CH_2 \cdot CO_2)_2Cd, CdCl_2, 4H_2O$, to crystallise. This on treatment with hydrochloric acid gives the *acid cadmium salt*, $C_6H_{12}N_4Cl \cdot CH_2 \cdot CO_2H, CdCl_2, H_2O$. By the action of zinc chloride and mercuric chloride respectively on the solution of the sodium salt, double salts, $C_6H_{12}N_4Cl \cdot CH_2 \cdot CO_2Na, ZnCl_2, H_2O$ and $(C_6H_{12}N_4Cl \cdot CMe \cdot CO_2)_2Hg, HgCl_2$, were obtained. P. M.

The Chlorination of Esters of Amino-acids. WILHELM TRAUBE and HEINRICH GÖCKEL (*Ber.*, 1923, 56, [B], 384—391).—Ethylurethane can be smoothly converted by chlorine or hypochlorous acid in aqueous solution into *N*-chloroethylurethane, $NHCl \cdot CO_2Et$. Under similar conditions, the conversion of the esters of amino-acids into the corresponding monochlorinated derivatives does not appear to be possible, the dichloro-compounds being almost invariably produced.

Ethylurethane dissolved in water is converted by gaseous chlorine at the atmospheric temperature into *N-chloroethylurethane*, b. p. 101—102°/30 mm., the yield being 80% of that theoretically possible. It solidifies at 0°. The *potassium salt*, $C_3H_5O_2NClK, 2H_2O$, lustrous prisms which explode at 300°, the hygroscopic *sodium salt*, and the *silver salt*, a colourless powder, are described. *N-Chloro-N-methylethylurethane*, $NMeCl \cdot CO_2Et$, a colourless liquid, b. p. 57°/30 mm., is prepared by the chlorination of *N*-methylethylurethane or by the action of methyl sulphate and potassium hydroxide on chloroethylurethane. The latter is transformed by potassium hydroxide and benzoyl chloride into *N-chloro-N-benzoylethylurethane*, a pale yellow liquid which was not prepared in the homogeneous condition; its formation is established by the reduction of the product of the reaction to *N*-benzoylethylurethane, m. p. 110°. The action of ethyl chloroformate on chloroethylurethane in aqueous alkaline solution leads to the production of a mixture of *N*-dichloroethylurethane, b. p. 73°/20 mm., and ethyl iminodicarboxylate, m. p. 50°; the primarily formed ethyl chloroiminodicarboxylate appears to react with a portion of the chloroethylurethane liberated by hydrolysis of the potassium salt in accordance with the scheme: $NCl(CO_2Et)_2 + Cl \cdot NH \cdot CO_2Et \rightarrow NH(CO_2Et)_2 + NCl_2 \cdot CO_2Et$.

The action of chlorine on an aqueous solution of ethyl amino-

acetate leads to the formation of *ethyl dichloroaminoacetate*, $\text{NCl}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$, a yellow liquid. *Ethyl dibromoaminoacetate* is prepared from ethyl aminoacetate and sodium hypobromite; both dihalogenated compounds are unstable. *Ethyl α -dichloroamino-propionate*, $\text{NCl}_2 \cdot \text{CHMe} \cdot \text{CO}_2\text{Et}$, is an extremely unstable, pale yellow liquid. H. W.

Synthesis of γ -Amino- β -hydroxybutyric Acid. MASAJI TOMITA (*Z. physiol. Chem.*, 1923, **124**, 253—258).— γ -Phthalimido- β -hydroxybutyronitrile, m. p. 132° , is prepared by the action of potassium cyanide on α -chloro- γ -phthalimido- β -hydroxypropane. When hydrolysed with concentrated sulphuric acid at water-bath temperature, it yields γ -amino- β -hydroxybutyric acid, m. p. 214° , which gives a marked biuret reaction, and forms a crystalline copper salt. When heated just above its melting point, it loses water to form 4-hydroxy-2-pyrrolidone, m. p. 118° , and on exhaustive methylation the betaine is formed, isolated as its chloroaurate, $\text{C}_7\text{H}_{15}\text{O}_3\text{N}, \text{HAuCl}_4$, citron-yellow needles, m. p. 180 — 182° . It has been suggested that carnitine may be the betaine of γ -amino- β -hydroxybutyric acid, but carnitine chloroaurate melts about 30° lower than that of the betaine described above. There remains, however, the possibility that carnitine may be the optically active form. W. O. K.

A Polymeride of Hydrocyanic Acid. CH. BEDEL (*Compt. rend.*, 1923, **176**, 168—171).—When azulmin, resulting from the polymerisation of hydrocyanic acid, is extracted with ether, a yellowish-brown, crystalline substance is obtained. If this material is crystallised from aqueous solution after decolorising it with animal charcoal and the resulting mother-liquors are concentrated in the presence of charcoal, a colourless, crystalline substance is obtained. It has m. p. 179° (decomp.), and molecular-weight determinations show it to be a tetrameride of hydrogen cyanide. When decomposed by dilute mineral acids, it gives for each molecule one molecule of hydrogen cyanide. When decomposed by barium hydroxide, it gives glycine, ammonia, and a small amount of barium carbonate, but principally barium oxalate. With alcoholic potassium hydroxide and chloroform, it gives the odour of carbylamine. From its behaviour the author considers it to be a hydrocyanide of aminopropanedinitrile (cf. Wippermann, *Ber.*, 1874, **7**, 767). W. G.

The Nitriles of Fluoro- and Difluoro-acetic Acids. FRED SWARTS (*Bull. Soc. chim. Belg.*, 1922, **31**, 364—365).—These substances were prepared by distillation of the corresponding amides with phosphoric oxide. *Fluoroacetonitrile* is a colourless liquid of penetrating odour, b. p. 81.8 — 82° , d_4^{20} 1.0730. It is slightly soluble in water and reacts rapidly with potassium hydroxide. *Difluoroacetonitrile*, b. p. 22.8 — 23.4° , is a colourless, mobile liquid, d_4^{25} 1.1130, very sparingly soluble in water and reacting vigorously with potassium hydroxide. A specimen kept for several years did not undergo polymerisation. H. J. E.

The Action of Organomagnesium Compounds on Nitriles. *n*-Butyronitrile. FRANTZ BAERTS (*Bull. Soc. chim. Belg.*, 1922, 31, 421—426).—The results obtained with *n*-butyronitrile are exactly parallel to those previously obtained by the author with propionitrile (A., 1922, i, 817). The chief product of *n*-butyronitrile and magnesium ethyl bromide was ethyl propyl ketone (about 40%). Diethylpropylcarbinol was also formed together with termolecular cyanopropane, $(\text{PrCN})_3$, and a substance not previously isolated which proved to be α -butyrylbutyronitrile, a liquid, b. p. 216° , semicarbazone, m. p. 88 — 90° . P. M.

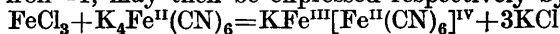
Constitution of Allyl Cyanide. P. BRUYLANTS (*Bull. Acad. roy. Belg.*, 1920, 479—486).—Pyridine and γ -chlorobutyronitrile when heated together give allyl cyanide, b. p. 114 — $116^\circ/757$ mm., d_4^{20} 0.8318, n_D^{20} 1.41438. The product is not accompanied by the nitrile of cyclopropanecarboxylic acid, which, however, is formed by the action of dry potassium hydroxide on the above chloro-compound, whilst the latter with sodium ethoxide affords a mixture of the cyclic nitrile and γ -ethoxybutyronitrile.

By the removal of the elements of water from α -hydroxybutyronitrile, a product (b. p. 115 — $116^\circ/763$ mm., n_D^{20} 1.41692) is obtained, which, from its convertibility into two known dibromo-amides is thought to be a mixture of crotononitrile and isocrotononitrile. Potassium cyanide and allyl bromide interact to give the same mixture. E. E. T.

Prussian Blue and Turnbull's Blue. V. ERICH MÜLLER [with HANS LAUTERBACH] (*J. pr. Chem.*, 1922, [ii], 104, 241—258).—The insoluble Prussian blue, precipitated by adding potassium ferrocyanide solution to ferric chloride solution in the proportion non-ionisable iron : ionisable iron = 0.75, consists of ferric ferrocyanide, which is converted by further addition of potassium ferrocyanide into potassium ferric ferrocyanide. Equimolecular proportions of potassium ferrocyanide and ferric chloride do not, however, give pure potassium ferric ferrocyanide, because the reaction $\text{Fe}_4^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]_3^{\text{IV}} + \text{K}_4\text{Fe}^{\text{II}}(\text{CN})_6 \rightleftharpoons 4\text{KFe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]_3^{\text{IV}}$ is reversible, and the further change $\text{KFe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]_3^{\text{IV}} + \text{K}_4\text{Fe}^{\text{II}}(\text{CN})_6 = \text{K}_3\text{Fe}^{\text{III}}(\text{CN})_6 + \text{K}_2\text{Fe}^{\text{II}}[\text{Fe}^{\text{II}}(\text{CN})_6]_3^{\text{IV}}$ occurs, so that the main product, $\text{KFe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]_3^{\text{IV}}$, contains traces of potassium ferrous ferrocyanide and ferric ferrocyanide in solid solution. The insoluble Turnbull's blue, formed by adding potassium ferricyanide to ferrous chloride solution in the proportion non-ionisable iron : ionisable iron = 0.75, is $\text{KFe}^{\text{II}}\text{Fe}_3^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]_3^{\text{IV}}$, which with further amounts of potassium ferricyanide passes into potassium ferric ferrocyanide :

$\text{KFe}^{\text{II}}\text{Fe}_3^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]_3^{\text{IV}} + \text{K}_3[\text{Fe}^{\text{III}}(\text{CN})_6]_3^{\text{III}} = 4\text{KFe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]_3^{\text{IV}}$. Again, the proportion non-ionisable iron : ionisable iron = 1.0 gives a solid solution, consisting mainly of $\text{KFe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]_3^{\text{IV}}$, with traces of $\text{KFe}^{\text{II}}\text{Fe}_3^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]_3^{\text{IV}}$, and also of $\text{Fe}_4^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]_3^{\text{IV}}$, formed according to the equation $\text{KFe}^{\text{II}}\text{Fe}_3^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]_3^{\text{IV}} + \text{K}_3\text{Fe}^{\text{III}}(\text{CN})_6 = \text{Fe}_4^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]_3^{\text{IV}} + \text{K}_4\text{Fe}^{\text{II}}(\text{CN})_6$. The formation of

Prussian blue and of Turnbull's blue, when non-ionisable iron : ionisable iron = 1, may then be expressed respectively by :



and



Suppose for the formation of Turnbull's blue a ferricyanide solution is used containing 1 mol. KCl per mol. FeCl_2 , so that there can be written $\text{FeCl}_2 + \text{K}_3\text{Fe}^{\text{III}}(\text{CN})_6 + \text{KCl} = \text{KFe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]^{\text{IV}} + 3\text{KCl}$, then both reactions become fully identical if the primary change is : $\text{FeCl}_2 + \text{K}_3\text{Fe}^{\text{III}}(\text{CN})_6 + \text{KCl} = \text{FeCl}_3 + \text{K}_4\text{Fe}^{\text{II}}(\text{CN})_6$. Equimolecular solutions of (a) FeCl_3 and $\text{K}_4\text{Fe}^{\text{II}}(\text{CN})_6$, (b) FeCl_2 and $\text{K}_3\text{Fe}^{\text{III}}(\text{CN})_6 + \text{KCl}$ therefore give the same end-product, the Prussian blue and Turnbull's blue formed under these conditions being identical.

These views, which agree with results already obtained analytically (cf. A., 1909, i, 142, 705, 706; 1911, i, 844; 1914, i, 504, 1058), have now been fully confirmed by following the various reactions potentiometrically; the potential of a platinum electrode immersed in one reagent is compared with that of a normal electrode ($\text{Hg}, \text{Hg}_2\text{Cl}_2, N - \text{KCl}$) after each addition of the second reagent. The results are shown graphically, the volume of the added constituent being plotted against the compensating ohmic resistance. The formation of solid solutions is deduced from the gradual slope of the relevant curves, whilst the intersection at the point "non-ionisable iron : ionisable iron = 1" of all four curves, corresponding with the pairs of reagents (1) FeCl_3 and $\text{K}_4\text{Fe}^{\text{II}}(\text{CN})_6$, (2) FeCl_2 and $\text{K}_3\text{Fe}^{\text{III}}(\text{CN})_6 + \text{KCl}$, is considered proof of the identity of the Prussian blue and the Turnbull's blue formed under these conditions.

W. S. N.

Derivatives of Semioxamazide. I. Ketonic Semioxamazones. FORSYTH JAMES WILSON and ERIC CHARLES PICKERING (T., 1923, 123, 394—397).

Oxidation of Cadets' Oil. Preparation of Cacodylic Acid. HENRI GUINOT (*J. Pharm. Chim.*, 1923, [vii], 27, 55—64).—The mixture of cacodyl and cacodyl oxide obtained by the dry distillation of potassium acetate and arsenious oxide is oxidised quantitatively to cacodylic acid by aqueous hypochlorite solutions, and the same reaction may be utilised for its estimation, the excess of hypochlorite added being determined by the addition of potassium iodide and titration of the liberated iodine with thiosulphate. For the preparation of cacodylic acid, the oil is agitated with the requisite amount of sodium hypochlorite solution in presence of hydrochloric acid, the completion of the oxidation being indicated by the disappearance of the odour of cacodyl or by the use of potassium iodide-starch paper. The acid solution thus obtained is neutralised with sodium hydroxide, using Congo-red as indicator, and is then evaporated to a small bulk, and the sodium chloride which separates is removed. The syrup is finally evaporated to dryness, and extracted with 96% alcohol. The alcoholic extract on cooling deposits pure cacodylic acid in 70% yield, and another 20% may

be obtained from the mother-liquors. Alternatively, cacodylic acid may be obtained in 80% yield by direct oxidation by means of oxygen of a solution of the oil in dry acetone to which slightly more than the amount of water theoretically required by the following equations is gradually added as the absorption of oxygen proceeds: $(\text{AsMe}_2)_2\text{O} + \text{H}_2\text{O} + \text{O}_2 = 2\text{AsMe}_2\text{O}\cdot\text{OH}$ and $2(\text{AsMe}_2)_2 + 2\text{H}_2\text{O} + 3\text{O}_2 = 4\text{AsMe}_2\text{O}\cdot\text{OH}$. The absorption of oxygen is very rapid and is with advantage moderated somewhat, otherwise a certain amount of arsenious acid will be formed. The cacodylic acid formed crystallises from the solution in an almost pure condition. The anodic oxidation of a solution of the oil in 20% sulphuric acid also gives a 70–80% yield of cacodylic acid, but this method does not present any practical advantage.

G. F. M.

Permanence of the Grignard Reagent. HENRY GILMAN and CHARLES H. MEYERS (*J. Ind. Eng. Chem.*, 1923, **15**, 61).—Observations extending over more than six months showed that the numerous Grignard reagents examined underwent no appreciable deterioration or decomposition during this period, when kept in ethereal solution (in some cases highly concentrated) and adequately protected from the moisture, carbon dioxide, and oxygen of the atmosphere by storage in glass-stoppered containers.

G. F. M.

The Optimum Condition for the Preparation of Magnesium Ethyl Iodide. HENRY GILMAN and CHARLES H. MEYERS (*J. Amer. Chem. Soc.*, 1923, **45**, 159–165).—Using the methods of analysis previously described (*ibid.*, 150) and a special reaction flask by means of which it was possible to withdraw aliquot portions for analysis, a study was made of the factors which influence the yield of magnesium ethyl iodide and, therefore, to some extent the yield of other Grignard reagents. The results indicate that there is a steady increase in the percentage of Grignard reagent formed when the rate of addition of ethyl iodide is progressively decreased, but that no advantage is gained by extending the time for the addition of 9.5 g. of ethyl iodide beyond forty-five minutes. Stirring during the addition of the ethyl iodide and for fifteen minutes after the addition is completed is desirable, and then it is not necessary to warm the mixture under a reflux condenser. Any large excess of magnesium does not affect the yield. When no precautions are taken to exclude the moisture and carbon dioxide of the air, the yield is lowered. Under a standard set of conditions the finer the grade of magnesium turnings used, the higher is the yield.

W. G.

Reducing Action of Grignard Reagents. B. A. BUYLLA and E. OLAY (*Anal. Fis. Quim.*, 1922, **20**, 599–600).—Metallic alkyl oxides react with Grignard reagents, giving hydrocarbons. For example, magnesium ethyl iodide and sodium methoxide in the presence of anhydrous xylene with ethyl ether or dimethylaniline as catalyst react as follows: $\text{MgEtI} + \text{MeONa} = \text{C}_2\text{H}_4 +$

$\text{CH}_4 + \text{MgO} + \text{NaI}$. Ethyl magnesium iodide and sodium amyl-oxide give ethylene and an unidentified liquid hydrocarbon.

G. W. R.

The Preparation of Methylmercuric Acetate and the Isolation of Methylmercuric Hydroxide. M. CANNON SNEED and J. LEWIS MAYNARD (*J. Amer. Chem. Soc.*, 1922, **44**, 2942—2947).—The substance described by Otto (*Annalen*, 1870, **154**, 199) as methylmercuric acetate, m. p. 142—143°, could not have been pure. The authors have obtained pure methylmercuric acetate by four different methods, namely, (1) the action of mercuric acetate on mercurydimethyl in methyl alcohol, (2) the neutralisation of methylmercuric hydroxide with glacial acetic acid, (3) the action of methylmercuric hydroxide on ethyl acetate, (4) the interaction of silver acetate and methylmercuric iodide. So prepared, it has, in all cases, m. p. 128°, and is very soluble in water, acetic acid, and ethyl alcohol. It is also one of the products of the thermal decomposition of mercurous acetate in an atmosphere of nitrogen.

Methylmercuric hydroxide, m. p. 95°, is readily obtained by the action of moist silver oxide on methylmercuric iodide in methyl alcohol. It is a very weak base, being alkaline to litmus but acid to phenolphthalein in aqueous solution. It is a strong vesicant even in dilute solutions.

W. G.

Ethyl Ether- and Ethanol-mercuri-salts. K. A. HOFMANN and KURT LESCHEWSKI (*Ber.*, 1923, **56**, [B], 123—129).—Hofmann and Sand have assigned the constitutions $\text{X} \cdot \text{Hg} \cdot \text{C}_2\text{H}_4 \cdot \text{OH}$ and $\text{X} \cdot \text{Hg} \cdot \text{C}_2\text{H}_4 \cdot \text{O} \cdot \text{C}_2\text{H}_4 \cdot \text{HgX}$ to the products obtained by the action of ethylene on mercury salts, whereas according to Manchot (A., 1920, **i**, 519, 720) they are to be regarded as additive products, $\text{C}_2\text{H}_4 \cdot \text{HgX} \cdot \text{OH}$, analogous to the compound obtained from cuprous chloride and carbon monoxide. The readiness with which they evolve ethylene appears to support Manchot's conception, but, on the other hand, the same tendency is observed with undoubtedly atomic compounds, such as ethylene dibromide, which yields ethylene when treated with magnesium or organomagnesium compounds and magnesium ethyl bromide, which evolves the gas when treated with manganese chloride. The mercuri-salts are somewhat sharply differentiated from Manchot's compounds of cuprous chloride with ethylene or carbon monoxide by their much greater stability towards non-acidic reagents and heat. The strongest argument in favour of the conception of the existence of an alcoholic group in ethanolmercuri-compounds lies in the observation that they evolve alcohol and aldehyde when boiled with potassium hydroxide solution and leave a residue of metallic mercury and mercuride, $\text{C}_2\text{H}_2\text{O}_4\text{Hg}_6$. The change proceeds slowly when potassium hydroxide alone is used, but can be greatly accelerated by the addition of potassium iodide; under the latter conditions, 50% of the organic portion of ethanolmercuri-chloride is obtained as alcohol and aldehyde, the production of the latter being attributable to the oxidising action of mercury oxide in the

strongly alkaline medium. The action is very difficult to explain Manchot's mode of formulation is adopted, since the persistence of portions of the mercuri-compound until the conclusion of the change shows that hydration of ethylene does not occur previously to its evolution and an alkaline suspension of mercury oxide is found to be without appreciable action on pre-formed ethylene.
H. W.

Primary Tar. I. FRANZ SCHÜTZ (*Ber.*, 1923, 56, [B], 162—169).—An examination of the tar formed by the carbonisation of coal obtained from the neighbourhood of Dortmund in rotary furnaces at 500—600°. The coal yields about 23% of volatile products (about 7% tar, 6% aqueous distillate, and 10% gas) and about 77% of semi-coke. It is found that the most volatile portions of the neutral oils contain only very small quantities of paraffins and larger amounts of unsaturated hydrocarbons. They consist mainly of aromatic and hydroaromatic hydrocarbons. The presence of benzene, toluene, and xylene is established, and that of their higher homologues is shown to be probable. The presence of considerable amounts of hydroaromatic hydrocarbons may be regarded as extremely probable. The absence of naphthalene is confirmed. Ketones, particularly acetone, are present. Phenol occurs in considerable quantity, its amount being very much greater than in coke-oven tar. Traces of acetaldehyde and acetonitrile are observed. Toly mercaptans are present in very small amount together with a sulphide, b. p. 150—160°, which appears to belong to the aliphatic series.
H. W.

Preparation of Petroleum from Rosin. SEIJI KWAI (*J. Chem. Ind. Japan*, 1922, 25, 1421—1424).—On distilling a mixture of rosin (acid value 162.1 and saponification value 178.3) and dried Japanese acid earth (ratio: 1:0.5—1:2) at 160° to 350° under ordinary pressure, an oily distillate, *d* 0.88, was produced; the yield being about 60% of the rosin used. This had an odour and a marked fluorescence similar to that of natural petroleum and is approximately composed of naphthenes, about 50%, aromatic hydrocarbons 40%, and unsaturated hydrocarbons (probably terpenes) 10%.
K. K.

Lely's Benzene Formula. S. C. J. OLIVIER (*Chem. Weekblad*, 1923, 20, 27).—A criticism of the triangular formula (this vol., i, 99). The synchronous rotation of the hydrogen atoms or substituents attached to the secondary carbon atoms is a dangerous conception; applied to the four dissimilar atoms or groups attached to an asymmetric carbon atom, it would invalidate the possibility of optical isomerism. Further, the existence of meta- and ortho-substituted benzenes is only possible if the phase of the synchronous rotation is unalterable in molecular collisions, reactions, etc. The facts with regard to substitution generally are only explained by Lely by arguments which could equally easily be employed to lead to exactly opposite conclusions.
S. I. L.

The Essentials of a Benzene Formula. H. J. PRINS (*Chem. Weekblad*, 1923, 20, 28; see preceding abstract).—Lely's formula fails entirely to explain the characteristic properties of the aromatic as contrasted with the aliphatic compounds; if benzene contained $-\text{CH}_2-$ groups, all the mono-substituted benzenes should act as if the substituent were united to a carbon atom still united to hydrogen, e.g., phenol like a secondary alcohol. Quinol would have the group $\text{C} \begin{smallmatrix} \text{OH} \\ < \\ \text{OH} \end{smallmatrix}$ and ring formation as in phthalic anhydride should occur equally readily with para-substituted derivatives, as terephthalic acid. S. I. L.

The Structural Formula for Benzene. H. A. J. SCHOUTISSEN (*Chem. Weekblad*, 1923, 20, 29; see preceding abstracts).—The four valencies of the primary carbon atoms in Lely's formula lie in one plane, and in an angle of $130^\circ 32'$, making with each other angles of $35^\circ 16'$ and 60° . The valencies of the three secondary carbon atoms lie along the edges of a tetrahedron. Such a distribution in a stable system like benzene is unthinkable.

A space-model of benzene based on the Lewis-Langmuir theory is suggested, which has the necessary symmetry and valency-distribution. In one phase it coincides with that of Pauly (A., 1919, i, 120), whilst by a rotation of each of the carbon atoms through 90° or 270° the configuration of Armstrong, Baeyer, and Claus is obtained. S. I. L.

Cymene as a By-product of the Hydrolysis of Wood. EMIL HEUSER, L. ZEH, and B. ASCHAN (*Z. angew. Chem.*, 1923, 36, 37—38).—*p*-Cymene occurs in appreciable quantities amongst the volatile products of the hydrolysis of wood with dilute mineral acids under pressure, and originates probably from the action of the acid on the α -pinene derived from the resins of the wood. It was isolated from the light oil which collects on the surface of the distillate. This was treated with sodium hydrogen sulphite to remove furfuraldehyde, and with 40% potassium hydroxide to remove volatile acids, and then fractionally distilled. The fraction boiling between 174° and 179° consisted largely of *p*-cymene which was identified by conversion into barium *p*-cymenesulphonate. The total content of *p*-cymene in the light oil was estimated at 4—5%. G. F. M.

1-Methyl-3-tert.-amylbenzene. G. CHARRIER [with M. GALLOTTI and E. ZAPPELLI] (*Gazzetta*, 1922, 52, ii, 317—323).—By the action of *tert.*-amyl chloride on toluene in presence of aluminium chloride, the author has obtained the compound prepared by Essner and Gossin (A., 1885, 517) by treating toluene in presence of aluminium chloride with either active or inactive amyl chloride or amylene. The conclusion drawn by these authors that this compound is 1-methyl-3-*tert.*-amylbenzene is confirmed, its description in Beilstein (edition III, ii, 36) as *m*-isoamyltoluene being inaccurate.

1-Methyl-3-*tert.*-amylbenzene is a colourless, mobile, refractive liquid with an odour of pine resin, d_4^{20} 0.8930, d_4^{20} 0.8673, d_4^{100} 0.8082.

When oxidised by either permanganate or dilute nitric acid, it yields isophthalic acid. The action of fuming nitric acid at -10° gives two isomeric mononitro-derivatives, which are uncrystallisable, pale yellow liquids with a pungent odour of musk: (1) b. p. $160-161^{\circ}/25$ mm., d_4^{20} 1.0675, and (2) b. p. $165-169^{\circ}/23$ mm., d_4^{20} 1.0825; the nitro-groups probably occupy the 2-, 4-, or 6-positions.

The action of chlorine on the hydrocarbon in presence of iodine yields two monochloro-derivatives, probably the 4- and 6-compounds: (1) a mobile, highly refractive liquid with a delicate odour of aniseed, b. p. $242-243^{\circ}/750.25$ mm., d_4^{20} 0.9769, and (2) a highly refractive liquid with a similar odour to the previous compound, b. p. $247-248^{\circ}/750.25$ mm., d_4^{20} 1.0111; neither isomeride solidifies at -25° .

The action of bromine on the hydrocarbon in the dark at 0° gives 4-(or 6) bromo-1-methyl-3-tert.-amylbenzene, which is a highly refractive liquid with a pleasing ethereal odour, b. p. $262-264^{\circ}/752.38$ mm., d_4^{20} 1.2143, and remains liquid at -25° . T. H. P.

The Influence of some Substituents in the Benzene Ring on the Mobility of the Chlorine in the Side-chain in its Relation to the Problem of Substitution in the Benzene Ring. II. S. C. J. OLIVIER (*Rec. trav. chim.*, 1922, **41**, 646—651; cf. A., 1922, i, 646).—A development of the work described in the previous paper. The influence of the position of the substituent is less pronounced the greater the retarding influence of that substituent on mobility. A table is given showing the values of the reaction constants calculated from the rate of saponification of various compounds, that for benzyl chloride itself being taken as unity. From this it is seen that at a higher temperature the reaction velocities generally tend to become of identical value, the smaller increasing with temperature, the greater remaining approximately constant. The retarding influence of the negative substituents is thus less pronounced at a higher temperature. The list of substituents in their order of influence as previously given (*loc. cit.*) is now amplified by addition of bromine and is $p\text{-Me} > o\text{-Me} > m\text{-Me} > \text{H} > p\text{-Cl} > p\text{-Br} > o\text{-Cl} > o\text{-Br} > m\text{-Cl} > m\text{-Br} > m\text{-NO}_2 > o\text{-NO}_2 > p\text{-NO}_2$.
H. J. E.

Some Constants of Phenylchloroform [Tri- ω -chlorotoluene]. FRED. SWARTS (*Bull. Soc. chim. Belg.*, 1922, **31**, 375—377).—A redetermination of some of the physical constants of tri- ω -chlorotoluene gave the following values: m. p. -4.75° ; b. p. $110.7^{\circ}/23$ mm.; $220.7^{\circ}/761$ mm.; d_4^{20} 1.3775. The cryoscopic constant has the notably high value 93.1. Moist air in contact with the substance causes rapid and considerable lowering of the freezing point, previous values for which are -22.5° (Haas, A., 1893, ii, 357), -17° (Altschul, A., 1895, ii, 206), and -8.1° (Timmermans, A., 1914, ii, 168).
H. J. E.

Aromatic Sulphinic Acids. E. KNOEVENAGEL and A. RÖMER (*Ber.*, 1923, **56**, [B], 215—217).—Sodium benzenesulphinic acid in the presence of ether is converted by one or less molecular proportion of phosphorus trichloride into phenyl benzenethiosulphonate,

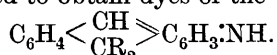
$\text{Ph}\cdot\text{SO}_2\cdot\text{SPh}$, m. p. 45° , which is reduced by an excess of the trichloride to diphenyl disulphide, m. p. 60° . Under similar conditions, thionyl chloride yields benzenesulphonyl chloride, phenyl benzenethiosulphonate, and some nitrogen sulphide. Sulphuryl chloride gives benzenesulphonyl chloride.

Salts of the type $\text{CHR}\cdot\text{NHR}'\cdot\text{SO}_2\text{Ph}$ are obtained by the action of molar amounts of benzenesulphinic acid and anils in the presence of ether at the atmospheric temperature. These are decomposed by solution in alcohol and subsequent addition of ether in accordance with the equations: $\text{CHR}\cdot\text{NHR}'\cdot\text{SO}_2\text{Ph} + \text{H}_2\text{O} = \text{R}\cdot\text{CHO} + \text{R}'\cdot\text{NH}_2 + \text{Ph}\cdot\text{SO}_2\text{H}$; $3\text{Ph}\cdot\text{SO}_2\text{H} = \text{Ph}\cdot\text{SO}_3\text{H} + \text{Ph}\cdot\text{SO}_2\cdot\text{S}\cdot\text{Ph} + \text{H}_2\text{O}$;

$\text{Ph}\cdot\text{SO}_3\text{H} + \text{Ph}\cdot\text{NH}_2 = \text{Ph}\cdot\text{NH}_2 < \begin{smallmatrix} \text{H} \\ \text{SO}_3\text{Ph} \end{smallmatrix}$. The salts derived from the following anils have the melting points placed in brackets: benzylideneaniline (82°); benzoinanil ($158-160^\circ$); acetophenoneanil (136°); dypnoneanil (130°). Acetoneanil and *N-isopropenyl-N-methylaniline* appear to react in a more complicated manner.

Ferrous and ferric benzene sulphinates are almost insoluble in water; the nickel, cobalt, copper, and cadmium salts dissolve to the extent of 10–15% in boiling water, the manganese salt to 20%, and the lead and silver salts to 40%. Aluminium and chromium salts do not give a precipitate with benzenesulphinic acid. The manganese, copper, and lead salts are soluble in dilute acetic acid; the cadmium salt dissolves in glacial acetic acid, whereas the nickel, cobalt, and iron salts require dilute mineral acids to bring them into solution. H. W.

Certain Derivatives of Anthracene. F. KEHRMANN, RAOUL MONNIER, and MARIE RAMM (*Ber.*, 1923, **56**, [B], 169–174).—Attempts are described to obtain dyes of the type



The nitration of 9:10:10-triphenyl-9:10-dihydroanthran-9-ol (Haller and Guyot, A., 1904, i, 660) could not be satisfactorily accomplished.

9-*Phenyl*-10:10-diethyl-9:10-dihydroanthran-9-ol, colourless needles, m. p. $111-112^\circ$, is prepared by the action of magnesium phenyl bromide on 10:10-diethyl-9-anthrone; it forms coloured carbonium salts with sulphuric, perchloric, and nitric acids. When dissolved in concentrated sulphuric acid it is converted by alcohol into 10-*phenyl*-9:9-diethyl-9:10-dihydroanthracene, colourless needles, m. p. $135-136^\circ$. 9:9-Diethyl-9:10-dihydroanthracene, slender, colourless needles, m. p. 210° , is obtained by the reduction of diethylanthrone with zinc dust and acetic acid.

9:10-Diphenyl-9:10-dihydroanthra-9:10-diol (Haller and Guyot, *loc. cit.*) gives an intense indigo-blue solution in concentrated sulphuric acid; it appears to be transformed thereby into anthraquinone, 9:10-diphenylanthracene, and an intensely reddish-yellow substance which has not been completely investigated. The nitration and reduction of the products will be described subsequently. H. W.

Preparation of Cyclic Amines. A. MAILHE (*Bull. Soc. chim.*, 1923, [iv], **33**, 83—86).—The direct hydrogenation of the hydrazones or ketazines of cyclic ketones over a nickel catalyst at 180° leads, as in the case of similar open-chain compounds, to the formation of primary amines accompanied by a small proportion of the corresponding secondary amines. Thus the hydrazone of 1:3-dimethyl-4-cyclohexanone is converted into 1:3-dimethyl-4-cyclohexylamine, a colourless liquid, b. p. 169—171°, d^{14}_4 0.8810, which rapidly absorbs carbon dioxide from the air and gives a hydrochloride, m. p. 278°, and a phenylcarbamide, m. p. 174°. Similarly, carvylamine is obtained together with a small quantity of dicarvylamine by the hydrogenation of carvone ketazine. Carvylamine boils at 205—210°, and forms a hydrochloride, m. p. 198°. Menthylamine obtained by the hydrogenation of menthonehydrazone, a colourless liquid, b. p. 243°, over nickel at 200°, is a strong base, b. p. 212°, giving a hydrochloride, m. p. 274°. Dimethylamine produced at the same time boils at 305—310°, and gives a hydrochloride, m. p. 207°. G. F. M.

Formation of Phenylcarbylamine and Nitrobenzene in Aqueous Aniline Solutions. HERMANN KUNZ-KRAUSE and PAUL MANICKE (*Ber. Deut. pharm. Ges.*, 1922, **32**, 232—236).—The formation of products with an odour of carbylamine when aniline and water are exposed for several months to sunlight does not take place if the aniline is pure, the products in this case being of a tarry nature and dissolving in concentrated sulphuric acid with a Bordeaux-red colour. Mono-methyl- and ethyl-anilines and toluidine behave in the same way as aniline. On the other hand, minute traces of nitrobenzene are formed even with pure aniline under the above conditions. P. M.

Action of Alcohols on Anilides. ALPHONSE MAILHE (*Bull. Soc. chim.*, 1923, [iv], **33**, 81—83).—Although the hydrogen atom of the $\text{NH}=\text{C}$ group of secondary arylamines is readily replaced by an alkyl group by the action of aliphatic alcohols in presence of dehydrating catalysts such as thoria or alumina, the aromatic amides cannot be similarly alkylated, as the water produced in the reaction causes the hydrolysis of the amides. So, for example, the catalysis of a mixture of acetanilide and methyl alcohol vapours over alumina at 370—380° results, not in the formation of methylacetanilide, but of a mixture of aniline, methylaniline, and dimethylaniline and acetic acid, together with small quantities of dimethyl ether. Other anilides and toluidides behave in a similar manner either with methyl or ethyl alcohol. With propyl alcohol, propylene and water are formed, and the anilide is hydrolysed; but no propylanilines are produced. G. F. M.

The Action of Sodammonium on Aniline and its Homologues. M. PICON (*Compt. rend.*, 1922, **175**, 1213—1216).—The action of sodammonium on cyclic amines in which the nitrogen is directly linked to the benzene ring affords a ready method of preparing the sodium derivatives of these amines. Only

monosodium derivatives were obtained; these are formed as readily with primary as with secondary amines. No reaction occurs with benzylamine. Monosodioaniline, NHPhNa , is a pale yellow, transparent solid decomposed by water with formation of aniline and sodium hydroxide and reacting with alkyl halides yielding substituted anilines (cf. Titherley, T., 1897, **71**, 464). *Sodio-ethylaniline*, NPhEtNa , is a pale yellow solid; *monosodio-o-toluidine*, $\text{C}_6\text{H}_4\text{Me}\cdot\text{NHNa}$, a pale yellow solid; *sodiodiphenylamine*, NPh_2Na , a white solid; they all show properties similar to those of monosodioaniline. The method of preparation consists in mixing the amine with sodammonium and an excess of liquid ammonia and allowing the mixture to remain in contact under pressure at the ordinary temperature for some days. Attempts to prepare disodium derivatives were unsuccessful. H. J. E.

Reaction between Aniline and Chloroacetic Acid. I. RYUZABURO NODZU and SHIGERU KOMATSU (*Mem. Coll. Sci. Kyoto*, 1922, **6**, 73—76).—Among the products of interaction of aniline (1.04 mol.) and chloroacetic acid (1 mol.) in a closed vessel at 100° were isolated and identified chloroacetanilide, diketodiphenylpiperazine, phenyliminodiacetic acid and its mono-anilide, and phenylglycine. The mono-anilide is probably formed by the interaction of phenylglycine and chloroacetanilide. E. H. R.

Optically Active Dyes. I. A. W. INGERSOLL and ROGER ADAMS (*J. Amer. Chem. Soc.*, 1922, **44**, 2930—2937).—In order to investigate the question as to whether the absorption of dyes by animal or vegetable fibres is a physical or chemical phenomenon the authors propose to prepare a number of optically active dyes and to examine the rate of absorption of the optical isomerides. With this purpose in view, they have prepared two such pairs of dyes. *d*- and *l*-aminoPhenylacetic acid have been condensed with *p*-nitrobenzoyl chloride and the products reduced to the corresponding amino-compounds, which were then diazotised and the diazo-compounds coupled with β -naphthol and dimethylaniline, respectively. Preliminary dyeing experiments have been carried out, and although the *d*- and *l*- β -naphthol dyes were absorbed in the same relative amounts over short as well as long periods, the experiments with the two dimethylaniline dyes indicated that one is absorbed more rapidly than the other. The following new compounds are described: *r-p-Nitrobenzamidophenylacetic acid*, m. p. 184° (corr.), its *ethyl* ester, m. p. 140° (corr.). *r-p-Aminobenzamidophenylacetic acid*, m. p. 152° (corr.), and its *hydrochloride*, m. p. 215° (decomp.). *l-p-Nitrobenzamidophenylacetic acid*, m. p. 163° (corr.), $[\alpha]_D^{20} - 86.56^\circ$, its *ethyl* ester, m. p. 155° (corr.), $[\alpha]_D^{20} - 67.7^\circ$. *l-p-Aminobenzamidophenylacetic acid*, m. p. 168—169° (corr.), $[\alpha]_D^{20} - 93.75^\circ$, and its *hydrochloride*, m. p. 220—222° (decomp.). *d-p-Nitrobenzamidophenylacetic acid*, m. p. 163° (corr.), $[\alpha]_D^{20} + 86.13^\circ$, its *ethyl* ester, m. p. 155° (corr.), $[\alpha]_D^{20} + 67.4^\circ$. *d-p-Aminobenzamidophenylacetic acid*, m. p. 168—169° (corr.), $[\alpha]_D^{20} + 93.63^\circ$, and its *hydrochloride*, m. p. 220° (decomp.). The

r-aminobenzoyl acid when diazotised and the product coupled with β -naphthol gave a *compound*, m. p. 252°, the *l*-acid similarly gave a *compound*, m. p. 238°, $[\alpha]_{25}^{25} - 27.25^\circ$, and the *d*-acid a *compound*, m. p. 238° (corr.), $[\alpha]_{25}^{25} + 28.50^\circ$. When diazotised and the product coupled with dimethylaniline, the *l*-acid gave a *compound*, m. p. 189—190°, and the *d*-acid a *compound*, m. p. 188—189°.

W. G.

Catalytic Preparation of *o*-Toluidine. C. O. HENKE and O. W. BROWNE (*J. Physical Chem.*, 1923, **27**, 52—64).—In continuation of previous work on the catalytic reduction of nitrobenzene to aniline (A., 1922, i, 445, 535; ii, 833), the authors have investigated the catalytic reduction of *o*-nitrotoluene to *o*-toluidine by means of hydrogen. A nickel catalyst is too active for this purpose, a large part of the *o*-nitrotoluene being reduced beyond the toluidine stage. The highest yield obtained with nickel was 86.8%. Lead catalysts gave slightly higher yields of *o*-toluidine than of aniline, the respective yields in the two cases being 94.6% and 93.4%. Silver, when first used, gave a yield of 99% of *o*-toluidine, but its activity decreased with use, especially at the higher rates of flow of *o*-nitrotoluene. A 97% yield of *o*-toluidine was obtained with a copper catalyst used at 260°, the activity of which had been decreased by use at too high a temperature (300°). A copper catalyst prepared by the ignition of copper nitrate at 415° and containing 0.023% of iron gave a yield of 98.3% of *o*-toluidine at 260°. The corresponding yield of aniline was 91.9%. The activity of copper catalysts did not decrease with use. *o*-Nitrotoluene is more easily reduced than nitrobenzene.

J. S. G. T.

The Isomerism of β -Benzylaminocrotonic Ester, its Reaction with Ferric Chloride, and that of Related Compounds. ERICH BENARY (*Ber.*, 1923, **56**, [B], 53—55).—The constitutions $\text{CH}_2\text{Ph}\cdot\text{N}\cdot\text{CMe}\cdot\text{CH}\cdot\text{C}(\text{OH})\cdot\text{OEt}$ and $\text{CH}_2\text{Ph}\cdot\text{N}\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ have been assigned by Rügheimer (A., 1916, i, 383) to the isomeric ethyl β -benzylaminocrotonates. The author considers this conception highly improbable, since it involves the enolisation of the carb-ethoxyl group in a series in which enolisation occurs only with difficulty and only when there is an accumulation of negative substituents around the carbon atom. The differing behaviour of the isomerides towards ferric chloride (Rügheimer, *loc. cit.*) is not directly related to their constitution, since the development of the coloration depends on their fission to base and ethyl acetoacetate. A similar dependence of the production of colour on the decomposition of the compound is observed in the cases of ethyl β -aminocrotonate, ethyl β -anilino(or *p*-toluidino)crotonate, methyl β -anilino-crotonate, and ethyl ethylenediaminoacetoacetate, but not of their acidic derivatives as far as they have been examined. The colour is not developed if ferric acetate is substituted for ferric chloride.

It is doubtful whether the existence of two forms of ethyl

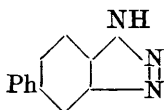
β -benzylaminocrotonate is to be ascribed to *cis-trans*-isomerism or to structural isomerism. H. W.

The Tertiary Amines Derived from Benzhydrylamine. MARCEL SOMMELET (*Compt. rend.*, 1922, **175**, 1149—1151; cf. A., 1922, i, 333).—The additive product of hexamethylenetetramine and diphenylbromomethane is converted by the action of formic acid into dimethylbenzhydrylamine, $\text{CHPh}_2\cdot\text{NMe}_2$, which combines very slowly in the cold with methyl iodide in methyl alcohol to give a *methiodide*, m. p. 211°. In hot solution, the hydriodide is obtained along with the methiodide and also a neutral, oily compound. Diethylbenzhydrylamine, benzhydrylpiperidine, and ethylbenzylbenzhydrylamine behave similarly towards methyl iodide, but in these cases very little, if any, of the methiodide is formed at 100°. If methyl bromide is used instead of methyl iodide, it is not possible to isolate any quaternary salt but only the hydrobromide. If dimethylbenzhydrylamine and methyl bromide are heated together in solution in methyl alcohol in a sealed tube at 100° for forty-eight hours, there is an abundant evolution of methyl ether, and benzhydryl methyl ether, $\text{CHPh}_2\cdot\text{OMe}$, and trimethylamine hydrobromide are obtained. If the methyl alcohol is replaced by butyl alcohol, the products are methyl butyl ether and benzhydryl butyl ether. These products may result as follows, $\text{MeBr} + \text{MeOH} + \text{CHPh}_2\cdot\text{NMe}_2 = \text{Me}_2\text{O} + \text{CHPh}_2\cdot\text{NMe}_2\cdot\text{HBr}$; $\text{CHPh}_2\cdot\text{NMe}_3\text{Br} = \text{CHPh}_2\text{Br} + \text{NMe}_3$, and $\text{CHPh}_2\text{Br} + \text{MeOH} + \text{NMe}_3 = \text{CHPh}_2\cdot\text{OMe} + \text{NMe}_3\cdot\text{HBr}$. W. G.

Diphenyl. III. Derivatives of Bromodiphenyl. A. GARCÍA BANÚS and L. MEDRANO (*Anal. Fis. Quím.*, 1922, **20**, 475—478; cf. A., 1922, i, 333).—By methylation of 4-bromo-4'-aminodiphenyl, using methyl alcohol and strong hydrochloric acid and heating in sealed tubes for ten hours at 140—150°, 4-bromo-4'-dimethylaminodiphenyl is obtained, which after recrystallisation has m. p. 205—208°. The mother-liquors from the crystallisation of this compound yield the corresponding *methochloride*, m. p. 180—185°. By nitration, 4-bromo-2-nitro-4'-dimethylaminodiphenyl is obtained; it forms large, orange-yellow plates, m. p. 107°. G. W. R.

Diphenyl. III. Derivatives of Anilindiphenyl. A. GARCÍA BANÚS and J. GUITERAS (*Anal. Fis. Quím.*, 1922, **20**, 479—485; cf. A., 1922, i, 333).—By boiling *p*-aminodiphenyl with fused sodium and 4:1:3-chlorodinitrobenzene in a reflux apparatus, 4-op-dinitroanilindiphenyl, $\text{C}_6\text{H}_4\text{Ph}\cdot\text{NH}\cdot\text{C}_6\text{H}_3(\text{NO}_2)_2$, is obtained; it has m. p. 147° and crystallises in two forms, namely, orange needles from acetic acid and red crystals from toluene. The transformation point from the orange to the red form is 95—105°. By reduction with sodium sulphide, *p*-nitro-o-aminoanilindiphenyl is obtained in platelets, m. p. 188°. 2-op-Dinitroanilindiphenyl is crystalline, m. p. 159°. The corresponding 2-p-nitro-o-aminoanilindiphenyl, obtained by reduction with sodium sulphide, forms dark orange platelets, m. p. 151—152°. 4'-Bromo-4-op-dinitroanilindiphenyl from 4:4'-bromoaminodiphenyl forms yellow

leaflets, m. p. 204—205°. 3:4-Diaminodiphenyl gives, with hydrochloric acid and sodium nitrite, 5-phenylbenziminazole (annexed formula); it forms white plates, m. p. 154—155°. 4'-Amino-4-op-dinitroanilinodiphenyl forms small prisms, m. p. 245—247°. 4'-Amino-4-p-nitro-o-aminoanilinodiphenyl forms red platelets, m. p. 201°. 4'-Amino-4-op-diaminoanilinodiphenyl forms grey platelets, m. p. 197°. G. W. R.



The Preparation of Phenylimido-phosgene [Phenylcarbylamine Chloride] and the Chlorination of Formanilide. R. S. BLY, G. A. PERKINS, and W. LEE LEWIS (*J. Amer. Chem. Soc.*, 1922, **44**, 2896—2903).—Good yields of phenylthiocarbimide were obtained from thiocarbaniide by heating it under a reflux condenser for several hours with three parts of dilute sulphuric acid (one of acid to 2.5 volumes of water) and subsequently distilling the product with steam. When the thiocarbimide is chlorinated to saturation in solution in carbon tetrachloride or carbon disulphide, a 95% yield of phenylcarbylamine chloride is obtained if the solvent is removed directly by fractional distillation at a pressure of 30 mm. By using the phenylcarbylamine chloride itself as a solvent for subsequent chlorinations the other solvents could be dispensed with.

When formanilide was chlorinated in the cold with or without solvents in the presence of sulphur chloride the product was in all cases 2:4-dichloroformanilide. If the chlorination was conducted in the presence of thionyl chloride, a series of products was obtained, namely, 2:4-dichloroformanilide, phenylcarbylamine chloride, *p*-chlorophenylcarbylamine chloride, b. p. 135—137°/30 mm., and 2:4-dichlorophenylcarbylamine chloride, b. p. 150—153°/30 mm. *p*-Chlorophenylcarbylamine chloride, when heated with glacial acetic acid, yielded *p*-chloroacetanilide, and with aniline yielded chlorotriphenylguanidine, m. p. 135—136°, as its hydrochloride, m. p. 247—250°. Similarly, 2:4-dichlorophenylcarbylamine chloride gave with acetic acid 2:4-dichloroacetanilide and with aniline 2:4-dichlorotriphenylguanidine, m. p. 129.5—130.5° (corr.) as its hydrochloride, m. p. 207—209° (corr.). The specific gravity of these substituted chlorides increases with the chlorine content but the lachrymatory effect diminishes. W. G.

New Derivatives of *p*-Phenetylcarbamide (Dulcin). MAX BERGMANN, FRANZESKO CAMACHO, and FERDINAND DREYER (*Ber. Deut. pharm. Ges.*, 1922, **32**, 249—258; cf. Speckan, A., 1922, i, 580).—Various derivatives of dulcin (*p*-phenetylcarbamide) have been prepared in an effort to find one which should be more soluble while retaining the sweet taste. *a*-*p*-Phenetyl-*a*-methylcarbamide is more soluble and very sweet, but has a very persistent unpleasant flavour as well. The unpleasant taste is less marked in *a*-*p*-phenetyl-*a*-hydroxyethylcarbamide, but is still sufficient to render it technically useless. These and other compounds of the same type were prepared by the action of potassium cyanate on the hydrochlorides of the corresponding bases in aqueous solution. Derivatives of

dulcin in which an alkyl group is introduced into the primary amino-group are sparingly soluble and have no appreciable sweet taste. The latter compounds were prepared by the action of the corresponding thiocarbimides on phenetidine, whereby the thiocarbamide derivatives were formed, which were converted into the corresponding carbamide compounds by the action of mercuric oxide in acetic acid.

a-*p*-Phenetyl-a-methylcarbamide, $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}\cdot\text{CO}\cdot\text{NH}_2$, was obtained in good yield from potassium cyanate and *N*-methylphenetidine hydrochloride. It forms long needles, m. p. 128—129°. Similarly, *N*-hydroxyethyl-*p*-phenetidine gave a-*p*-phenetyl-a-hydroxyethylcarbamide, $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{N}(\text{CH}_2\cdot\text{CH}_2\cdot\text{OH})\cdot\text{CO}\cdot\text{NH}_2$, needles, m. p. 113—115°. Dihydroxypropylphenetidine (*Ber.*, 1922, 55, 2796) gave a-*p*-phenetyl-a-dihydroxypropylcarbamide, $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{N}[\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}]\cdot\text{CO}\cdot\text{NH}_2$, crystals, m. p. 138—139°, without sweet taste. By the action of ethyl chloroacetate on *p*-phenetidine, *p*-phenetylglycine ethyl ester, $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$,

is formed, leaflets, m. p. 38°, b. p. 152°/1 mm. (*amide*, m. p. 146°).

The ester is converted by potassium cyanate into methyl-a-*p*-phenetylcarbamido-a-acetate, $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{N}(\text{CH}_2\cdot\text{CO}_2\text{Et})\cdot\text{CO}\cdot\text{NH}_2$, colourless needles, m. p. 86—87°, of slightly bitter taste. With alcoholic ammonia it gives the corresponding *amide*, m. p. 236—237°, without distinctive taste.

p-Phenetidine and allylthiocarbimide gave a-*p*-phenetyl-b-allylthiocarbamide, crystals, m. p. 94—95°. With mercuric oxide, it gives a-*p*-phenetyl-b-allylcarbamide, crystallising from alcohol, acetic acid, or ethyl acetate in fine needles, from chloroform in rectangular plates, m. p. 157°.

Similarly, a-*p*-phenetyl-b-methylthiocarbamide crystallises from alcohol in truncated prisms, m. p. 128—128·5°, and a-*p*-phenetyl-b-methylcarbamide forms fine, long, quadrilateral platelets, m. p. 159°. *N*-Methyl-*p*-phenetidine and methylthiocarbimide give a-*p*-phenetyl-ab-dimethylthiocarbamide, truncated prisms, m. p. 99—100°, and a-*p*-phenetyl-ab-dimethylcarbamide, prisms, m. p. 94—95°. Similarly, a-*p*-phenetyl-a-methyl-b-allylthiocarbamide forms long needles, m. p. 68—69°, and a-*p*-phenetyl-a-methyl-b-allylcarbamide, thin needles, m. p. 57—58°. P. M.

Hydrogenated Polycyclic Ring Systems. I. The Hydrogenation of Phenol and the By-products which are formed thereby. WALTHER SCHRAUTH, WILHELM WEGE, and FRITZ DANNER (*Ber.*, 1923, 56, [B], 260—268).—The hydrogenation of phenol in the gaseous state and under pressure has been studied in the presence of a nickel-copper catalyst. The arrangement of the apparatus for the first series of experiments is essentially that of Sabatier (*Die Katalyse*, 1914). Phenol is converted into a mixture of cyclohexanol (80—83%), cyclohexanone (6—9%), and smaller quantities of products of lower boiling point which have not been investigated fully; about 10% of the phenol remains unchanged. The results are closely similar to those obtained in

the presence of reduced nickel by Sabatier and Senderens (A., 1904, i, 156) and by Skita and Ritter (A., 1911, i, 272).

Hydrogenation under pressure in the presence of the nickel-copper catalyst is effected according to Schroeter's method (A., 1922, i, 122). It leads essentially to a mixture of *cyclohexanol* and *cyclohexanone*, containing about 9–14% of the latter. The volatile products formed during the hydrogenation in the vaporous phase are not observed, their place being taken by dark oils of high boiling point, the amount of which may rise to 10% when the action is unusually prolonged. A condensation appears therefore to occur in which *cyclohexanol* or more probably *cyclohexanone* takes part. Since the relative amounts of these substances is thereby undisturbed, it follows that the equilibrium between them is rapidly restored in the presence of the catalyst, which can also induce dehydrogenation (cf. Sabatier and Senderens, A., 1903, i, 393).

The liquids of high boiling point consist of di- and tri-cyclic condensation products consisting partly of saturated and partly of unsaturated ketones and aldehydes, which are readily converted by further hydrogenation into homogeneous saturated compounds of alcoholic character.

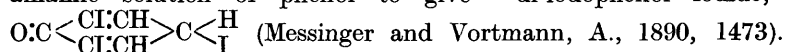
1 : 3-Dicyclohexylcyclohexane-2-one, $C_6H_{11} \cdot C_6H_8O \cdot C_6H_{11}$, long, colourless prisms, m. p. 131–132°, is obtained by the addition of alcohol to the least volatile fractions of the condensation products obtained by the hydrogenation of phenol under pressure. As in analogous cases, the presence of the ketonic group cannot be established by the help of semicarbazide hydrochloride or aminoguanidine hydrochloride, but the constitution of the product is placed beyond doubt by its production by the hydrogenation of 1 : 3-dicyclohexenylcyclohexane-2-one (cf. Mannich, A., 1907, i, 205). A solution of the ketone in methylcyclohexane is catalytically hydrogenated at 180–190° to a mixture of isomeric 1 : 3-dicyclohexylcyclohexane-2-ols, colourless needles, m. p. 117°, and a very viscous, colourless liquid, b. p. 220–221°/17 mm.; the latter is slowly converted into the solid variety when preserved. Either alcohol appears to be transformed into a mixture of the cis- and trans-acetate when acetylated. The liquid alcohol is dehydrated by zinc chloride at 200–210° with the formation of 1 : 3-dicyclohexyl- Δ^1 -cyclohexene, b. p. 204–207°/15 mm., d 0.9525; the hydrocarbon is also preparable from the solid alcohol, but it is uncertain whether a uniform product is obtained in this manner. It is transformed by hydrogenation in the presence of methylcyclohexane to a mixture of 1 : 3-dicyclohexylcyclohexanes, long, colourless needles, m. p. 66–67°, and a liquid, b. p. 192–196°/12 mm., d 0.9335. H. W.

The Synthesis of Phosphoric Acid Esters. I. SHIGERU KOMATSU and SHINICHIRO KUMAMOTO (*Mem. Coll. Sci. Kyoto*, 1922, 6, 45–48).—*cyclohexanol* when left in contact with phosphoric acid in presence of phosphoric oxide forms a *mono-ester*, $(C_6H_{11})H_2PO_4$, colourless crystals, m. p. 77–78°. The soluble
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barium salt, $C_6H_{11}BaPO_4$, is a white, crystalline substance; the *silver* salt is insoluble in water. When heated, the free ester and the barium salt are both decomposed into *cyclohexene* and phosphoric acid or phosphate. The di- and tri-*cyclohexyl* phosphates could not be obtained.
E. H. R.

The Action of Iodine on Alkaline Solutions of Phenol.

G. VORTMANN (*Ber.*, 1923, **56**, [B], 234—246).—In a previous communication it has been shown that iodine reacts with an alkaline solution of phenol to give “di-iodophenol iodide,”



The existence of this compound has been denied by Bougault (A., 1908, ii, 738), by Wilkie (A., 1911, ii, 546; 1912, i, 346), and by Hunter and Woollett (A., 1921, i, 238). Its isolation is now described.

The action of iodine on an alkaline solution of phenol takes place by the initial substitution of the halogen for the sodium atom of the phenoxide and its subsequent migration into the nucleus: $Ph \cdot O \cdot I \rightarrow C_6H_4I \cdot OH$. The process is then repeated until tri-iodophenol is produced. Even in the presence of a large excess of iodine, the nature of the product depends essentially on the quantity of alkali. Iodination therefore is effected by the alkali hypoiodite. Even in the presence of more than three molecular proportions of sodium hydroxide a compound more highly iodinated than tri-iodophenol is not produced; if the solution is acidified after not more than five minutes, this compound is quantitatively precipitated and is not further affected by the presence of much free iodine in the acid medium. If the phenol solution is not too dilute, tri-iodophenol separates previously to acidification; if it is shaken from time to time in the alkaline suspension, it gradually darkens in colour and passes into a mixture of “di-iodophenol iodide” and tetraiododiphenylenequinone (cf. Lautemann, *Annalen*, 1861, **120**, 309). Iodination of phenol in the presence of a large excess of alkali yields only di-iodophenol.

Di-iodophenol iodide is most conveniently prepared by the prolonged action of cold sodium hypoiodite solution on phenol. The brown mixture of the product with Lautemann's red is treated with acetone in which the former only is soluble to a yellowish-brown solution from which it is reprecipitated by the addition of much water and sodium chloride in the form of irregular, dark violet-brown leaflets or scales, m. p. 122°. It slowly loses iodine when exposed to air and gives a violet coloration when its dilute solution in acetone is treated with a little sodium thiosulphate solution.

The mechanism of the formation of Lautemann's red is discussed in detail and appears to be represented by the following equations: $C_6H_2I_3 \cdot OH + NaIO = C_6H_2I_3 \cdot OI + NaOH$; $C_6H_2I_3 \cdot OI \rightarrow C_6H_2I_2(O) \cdot I_2$, $C_6H_2I_2(O) \cdot I_2 + NaOH = C_6H_2I_2(O) \cdot IH + NaOI$; $2C_6H_2I_2(O) \cdot IH = 2HI + O \cdot C_6H_2I_2 \cdot C_6H_2I_2 \cdot O$.

Oxidation of tri-iodophenol by the requisite amount of potassium

persulphate in the presence of sodium carbonate gives a mixture of di-iodophenol iodide and Lautemann's red. Reduction of the latter in glacial acetic acid solution by stannous chloride and hydrochloric acid gives a colourless compound which appears to be a hydrogenated derivative (cf. Hunter and Woollett, *loc. cit.*).

Phenol may be estimated by treating its solution, which must contain at least four molecular proportions of sodium hydroxide, with an excess of iodine solution; after five minutes the solution is acidified with dilute sulphuric acid, whereby tri-iodophenol is precipitated. The excess of iodine is estimated in an aliquot portion of the supernatant liquor. If the time of action is prolonged beyond five minutes, the precipitate is more or less discoloured, but the consumption of iodine is not thereby changed. H. W.

The Decomposition of Ethers by Metallic Sodium. PAUL SCHORIGIN (*Ber.*, 1923, 56, [B], 176—186; cf. A., 1910, i, 547).—Diphenyl ether reacts exothermally with sodium wire at 180—200°, giving phenol (60—75%), benzene (30%), a small quantity of diphenyl, phenol-like products of high boiling point, and carbonised substances. The reaction also occurs in the presence of neutral solvents of suitable boiling point. The reaction is considered to involve the primary addition of sodium to yield the product Ph_2ONa_2 , and immediate scission of the latter into sodium phenoxide and sodium phenyl. The latter is decomposed by water (evolved during the production of the complex, pitch-like products) with the formation of benzene and sodium hydroxide. The formation of diphenyl may be ascribed to the direct removal of oxygen from the ether by sodium or to the interaction of sodium phenoxide and sodium phenyl, $\text{PhNa} + \text{PhONa} = \text{Ph} \cdot \text{Ph} + \text{Na}_2\text{O}$. The intermediate formation of organo-metallic sodium derivatives is rendered probable by the observation that an extremely vigorous action takes place when dry air is bubbled through the mixture, but, on the other hand, salicylic acid is produced when carbon dioxide is introduced into it, whereas sodium phenyl would be expected to yield benzoic acid.

α -Naphthyl ethyl ether reacts vigorously with sodium at 230—270°, yielding naphthalene, α -naphthol, carbonised and pitch-like products, ethylene, ethane, and hydrogen. The volume of ethylene formed exceeds that of ethane; the production of butane or butylene could not be established. β -Naphthyl ethyl ether reacts more energetically than the α -isomeride with sodium, but yields similar products, naphthalene, β -naphthol, ethylene, ethane, and hydrogen.

Phenetole does not react to an appreciable extent with sodium at any temperature below its boiling point. At 200—260°, it becomes decomposed into phenol, ethane, ethylene, hydrogen, products of high boiling point, carbonised material, and small quantities of ethyl alcohol. The intermediate formation of organo-metallic substances is established by the observations that the product of reaction becomes heated, sometimes to the point of ignition, when exposed to air, and that propionic acid is produced when it is treated with carbon dioxide.

Benzyl ethyl ether reacts with sodium at 140°, this temperature being much below its boiling point; benzyl alcohol appears to be produced, but owing to an accident, the products could not be fully investigated. *iso*Amyl ether yields small amounts of *iso*amyl alcohol when heated with sodium at 200–220° and subsequently at 235–275°.

The experiments show that the desiccation of simple ethers by distillation over sodium is open to suspicion, and that the process is quite unsuitable for fatty-aromatic and aromatic ethers of high boiling point. If the use of sodium is desired, milder conditions should be adopted, and the metal should be removed previously to the distillation of the ether. H. W.

Simplified Methods of Preparing certain Organic Substances. I. Nitrophenetoles and Nitroanisoles. H. VAN ERP (*Ber.*, 1923, 56, [B], 217–221).—The substances are prepared by the action of potassium alkyl sulphates on potassium nitrophenoxides in the presence of a small quantity of glycerol. The latter, after being purified and dehydrated by distillation under diminished pressure, is placed in a $\frac{1}{2}$ -litre flask provided with a reflux condenser filled with cold water, but with both tubes closed; an intimate mixture of the potassium compounds, previously desiccated at 140° and 100°, respectively, is added; and the mixture is heated in an oil-bath, usually at about 180° to 210°, until the change appears to be complete. The yields obtained are as follows: *o*-nitrophenetole, above 90%; 2:4-dinitrophenetole, 56%; 6-chloro-2:4-dinitrophenetole, 0%; *p*-nitroanisole, 87%.

Contrary to the statements in the literature, pure methyl sulphate has b. p. 76°/15 mm., d_{15}^{15} 1.3348.

Contrary to statements in Beilstein's *Handbuch*, crystalline potassium methyl sulphate is anhydrous and not deliquescent.

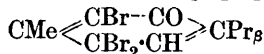
H. W.

Certain Bromine Derivatives of Thymol. HANS JOST and FRIEDRICH RICHTER (*Ber.*, 1923, 56, [B], 119–123).—The action of bromine on thymol dissolved in glacial acetic acid has been examined by Dannenberg (*A.*, 1903, i, 338), who has thereby isolated a product which he considers to be the keto-bromide, $\text{CMe} \begin{smallmatrix} \text{CBr} \cdots \text{CO} \\ \text{CHBr} \cdots \text{CH} \end{smallmatrix} \text{CPr}^s$. The remarkable constitution of the compound has led the authors to re-examine the reaction; they draw the conclusion that the substance described by Dannenberg does not exist.

The action of bromine on thymol under the conditions adopted by Dannenberg proceeds beyond the formation of a dibromocompound, and gives also a true keto-bromide, $\text{C}_{10}\text{H}_{11}\text{OBr}_3$ (see later), which renders the product of the reaction incompletely soluble in solutions of alkali hydroxide; if a smaller proportion of bromine is used, its production is avoided and the dibromothymol is completely soluble; it crystallises in long, colourless prisms, m. p. +3.5–4°, b. p. 160–161°/16 mm., 175°/25 mm.,

d_{13}^{19} 1.6631, d_{14}^{19} 1.6618, d_{17}^{19} 1.6588; the corresponding benzoate forms small, colourless needles, m. p. 89–90°, whereas Dannenberg gives m. p. 80–81°.

Thymol is converted by a solution of calcium bromohypobromite into tribromo-*p*-menthadienone, $\text{CMe} \begin{smallmatrix} \text{CBr}_2 \cdot \text{CO} \\ \text{CBr} \cdot \text{CH} \end{smallmatrix} \text{CPr}^s$ or



(see above), large, dark yellow plates, m. p. 59–60° after softening at 55°. The substance decomposes somewhat readily when preserved. It liberates two atomic proportions of iodine from neutral potassium iodide solution, and is reduced by stannous chloride in the presence of hydrogen chloride and acetic acid to dibromothymol. It is converted by cold, concentrated sulphuric acid into 2:4:6-tribromo-*m*-cresol, its behaviour in this respect being similar to that of trichloro-*p*-menthadienone (Crowther and McCombie, T., 1913, **103**, 539, 545). The keto-bromide is also obtained by the action of sodium hypobromite or of an excess of bromine on thymol. When dissolved in carbon tetrachloride and shaken with aqueous potassium hydroxide solution (4%), it is transformed into a brown, amorphous powder, m. p. 220–230° (decomp.) after darkening at 200°. H. W.

Amino-alcohols of Tetralin [Tetrahydronaphthalene].

A. GONZÁLEZ and M. CAMPOY (*Anal. Fis. Quím.*, 1922, **20**, 534–538).—By the action of hypobromous acid on 1:4-dihydronaphthalene, 3-bromo-2-hydroxytetrahydronaphthalene is obtained. It is crystalline, and has m. p. 107°. By acting on it with anhydrous dimethylamine in benzene solution in a sealed tube at 120°, 3-dimethylamino-2-hydroxytetrahydronaphthalene is obtained, b. p. 165–170°/14 mm. 2-Dimethylamino-1-hydroxytetrahydronaphthalene has b. p. 157–158°/13 mm. The following compounds were also prepared: 2-benzoyl-3-dimethylaminotetrahydronaphthalene hydrochloride, m. p. 228°; 2-valeryl-3-dimethylaminotetrahydronaphthalene hydrochloride, m. p. 173°; 2-cinnamoyl-3-dimethylaminotetrahydronaphthalene hydrochloride, m. p. 178°; 2-pyromucyl-3-dimethylaminotetrahydronaphthalene hydrochloride; 1-benzoyl-2-dimethylaminotetrahydronaphthalene hydrochloride, m. p. 176°; 1-valeryl-2-dimethylaminotetrahydronaphthalene hydrochloride, m. p. 165°; 1-cinnamoyl-2-dimethylaminotetrahydronaphthalene hydrochloride, m. p. 176.5°; 1-pyromucyl-2-dimethylaminotetrahydronaphthalene hydrochloride, m. p. 172°. Hydrochlorides of the 1:2-series are more soluble and have a lower melting point than those of the 2:3-series. G. W. R.

A New Class of Derivatives of β -Naphthol, the 1-Arylamino- β -naphthols. A. WAHL and ROBERT LANTZ (*Bull. Soc. chim.*, 1923, [iv], **33**, 93–110).—Certain atoms and groups which in the benzene nucleus are only displaced at high temperatures or not at all are extremely reactive when substituted in the α -position in β -naphthol. Thus the sulphonic group of β -naphthol- α -sulphonic acid is eliminated when the substance is treated in aqueous solution

with *p*-nitrobenzenediazonium chloride. In alkaline solution, the reaction occurs in two stages with the intermediate formation of an extremely unstable compound, which is thought to be a diazo-oxide of the formula $\text{SO}_3\text{Na}\cdot\text{C}_{10}\text{H}_6\cdot\text{O}\cdot\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$. In presence of the least trace of acid, this yellow, water-soluble substance is instantly converted into *p*-nitraniline-red,



with liberation of sulphuric acid. With α -chloro- β -naphthol, the intermediate product cannot be isolated, the dye being produced at once with the elimination of the chlorine atom. The mobility of the halogen atom in the α -position is further illustrated by the action of sodium sulphite in weak alcoholic solution, β -naphthol being formed and the halogen eliminated. α -Chloro- or α -bromo- β -naphthol also reacts vigorously with primary aromatic amines, and, moderating the reaction by using a large excess of the amine, quantitative yields of 1-arylamino-2-hydroxynaphthalenes are obtained. 1-*Anilino*- β -naphthol forms white needles, m. p. 155—156°, which darken on exposure to air. The *hydrochloride* forms a white, crystalline powder, and the *methyl ether* colourless needles, m. p. 82—83°. 1-*p-Toluidino*- β -naphthol forms white prisms, m. p. 138—139°, and its *methyl ether* white needles, m. p. 94°. 1-*o-Toluidino*- β -naphthol, crystallised from acetic acid, melts at 114—115°. 1-*o-Anisidino*- β -naphthol crystallises in small needles, m. p. 110°. 1-*o-Methoxy-m-toluidino*- β -naphthol forms white needles, m. p. 118°. 1- α -Naphthylamino- β -naphthol forms grey needles, m. p. 171°, and the corresponding β -derivative a grey powder, m. p. 166—167°. G. F. M.

The Influence of Boric Acid on some Polyhydroxy-derivatives of Naphthalene and Anthraquinone. J. BÖESEKEN [with (MLLE) K. C. ANEMA and (MLLE) M. A. J. BREVET] (*Rec. trav. chim.*, 1922, **41**, 778—783; cf. A., 1915, ii, 667).—Two *o*-dihydroxynaphthalenes, similarly to dihydroxyphenols (cf. Böeseken and Van Rossem, A., 1912, ii, 147), considerably increase the electrical conductivity of solutions of boric acid, but the increase due to the 2:3-dihydroxy-compound is much greater than that conferred by its 1:2-isomeride. This difference is attributed to greater freedom of the hydroxyl groups in the former compound. The hydroxy-derivatives of anthraquinone were found to be insufficiently soluble in water for similar measurements of conductivity to be made, but a coloration was observed in each case on the addition of boric acid to a solution of the substance in dilute alcohol. The suggestion is made that the coloration depends on the presence of two hydroxyl groups in the ortho-position with respect to each other, or, alternatively, that it is correlated with the presence of a hydroxyl group next to a carbonyl group.

H. J. E.

Preparation of Benzyl Esters of some Acids of High Boiling Point. T. J. THOMPSON and GERALD J. LEUCK (*J. Amer. Chem. Soc.*, 1922, **44**, 2894—2896).—Benzyl esters of certain

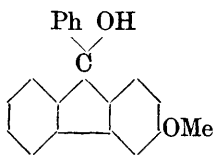
acids which boil at above 100° without decomposition have been prepared by heating together the alcohol and acid in the requisite proportions in a flask fitted with an air condenser of such a length that the benzyl alcohol vapour condenses just below its upper end, whilst it is not long enough to cause the condensation of the water vapour arising from the interaction of the alcohol and acid. Pure benzyl alcohol, free from traces of benzaldehyde, must be used. Good yields were obtained in the case of eight esters, but in two cases it was necessary to vary the pressure in the flask. Other high boiling point alcohols were tried instead of benzyl alcohol, but they did not give satisfactory results.

W. G.

Triphenylmethyl. XXXII. *p*-Benzyloxy- and *p*-Methoxytriphenylmethyl. M. GOMBERG and C. C. BUCHLER (*J. Amer. Chem. Soc.*, 1923, **45**, 207—222).—*p*-Benzyloxytriphenylcarbinol, m. p. 94°, was prepared from the corresponding hydroxy-compound by the Schotten-Baumann reaction. When reduced with zinc and acetic acid, it yielded *p*-benzyloxytriphenylmethane, m. p. 116·5°, and with hydrogen chloride gave *p*-benzyloxytriphenylmethyl chloride, m. p. 77°, from which, by the action of sodium ethoxide, *p*-benzyloxytriphenylmethyl ethyl ether, m. p. 89°, was obtained. *p*-Benzyloxytriphenylmethyl bromide had m. p. 90°. When the chloride was shaken with molecular silver in dry benzene, *p*-benzyloxytriphenylmethyl, m. p. 142—145°, was obtained; it rapidly absorbed oxygen from the air, giving a *peroxide*, m. p. 171°, and absorbed iodine from its solution giving an unstable *iodide*. In benzene solution, the free radicle reacts with hydrogen chloride to give a mixture of the carbinyl chloride and the triarylmethane, and these interact only to a very slight extent to give a dialkyloxy-*p*-benzhydryltetraphenylmethane. A benzene solution of the free radicle exposed in a quartz tube to sunlight undergoes auto-oxidation and reduction to form a biphenylene free radicle and *p*-benzyloxytriphenylmethane. The free radicle was crystallised from a number of different types of solvents, but only in one case, namely, with ether, was an additive compound formed. The degree of dissociation of di-*p*-benzyloxyhexaphenylethane in six different solvents over a temperature range from -17° to +53° and in concentrations from 1 to 6%, was found to vary from 26 to 56% with the concentration, the temperature, and the nature of the solvent.

p-Methoxytriphenylcarbinol gave a chloride and a *bromide*, m. p. 143°, and from the chloride the free radicle *p*-methoxytriphenylmethyl, m. p. 145—150°, was obtained. It absorbs oxygen, giving a *peroxide*, m. p. 157°, and iodine, giving an *iodide*. Like the benzyloxy-compound, the main reaction with hydrogen chloride in benzene solution is to yield the carbinyl chloride and the triarylmethane. When exposed to sunlight in the same solvent a mixture of *p*-methoxytriphenylmethane and a biphenylenetriarylmethyl result, and from this solution on exposure to air 9-phenyl-3-methoxyfluoroyl peroxide, m. p. 200° (decomp.), was obtained. This peroxide was synthesised by a different method as follows:

3-methoxy-9-fluorenone was converted by the action of magnesium phenyl bromide into the *carbinol* (annexed formula), m. p. 84°, giving a *chloride*, m. p. 119°. From this by shaking with molecular silver the free radicle was obtained, and this on exposure to air gave the required peroxide. *p*-Methoxy-triphenylmethyl did not give any additive compounds with the various solvents tried. The degree of dissociation of di-*p*-methoxyhexaphenylethane, determined as in the case of the benzyloxy-compound, varied from 22 to 42%.



W. G.

Triphenylmethyl. XXXI. Tautomerism of *o*-Hydroxytriphenylcarbinol; *o*-Hydroxy- and Alkyloxy-triphenylmethyl. M. GOMBERG and D. NISHIDA (*J. Amer. Chem. Soc.*, 1923, **45**, 190—207).—When *o*-hydroxytriphenylcarbinol in solution in glacial acetic acid, carbon tetrachloride, benzene, toluene, or xylene is warmed, the solution becomes brown, the coloration beginning at 50—80°, according to the nature of the solvent, and increasing in intensity with rise in temperature or concentration of the solution. This coloration is due to tautomerisation of the carbinyl to the quinonoid form, and the change is reversible if the temperature does not exceed 110°. Above 110°, the carbinol, in solution, slowly loses water and yields, not the expected *o*-fuchsone, but a rearrangement product, namely, 9-phenylxanthane. The carbinyl chloride undergoes similar changes, but at much lower temperatures, and loses hydrogen chloride instead of water. *o*-Benzyloxytriphenylcarbinyl chloride is considerably more stable than the *o*-hydroxy-compound, but even at ordinary temperatures it undergoes a gradual spontaneous decomposition. *o*-Hydroxy-, *o*-benzyloxy-, and *o*-methoxy-triphenylcarbinyl chlorides are all decomposed by molecular silver, giving the free radicle, but in the cases of the first two the free triarylmethyls could not be isolated owing to secondary changes, but *o*-methoxytriphenylmethyl was isolated and its physical and chemical properties were determined. It exists in solution in the unimolecular state to the extent of 26—49%, depending on the temperature. At ordinary temperatures only about one-third of the total amount of the unimolecular triarylmethyl is in the quinonoid state, the remaining two-thirds being benzenoid.

o-Hydroxytriphenylchloromethane was obtained by dissolving the carbinol in ether, adding calcium chloride, and saturating the solution with hydrogen chloride. Colourless crystals were obtained, which rapidly became brown even in a desiccator. When shaken in benzene solution with molecular silver in the presence of air, the polymerised *o*-hydroxytriphenylmethyl, m. p. 237°, was obtained, together with a peroxide, $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{CPh}_2\cdot\text{O}\cdot\text{O}\cdot\text{CPh}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, m. p. 131°. *o*-Benzyloxytriphenylcarbinol, m. p. 172°, was prepared from the hydroxy-compound, and gave the carbinyl chloride, m. p. 146°, which with molecular silver gave the polymeride, m. p. 207°, of the triarylmethyl, and also a peroxide, m. p. 153°.

o-Methoxytriphenylcarbinol gave a stable chloride and *bromide*, m. p. 127—128°. The chloride when decomposed by molecular silver gave a mixture of *di-o-methoxyhexaphenylethane*, m. p. 117—121°, and *o-methoxytriphenylmethyl*. The free radicle, when exposed to air, rapidly absorbs oxygen and gives its *peroxide*, m. p. 160—161° (decomp.), and, similarly, it absorbs iodine to give its *iodide*. Both the free radicle and its chloride and bromide show decided electrical conductivity in liquid sulphur dioxide. W. G.

Pinacolic and Semi-pinacolic Transpositions. Comparative Migratory Aptitudes of Different Radicles. M. TIFFENEAU and (Mlle) J. LEVY (*Compt. rend.*, 1923, 176, 312—314).—From examples of pinacolic and semi-pinacolic transpositions of substituted glycols and iodohydrins quoted, it is shown that ethyl and benzyl groups have a much more marked aptitude for migration than has the methyl group, and in many cases the migration of the former groups is exclusive. W. G.

Compounds containing the Trimethylene [*cyclo*Propane] Ring. P. BRUYLANTS and A. STASSENS (*Bull. Acad. roy. Belg.*, 1921, 702—719).—*cyclo*Propanecarboxylonitrile, when prepared from γ -chlorobutyronitrile by distilling with dry potassium hydroxide, contains crotono- or isocrotono-nitrile. The pure *cyclo*-nitrile boils at 134—134.2°/762.5 mm. Pure *cyclo*propanecarboxylic acid has m. p. 18.1° and b. p. 181.8—182.0°/766 mm. The corresponding chloride, on chlorination, at the b. p. gives (a) 1-chlorocyclopropanecarboxyl chloride, b. p. 141—143°, d_4^{20} 1.336, n_D^{20} 1.4759, and (b) a small amount of what is apparently α -dichlorobutyryl chloride, b. p. 212—214°. The former (a) was converted by water into 1-chlorocyclopropanecarboxylic acid, colourless needles, m. p. 70—71°, b. p. 206°; sodium salt, colourless, hygroscopic needles; methyl ester, b. p. 152—153°/761 mm., d_4^{20} 1.179; ethyl ester, b. p. 65—66°/15 mm. or 162—163°/762.5 mm., d_4^{20} 1.126, n_D^{20} 1.4417; amide, white crystals, m. p. 131—132°.

Ethyl 1-chlorocyclopropanecarboxylate by treatment with magnesium methyl bromide is converted into a *chlorohydrin*, $C_3H_4Cl \cdot CMe_2 \cdot OH$. The latter has b. p. 156.5—157°/756 mm., d_4^{20} 1.065, forms an *acetyl* derivative, d_4^{20} 1.086, and is almost unaffected by hot aqueous potassium hydroxide.

The chlorine atom in 1-chlorocyclopropanecarboxylic acid is not reactive enough to permit of the preparation of derivatives by its replacement. The constitution of the acid was decided from conductivity measurements with the acid and its sodium salt, whence the dissociation constant (100 *k*) was found to be between 0.05 and 0.06, a value only to be explained if the chloro-group is in the α -position.

By treating the higher boiling fractions of the above chlorination with methyl alcohol in presence of a little sulphuric acid, methyl α -chlorocyclopropanecarboxylate and methyl α -dichlorobutyrate, b. p. 212—214°, were obtained.

The molecular heats of combustion of cyclopropanecarboxylic

acid at constant volume and at constant pressure were found to be 486.1 and 486.4 cal., respectively, whereas for crotonic acid the value is 478.0 cal. The heat of formation of the acid in the liquid state is 97.8 cal. (crotonic acid, 102.3 cal.).

Determinations of the viscosities and melting points of mixtures of cyclopropanecarboxylic acid with water are described, and point to the existence of a hydrate, $C_4H_6O_2 \cdot H_2O$. E. E. T.

4-Fluoro-3-nitrobenzoic Acid. H. ROUCHE (*Bull. Acad. roy. Belg.*, 1921, 534—547).—4-Fluorobenzoic acid, on treatment with nitric acid (d 1.495), is converted to the extent of 80% into 4-fluoro-3-nitrobenzoic acid, white needles, m. p. 121.5° , 4-fluoronitrobenzene also being formed as the result of the displacement of the carboxyl group by the nitro-group. The new acid forms soluble and highly coloured salts (alkali metals, red; alkaline-earth metals, yellow or orange). The silver salt is unstable. The ethyl ester, yellow crystals, melts at 45.3° . The chloride, b. p. $210^\circ/130$ mm., on treatment with aqueous ammonia, gives 3-nitro-4-aminobenzamide, dry ammonia in ethereal solution, however, giving 4-fluoro-3-nitrobenzamide, a waxy mass, m. p. 153° .

The solubilities of 4-fluoro-, 4-chloro-, and 4-bromo-3-nitrobenzoic acids have been compared.

The dissociation constants (100 k) of 4-fluoro- and 4-chloro-3-nitrobenzoic acids were found to be respectively 0.0433 and 0.048 (cf. A., 1890, 1209), the corresponding 4-bromo-acid being stronger than these two acids. *p*-Fluorobenzoic acid, used in comparison, gave 100 k 0.00735. Owing to the labile nature of the fluoro-group in fluoronitrobenzoic acid, conductivity determinations with the latter were carried out in presence of hydrochloric acid.

A study of the velocities of reaction with sodium methoxide of sodium fluoronitrobenzoate and *o*-fluoronitrobenzene showed that the carboxyl group renders a para-fluoro-group more labile.

E. E. T.

α -Nitrophenylacetamide and some of its Derivatives. A. J. VAN PESKI (*Rec. trav. chim.*, 1922, 41, 687—700; cf. A., 1909, i, 647).—On treatment of α -isonitrophenylacetamide with concentrated sodium hydroxide solution, the sodium derivative of the amide which is first formed gradually disappears and sodium nitrophenylacetamide is formed. This reacts with bromine to give α -bromo- α -nitrophenylacetamide, which is easily obtained pure. The action of dilute sulphuric acid on the aqueous solution of the sodium derivative gives a white precipitate which becomes viscid and then solidifies. This consists of α -nitrophenylacetamide, which on crystallisation from benzene or chloroform is obtained in the form of white needles, m. p. 82.5 — 83° . These remain unchanged for a considerable time; decomposition may be detected by a lowering of the melting point, and after some months the substance is transformed into a thick brown syrup. Complete decomposition may be effected in less than two hours by heating

on the water-bath : among the decomposition products are nitrogen, nitrous oxide, phenylglyoxylic acid, phenylglyoxylamide, benzonitrile, water, and two unidentified derivatives of phenylglyoxylamide. On boiling in contact with water, the products are phenylglyoxylic acid and its amide, benzoic acid and the oxime of phenylglyoxylamide. The chloro-derivative of α -nitrophenylacetamide is prepared in a similar manner to the bromo-derivative, but the corresponding iodine compound is obtained in ethereal solution of iodine by reaction with the silver salt of the amide. All three halogen derivatives liberate nitric oxide and the halogen on being heated; the decomposition may take place explosively. The following descriptions are given : α -chloro- α -nitrophenylacetamide, white prisms, m. p. 107—115°; α -bromo- α -nitrophenylacetamide, crystals, m. p. 108—116°; α -iodo- α -nitrophenylacetamide, yellow, rod-shaped crystals, m. p. 97—100°; o-bromo- α -nitrophenylacetamide, white, rod-shaped crystals, m. p. 125°; p-bromo- α -nitrophenylacetamide, white, rod-shaped crystals, m. p. 101.5°; ethyl imidophenylperacetate, $\text{CH}_2\text{Ph}\cdot\text{C}(\text{NH})\cdot\text{O}\cdot\text{OEt}$, small, rod-shaped crystals, m. p. 180°.

H. J. E.

Asymmetrical Synthesis. EMIL ERLÉNMEYER and HANS ERLÉNMEYER (*Biochem. Z.*, 1922, **133**, 52—62).—If bromine be added to a solution containing cinnamic acid, a sugar, and a zinc salt, the dibromophenylpropionic acid formed is optically active, except in the case of lactose, where the resulting acid is inactive. Presumably a complex salt of zinc with cinnamic acid on the one hand, and with the sugar on the other, is formed, and this optically active compound adds on bromine asymmetrically. With dextrose, lævulose, and sucrose excess of the *l*- α - β -dibromo- β -phenylpropionic acid is formed, and with *l*-arabinose excess of the *d*-acid. Lævulose is particularly effective, and it is likewise active if α -methylcinnamic acid is used instead of cinnamic acid.

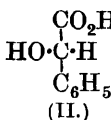
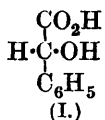
W. O. K.

The Iodination of *m*-Hydroxybenzoic Acid. P. H. BELJER (*Rec. trav. chim.*, 1922, **41**, 701—702).—Monoiodohydroxybenzoic acid was prepared by Wieselsky's method (*Annalen*, 1874, **174**, 105). An identical acid was obtained from 4-nitro-3-hydroxybenzoic acid by reduction of the nitro-group, diazotisation, and treatment with potassium iodide. The acid is thus 4-iodo-3-hydroxybenzoic acid, so that the action of iodine yields a derivative substituted similarly to that obtained on bromination. This was confirmed by the preparation of 6-iodo-3-hydroxybenzoic acid (cf. Limpricht, A., 1891, 1036) which is not identical with the acid obtained by Wieselsky.

H. J. E.

The Configuration of Mandelic Acid and other α -Hydroxyacids. KARL FREUDENBERG, FRITZ BRAUNS, and HEINRICH SIEGEL (*Ber.*, 1923, **56**, [B], 193—200).—The hypothesis that the optical activity of similarly constituted substances of the same configuration is influenced in a uniform manner by change of temperature, dilution, or addition of neutral salts has led Clough

(T., 1918, 113, 526) to assign *l*-mandelic acid to the *d*-series (configuration I), whereas Hudson (A., 1918, i, 292), on the consideration that all hydroxy-acids which yield dextrorotatory amides and hydrazides belong to the *d*-series, has assigned to it the configuration II (*l*-mandelamide is lævorotatory). *l*-Hexahydromandel-



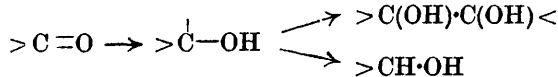
amide has now been prepared, and shown to be strongly dextrorotatory. Since, therefore, *l*-mandelic and *l*-hexahydromandelic acids are configurationally related, Hudson's rule appears to be broken. A consideration of the optical activities of α -hydroxy-acids of known configuration and of their amides confirms the validity of Clough's deductions. Hudson's rule appears merely to require a slight modification in the sense that α -hydroxy-acids are considered to belong to the *d*-series when their specific rotation is displaced in the dextro-direction on conversion into the amide. An actual transition from lævo to dextro is only observed with substances of low rotatory power, such as the monocarboxylic acids of the sugar group, from a study of which the rule was first developed.

dl-cycloHexylglycollic acid, m. p. 134—135° [Godchot (A., 1910, i, 480) gives 130—131°], is prepared by the catalytic hydrogenation of *dl*-mandelic acid in aqueous solution in the presence of platinum with gum arabic or gelatin as protective colloid. It is smoothly esterified to *methyl dl*-cyclohexylglycollate, b. p. 122—123°/18 mm., from which the corresponding amide, m. p. 156° (Godchot gives m. p. 155°) is prepared. *dl*-cycloHexylglycollophenylhydrazide has m. p. 213°. *d*(-)-cycloHexylglycollic acid, prepared by hydrogenation of *l*-mandelic acid, has m. p. 128—129°, $[\alpha]_{\text{Hg yellow}}^{23} -26.6^\circ$, $[\alpha]_{\text{Hg yellow}}^{27} -25.8^\circ$ in glacial acetic acid solution. The corresponding *methyl* ester has b. p. 123°/19 mm., $[\alpha]_{\text{Hg yellow}}^{25} -4.7^\circ$; the *phenylhydrazide*, m. p. about 215° (decomp.), $[\alpha]_{\text{Hg yellow}}^{30} +55.25^\circ$ in glacial acetic acid, and the *amide*, m. p. 158°, $[\alpha]_{\text{Hg yellow}}^{25} +47.4^\circ$ in alcohol, $[\alpha]_{\text{Hg yellow}}^{25} +41.16^\circ$ in aqueous (20%) alcohol are described.

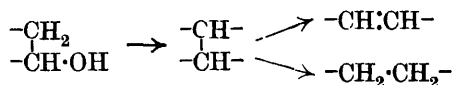
d(-)-Lactic acid, prepared by the resolution of the *r*-acid with morphine (cf. Irvine, T., 1906, 89, 935), is converted into the *methyl* ester, b. p. 50—60°/25 mm., $[\alpha]_{\text{Hg yellow}}^{20} +7.3^\circ$, and thence into the *amide*, m. p. 49—51°, $[\alpha]_{\text{Hg yellow}}^{18} +22.2^\circ$; it is remarkable that the active amide is very deliquescent and that this property is not shared by the *r*-amide. H. W.

The Theory of Reduction. The Reduction of the Carbonyl Group by Zinc Amalgam. WILHELM STEINKOPF and ARTHUR WOLFRAM (*Annalen*, 1923, 430, 113—161).—A careful study of the action of zinc amalgam and aqueous or alcoholic hydrochloric acid on a variety of carbonyl compounds has shown that products of several distinct types may be obtained, and that the formation of these may be accounted for by ascribing to the process the following general mechanism. In the first place, hydrogen becomes attached to the oxygen of the carbonyl group, giving a radicle (containing tervalent carbon) which may react either with

itself, yielding a pinacone or with more hydrogen, forming an alcohol :



Secondly, if the alcohol contains a CH_2 residue next to the carbinol group, water may be eliminated, giving first a compound containing two tervalent carbon atoms, and ultimately either a saturated or unsaturated substance :



Stress is laid on the view that the formation of the saturated and unsaturated substances is simultaneous and not successive, at least in the main. The constitution of the original carbonyl compound and the conditions of the reduction may determine which of the above four side reactions takes place preferentially, but the above mechanism is considered to be generally applicable.

Benzophenone, on reduction with zinc amalgam and aqueous hydrochloric acid, yields benzpinacone and traces of diphenylmethane; by reduction in alcoholic solution, tetraphenylethylene, α - and β -benzpinacolin, and diphenylmethane may be obtained. Benzhydrol on reduction in alcoholic solution gives diphenylmethane, and the benzpinacolins give tetraphenylethylene.

Ethyl acetoacetate, on reduction in alcohol, gives ethyl crotonate and ethyl butyrate. Ethyl crotonate is not reduced to ethyl butyrate under similar conditions.

Ethyl lævulate yields ethyl valerate and an unsaturated ester, probably β -ethylidenepropionic ester.

Ethyl benzoylacetate on reduction in alcohol with amalgamated zinc yields $\beta\gamma$ -diphenylpentadilactone (A., 1912, i, 889), ethyl β -phenylpropionate, and an oil, b. p. 210—212°/<1 mm. Using unamalgamated zinc, the products are the dilactone, ethyl cinnamate, ethyl β -phenylpropionate, $\beta\gamma$ -diphenyl- Δ^a -crotonolactone- γ -acetic acid, and probably *meso*- $\beta\beta'$ -dihydroxy- $\beta\beta'$ -diphenyladipic acid. Ethyl cinnamate on reduction with amalgamated zinc in alcoholic hydrogen chloride gives ethyl β -phenylpropionate.

Ethyl phenylglyoxylate gives ethyl mandelate and ethyl diphenyltartrate, and phenylglyoxylic acid yields mandelic acid.

Reduction of acetophenone in aqueous solution leads to ethyl benzene, acetophenonepinacolin, and styrene and its polymerisation products, along with small amounts of acetophenonepinacone, and $\alpha\gamma$ -diphenylbutane (?). In alcoholic solution, the products are styrene and its polymerides, acetophenonepinacone and α -chloroethylbenzene.

The products of reduction of benzaldehyde in aqueous solution are toluene, benzyl alcohol, stilbene, and hydrobenzoin. The action of zinc chloride on benzyl alcohol gives rise to stilbene hydrochloride.

C. K. I.

The Isomeric Esters of Benzoylacrylic Acid. GRACE POTTER RICE (*J. Amer. Chem. Soc.*, 1923, **45**, 222—238).—The yellow methyl benzoylacrylate, obtained by Kozniewski and Marchlewski (cf. A., 1906, i, 759) can be converted into a colourless *stereoisomeride*, m. p. 67°, by exposure to sunlight. The reverse change occurs if the colourless isomeride is exposed to sunlight in a solution containing a trace of iodine or bromine. Both the esters behave alike on oxidation by potassium permanganate in cold acetone solution, and they give the same product on treatment with nitromethane. Their behaviour towards alkaline reagents is not, however, the same. On boiling the yellow ester with dilute sodium carbonate solution, almost complete decomposition takes place, and it is not possible to isolate any benzoylacrylic acid. The colourless ester, under similar conditions, gives a 60% yield of benzoylacrylic acid. With concentrated hydrochloric acid, both the esters give a mixture of benzoylacrylic and α -hydroxybenzoylpropionic acids. The benzoylacrylic acid obtained in either of these cases corresponds, in configuration, with the yellow ester.

The colourless ester reacts with two molecules of semicarbazide hydrochloride to give the *semicarbazone of methyl α -semicarbazidobenzoylpropionate*, m. p. 177—178°. If, however, only one molecule of semicarbazide is used then the product is *methyl α -semicarbazidobenzoylpropionate*, m. p. 150—150.5°, which when treated in cold acid solution with sodium nitrite gives *methyl nitroso- α -semicarbazidobenzoylpropionate*, m. p. 125°. With one molecule of semicarbazide the yellow ester gives the same product as the colourless ester, but with two molecules it yields *methyl α -semicarbazido-3-phenylpyrazolone-4-acetate*, m. p. 172°, which when decomposed by hydrochloric acid gives the methyl semicarbazidobenzoylpropionate described above.

Ethyl benzoylacrylate was obtained in a yellow form, b. p. 184—185°/25 mm., and in a colourless form, m. p. 54°. As in the case of the methyl esters, the following products were prepared: the *semicarbazone of ethyl α -semicarbazidobenzoylpropionate*, m. p. 187°; *ethyl α -semicarbazidobenzoylpropionate*, m. p. 151—152°; *ethyl nitroso- α -semicarbazidobenzoylpropionate*, m. p. 127°; *ethyl α -semicarbazido-3-phenylpyrazolone-4-acetate*, m. p. 171°.

Benzoylacrylic acid reacts with semicarbazide, and gives the same products whether one or two molecules of the latter are used, namely, two isomeric *semicarbazones*, m. p. 205° and 225°, respectively, and a *hydrate* of the former, m. p. 190°. All three compounds react with bromine as unsaturated compounds and two atoms of bromine are added on to the molecule, and a *compound*, m. p. 171°, is obtained. W. G.

Dyes derived from Diphenic Anhydride. SIKHIBHUSHAN DUTT (T., 1923, **123**, 225—228).

The Action of Bromine on Methylcoumaric and Methylcoumarinic Acids. EINAR BILLMANN and HAKON LUND (*Ann. Chim.*, 1922, [ix], **18**, 263—282).—The addition of bromine in anhydrous solution to methylcoumaric and methylcoumarinic

acids apparently results in the formation of a single product (cf. Fittig and Ebert, A., 1883, 474; Werner, A., 1906, i, 180), but Perkin (T., 1881, 39, 420) and Stoermer and Friemel (A., 1911, i, 632) have obtained indications of two acids resulting. The last-named workers isolated an acid, m. p. 170° ; the authors' work confirms the formation of this single compound, but they were unable to determine its constitution with certainty, although the substance is presumed to be $\alpha\beta$ -dibromo- β -methoxyphenylpropionic acid. This acid on treatment with powdered zinc was converted into methylcoumaric acid, whilst water readily effected its hydrolysis into α -bromo- β -hydroxy- β -methoxyphenylpropionic acid, crystals, m. p. 134° , which yields on dehydration α -bromo- β -methoxyphenylacrylic acid, obtained directly from $\alpha\beta$ -dibromo- β -methoxyphenylpropionic acid by Perkin (*loc. cit.*). The hydrolysis by which the acid was obtained must not be effected at a high temperature, otherwise carbon dioxide is evolved with formation of *methoxybromostyrene*, a light yellow oil, b. p. $142\text{--}143^{\circ}/14\text{--}16$ mm., whilst hydrobromic acid in acetic acid solution reverses the hydrolysis. Treatment of the acid with zinc powder results in the formation of methylcoumaric acid. The last-named substance yields on bromination by means of solution of bromine in aqueous potassium bromide, $\alpha\beta$ -5-tribromo- β -methoxy-5-phenylpropionic acid, which was also obtained from $\alpha\beta$ -dibromo- β -methoxyphenylpropionic acid and bromine water, and also by the action of hydrobromic acid on α -5-dibromo- β -hydroxy- β -methoxyphenylpropionic acid. The latter was prepared by the action of bromine water on α -bromo- β -hydroxy- β -methoxyphenylpropionic acid and forms crystals, m. p. 137° , isomeric with and transformed by heating into an acid of m. p. 155° identical with that prepared by Read and Andrews (T., 1921, 119, 1782). This acid may also be obtained by hydrolysis of $\alpha\beta$ -5-tribromo- β -methoxyphenylpropionic acid, the reaction being reversed by hydrobromic acid. Mercuric acetate and methylcoumarinic acid combine to form a mercuric compound (cf. A., 1900, i, 431). This was not isolated, but was used as an intermediate in the preparation of β -hydroxy- β -methoxyphenylpropionic acid, which resulted from the elimination of the mercury by means of hydrogen sulphide. This acid has m. p. $88\text{--}5^{\circ}$ and is quantitatively converted into methylcoumaric acid when boiled with dilute sulphuric acid, whilst bromine water yields a ring-substituted derivative, 5-bromo- β -hydroxy- β -methoxyphenylpropionic acid, m. p. 108° . All the ring-substituted bromo-compounds dealt with are converted on oxidation with permanganate into 2-methoxy-5-bromobenzoic acid, and the same substance was obtained by oxidation of methylcoumaric acid with permanganate and subsequent treatment of the methoxybenzoic acid so formed with bromine water.

H. J. E.

The Chemistry of the Glutaconic Acids. XIV. Three-carbon Tautomerism in the *cyclo*Propane Series. FRANK ROBERT GOSS, CHRISTOPHER KELK INGOLD, and JOCELYN FIELD THORPE (T., 1923, 123, 327—361).

The Thermal Decomposition of certain Hydroaromatic Dicarboxylic Acids. A. WINDAUS, W. HÜCKEL, and G. REVEREY (*Ber.*, 1923, 56, [B], 91—98).—Blanc's rule (A., 1907, i, 710), according to which pimelic and adipic acids are converted into cyclic ketones when heated at about 300° (in the presence of acetic anhydride if necessary), whereas glutaric and succinic acids give internal anhydrides under similar conditions, appears to be generally applicable in the aliphatic series. An experimental examination of the possibility of applying it in the hydroaromatic series has been undertaken, and the behaviour of certain hydroaromatic o-dicarboxylic acids is now described.

cis-cyclo-Hexane-1 : 2-dicarboxylic anhydride is decomposed at 380° into carbon dioxide, water, anthraquinone, and various hydrogenated derivatives of anthracene; its behaviour is thus similar to that of calcium succinate.

Homophthalic [*o*-carboxyphenylacetic] acid is smoothly hydrogenated in glacial acetic acid solution in the presence of platinum black to a mixture of *cis*- and *trans*-*o*-carboxycyclohexanecarboxylic acids from which the pure *cis*-acid is isolated by fractional crystallisation; it forms aggregates of prisms, m. p. 146°, and is converted by acetic anhydride into the corresponding *anhydride*, rectangular plates, m. p. 57°. The *cis*-acid is isomerised by hydrochloric acid at 200° to the *trans*-acid, colourless crystals, m. p. 157° (*anhydride*, short needles, m. p. 80—81°). When either anhydride is heated for a considerable time at 220°, an equilibrium mixture containing about 25% of the *cis*- and 75% of the *trans*-variety is produced.

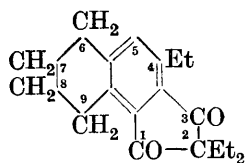
o-Carboxyphenylpropionic acid is catalytically hydrogenated to *cis*-*o*-carboxycyclohexanecarboxylic acid, prisms, m. p. 103°; the calcium salt and the *di-anilide*, lustrous leaflets, m. p. 159°, are described. The acid is isomerised by concentrated hydrochloric acid at 180° to *trans*-*o*-carboxycyclohexanecarboxylic acid, prisms, m. p. 143°. The corresponding *di-anilide*, m. p. 212°, is prepared from the acid and aniline or by heating the *cis*-*di-anilide* at 250°; it can be distilled unchanged in a high vacuum. The *cis*- or the *trans*-acid is not converted into an alicyclic ketone containing one less atom of carbon when heated alone, but either acid is transformed by distillation with acetic anhydride into *hexahydro- α -hydrindone*, $C_6H_{10} \begin{smallmatrix} CH_2 \\ CO \end{smallmatrix} > CH_2$, a colourless liquid, b. p. 216°/758 mm., d_4^{20} 0.9982, n_D 1.47915, n_D 1.48117, n_D 1.48827, n_D 1.49342. The corresponding *semicarbazone* crystallises in needles, m. p. 214—215° (decomp.) when rapidly heated; the *oxime*, lustrous needles, m. p. 79—80°, is described. H. W.

Total Hydrogenation of Naphthalic [Naphthalene-1 : 8-dicarboxylic] Acid. J. CASARES and J. RANEDO (*Anal. Fis. Quím.*, 1922, 20, 519—526).—Naphthalene-1 : 8-dicarboxylic acid was hydrogenated to the tetrahydro- and decahydro-acids by the action of hydrogen in the presence of platinum. Specially purified reagents were used, and repeated activations were necessary.

The decahydronaphthalene-1 : 8-dicarboxylic acid thus obtained has no definite melting point, and is probably a mixture of *cis*- and *trans*-isomerides. Hydrogenation was effected more easily and without activations by use of the methyl and ethyl esters of naphthalic acid. *Methyl tetrahydronaphthalene-1 : 8-dicarboxylate* thus obtained from methyl naphthalate forms crystals, m. p. 74°. *Ethyl tetrahydronaphthalene-1 : 8-dicarboxylate* forms crystals, m. p. 52°, and has b. p. 193°/17 mm. *Methyl decahydronaphthalene-1 : 8-dicarboxylate* forms crystals, m. p. 103—105°. G. W. R.

The Preparation of Benzenepentacarboxylic Acid. KARL FLEISCHER and EWALD RETZE (*Ber.*, 1923, 56, [B], 228—234).—A new method of preparing benzenepentacarboxylic acid (cf. Fleischer and Siefert, A., 1920, i, 621), which starts from tetrahydronaphthalene, is described.

2-Ethyl-5 : 6 : 7 : 8-tetrahydronaphthalene condenses with diethylmalonyl chloride in the presence of aluminium chloride and carbon disulphide to yield 2 : 2 : 4-triethyltetrahydronaphth- $\alpha\beta$ -indane-1 : 3-dione (annexed formula), colourless crystals, m. p. 39°. The substance is oxidised by nitric acid at 125—150° to 2 : 2-diethylindane-1 : 3-dione-4 : 5 : 7-tricarboxylic



acid, colourless crystals, m. p. 249° (decomp.) after slight previous softening; when more drastically treated with nitric acid, it gives benzenepentacarboxylic acid, m. p. 232—233°.

2 : 2 : 4-Triethyltetrahydronaphth- $\alpha\beta$ -hydrindene, a colourless liquid, b. p. 203—205°/19 mm., d_4^{20} 0.9673, n_D^{20} 1.5352, is isolated from the products of the action of amalgamated zinc and hydrochloric acid on 2 : 2 : 4-triethyltetrahydronaphth- $\alpha\beta$ -indane-1 : 3-dione. It condenses with acetyl chloride in the presence of aluminium chloride and carbon disulphide to yield 5-acetyl-2 : 2 : 4-triethyltetrahydronaphth- $\alpha\beta$ -hydrindene, colourless needles, m. p. 66° after softening at 63°, which, with *p*-nitrobenzaldehyde and potassium hydroxide solution, gives the corresponding *p*-nitrobenzylidene derivative, $C_{28}H_{33}O_3N$, canary-yellow needles, m. p. 161.5°. The acetyl compound is reduced by zinc and hydrochloric acid to 2 : 2 : 4 : 5-tetraethyltetrahydronaphth- $\alpha\beta$ -hydrindene, a pale yellow, very viscous liquid, b. p. 220—222°/20 mm., d_4^{27} 0.9647, n_D^{27} 1.5365.

H. W.

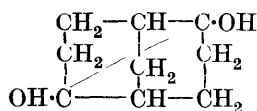
Dicyclic and Polycyclic Compounds with Bridged Linking. *dicyclo*-[1,3,3]-Nonane and its Derivatives. HANS MEERWEIN [with FRANZ KIEL, GUSTAV KLÖSGEN, and EDWIN SCHOCH] (*J. pr. Chem.*, 1922, [ii], 104, 161—206; cf. A., 1913, i, 869).—*dicyclo*-[1,3,3]-Nonan-2 : 6-dione, the preparation of which has now been slightly improved, has been further characterised by the formation of the unsaturated *diacetyl* derivative of the dienol form, colourless needles, m. p. 78—79°. When the *disemicarbazone*, a white, crystalline powder, m. p. 226°, is heated for six hours at 220° with 10% ethyl-alcoholic sodium ethoxide solution (cf. Wolff,

A., 1912, i, 988), dicyclononane (annexed formula), snow-white, feathery, plastic crystals, m. p. 145—146°, b. p. 168·5—170°, may be isolated from the product in 40% yield by distillation in steam.

Reduction of the dicyclononandione with sodium amalgam gives a mixture of a tri-cyclononandiol (see below) and trans-dicyclo-

[1,3,3]-nonan-2 : 6-diol, m. p. 219°, which gives a reddish-violet coloration with alcohol and sulphuric acid, and a sapphire-blue coloration with acetic anhydride and sulphuric acid. The diacetate, m. p. 35°, b. p. 173—174°/17 mm., and the dibenzoate, glistening, white leaflets, m. p. 96—97°, are described. On oxidation with chromic acid, the dicyclo-glycol is reconverted into the diketone. When dehydrated with sulphuric acid, it gives dicyclo-[1,3,3]- Δ^6 -nonen-2-ol, m. p. 133°, b. p. 224—226°, which has an intense camphor-like odour, is plastic, gives the same colour reactions as the dicyclo-glycol, and forms a liquid acetate, b. p. 111—112°/12 mm., having an intense odour resembling that of pine needles. This unsaturated alcohol, when reduced by means of hydrogen and platinum black, gives an 88% yield of dicyclo-[1,3,3]-nonan-2-ol, colourless crystals, m. p. 185°, which forms a liquid acetate, b. p. 128°/20 mm., and is oxidised by chromic acid mixture to dicyclo-[1,3,3]-nonan-2-one, plastic, colourless crystals, m. p. 150°; the ketone is characterised by the semicarbazone, colourless, needle-shaped crystals, m. p. 180—181°, the benzylidene derivative, m. p. 127—128°, which dissolves in concentrated sulphuric acid with a lemon-yellow coloration, and the cinnamylidene derivative, yellow needles, m. p. 116—117°, which similarly gives an orange-red coloration. Attempts to eliminate two molecules of water from the dicyclo-glycol have led only to resinous products, probably because the second double bond appears in the 5 : 6, and not the 6 : 7, position, the resulting hydrocarbon then isomerising to cyclooctatetrene, which is well known to polymerise easily.

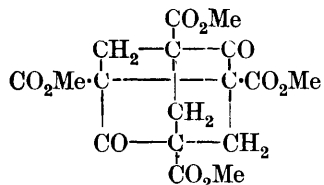
As mentioned above, the reduction of the dicyclo-diketone leads also to tricyclo-[1,3²,3⁶,0]-nonan-2 : 6-diol (annexed formula), which



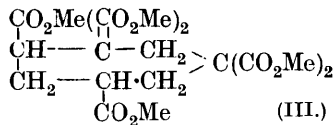
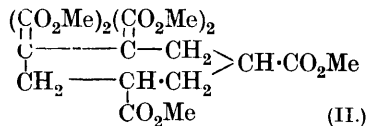
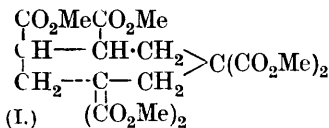
may most readily be obtained by using the crude reduction product for the preparation of the dicyclononanol, it being then isolated from the sulphuric acid residue after the unsaturated alcohol has been removed in a current of steam. It forms glistening needles, m. p. 141°, is appreciably volatile in steam, dissolves without any coloration in concentrated sulphuric acid, and is oxidised by chromic acid in glacial acetic acid solution to the original dicyclo-diketone. The diacetate, tabular crystals, m. p. 121°, the dibenzoate, needles, m. p. 153—154°, and the diphenylurethane, fine needles, m. p. 201°, are described.

Methyl dicyclo-[1,3,3]-nonan-2 : 6-dione-1 : 3 : 5 : 7-tetracarboxylate forms with sodium methoxide (1 mol.) a white, crystalline monosodium derivative, which is decomposed by water into the free ester (1 mol.) and the disodium derivative (1 mol.); the latter, which

is directly produced from the ester and sodium methoxide (2 mols.), is a colourless, crystalline, hygroscopic powder, dissolving in water with opalescence. The action of bromine (2 atoms) on the monosodium derivative gives *methyl 3-bromodicyclo-[1,3,3]-nonan-2:6-dione-1:3:5:7-tetracarboxylate*, rhombohedra, m. p. 154°, which is soluble in dilute alkalis and gives a reddish-violet coloration with ferric chloride. *Methyl 3:7-dibromodicyclo-[1,3,3]-nonan-2:6-dione-1:3:5:7-tetracarboxylate*, colourless prisms, which is formed from the above-mentioned disodium derivative and bromine (5 atoms), is insoluble in alkalis, does not give a coloration with ferric chloride, and melts at 142° with elimination of bromine, giving *methyl tricyclo-[1,3³,3⁷,0]-nonan-2:6-dione-1:3:5:7-tetracarboxylate* (annexed formula), colourless prisms from xylene and

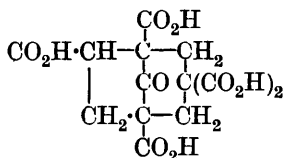


glacial acetic acid, leaflets from amyl-alcohol, m. p. 247—248°. The same compound is produced by the action of sodium and zinc dust in xylene solution on the dibromo-ester, by the action of bromine on the disodium derivative, or by the thermal decomposition of the *copper* compound of the *dicyclo-tetracarboxylic* ester (A., 1913, i, 869), but is most readily prepared by treating the monobromo-ester with sodium methoxide (1 mol.), care being taken to avoid excess of alkali during the reaction. The tricyclic ester undergoes fission with methyl-alcoholic sodium methoxide, two molecules of methyl alcohol being taken up, with formation of a *methyl cycloheptanehexacarboxylate*, white needles from amyl alcohol, large prisms from methyl or ethyl alcohol, m. p. 128°, which must have one of the formulæ (I), (II), or (III), according as fission occurs in the positions 2:3 and 6:7, 1:2



and 5:6, or 1:2 and 6:7, respectively. The corresponding *cycloheptanehexacarboxylic acid*, obtained by hydrolysing the ester with aqueous barium hydroxide, separates from glacial acetic acid or anhydrous formic acid as a microcrystalline powder, m. p. 177° (decomp.), and loses carbon dioxide when heated with water and a trace of hydrochloric acid, giving *cycloheptane-1:3:5:6-tetracarboxylic acid*, m. p. 233°, which is probably a mixture of several of the five possible stereoisomeric forms, and may be derived equally well from any of the three possible hexacarbomethoxy-esters. Alternate formulæ are suggested for the *dianhydride*, m. p.

197—198°. When the *tricyclo*-ester is heated with aqueous barium hydroxide, hydrolytic fission of the bond 2 : 3 (?) occurs, with formation of dicyclo-[1,2,3]-*octan-8-one-pentacarboxylic acid* (probable formula annexed), beautiful transparent prisms, which melt at 184—185° with evolution of carbon dioxide, but not of water.



Oxidation of the *dicyclononenol* (above) with chromic anhydride in glacial acetic acid solution gives dicyclo-[1,3,3]- Δ^6 -*nonen-2-one*, a white, plastic mass, of camphor-like odour, m. p. 82°, b. p. 213—217°; it forms a *semicarbazone*, star-shaped clusters of needles, m. p. 190·5—191°, and a *cinnamylidene* derivative, yellow needles, m. p. 117°, which dissolves in concentrated sulphuric acid with an orange-red coloration. By the reduction of the dioxime of the *dicyclononandione* (A., 1913, i, 869) by means of sodium and alcohol, trans-2 : 6-*diaminodicyclo*-[1,3,3]-*nonane* is produced as a transparent, crystalline, hygroscopic mass, b. p. 125—130/14 mm., which has a strong odour characteristic of bases and rapidly liquefies in contact with the air. The dihydrochloride, colourless, non-hygroscopic, crystalline powder, the *diacetyl* derivative, glistening clusters of needles, m. p. 214°, and the *dibenzoyl* derivative, indefinite crystals, m. p. 351°, are described. Distillation of the dihydrochloride gives 2-*aminodicyclo*-[1,3,3]- Δ^6 -*nonene*, a colourless, translucent, crystalline mass, m. p. 37·5°, b. p. 104°/17 mm., which rapidly liquefies on exposure to the air, possesses a strong odour reminiscent of both conine and nicotine, and is immediately oxidised by potassium permanganate in sulphuric acid solution.

Space formulæ are used to indicate the absence of strain, not only in dicyclo-[1,3,3]-*nonane* itself, but also in the *tricyclopinacone*, the 2 : 6 bridge-bond of which is opened and closed with extraordinary ease, and in the *tricyclo*-tetracarboxylic ester, the production of which by the thermal elimination of free bromine provides an entirely new type of ring formation. Since the *tricyclononandionetetracarboxylic ester* is nearly "spannungslos," the ready formation by the action of sodium methoxide of a *cycloheptane* ring is taken to indicate that the latter is also free from strain, and therefore probably lies in more than one plane.

The stability of the *dicyclononandionetetracarboxylic ester*, and the ready fission of the *tricyclo*-ester, with alkaline reagents, are ascribed to the presence in the former, but not in the latter, of hydrogen attached to the ring-atoms 3 and 7 (cf. Dieckmann, A., 1901, i, 539).

A similarity is indicated between the physical properties of the *dicyclononane* derivatives and compounds of the camphor series; this does not, however, extend to the physiological properties, examples of which, contributed by Schüller, are quoted.

W. S. N.

Cryoscopic Investigations on the Capacity to form Schiff's Bases. BERNARDO ODDO and FRANCESCO TOGNACCHINI (*Gazzetta*, 1922, 52, ii, 347—361).—The method previously used (A., 1913, i,

1233; 1915, ii, 414, 415, and this vol., i, 255) has now been applied to the investigation of the course of the reaction between aniline and a number of aliphatic and aromatic aldehydes and ketones. The molecular weight, calculated from the depression of the freezing point of the aniline, is expressed as a percentage of the theoretical value for the aldehyde or ketone taken, and the result plotted as a function of the time.

Like all aromatic aldehydes, *p*-tolualdehyde reacts promptly with aniline, whereas phenylacetaldehyde reacts decidedly more slowly; with cinnamaldehyde, the reaction takes place more easily. As in the reaction with phenylhydrazine, anisaldehyde reacts with aniline far more rapidly than does vanillin, the hydroxyl group apparently exerting a retarding effect; a similar effect is exercised by a nitro-group in the meta-position to the aldehyde group. Anisaldehyde, cuminaldehyde, *p*-nitrobenzaldehyde, and *p*-tolualdehyde, all of which are substituted in the para-position, exhibit similar molecular weight-time curves.

The reaction is relatively slow with aromatic, and more rapid with aliphatic, ketones, mixed ketones showing intermediate behaviour. The results given by benzil, acetylacetone, and acetonylacetone show that the reactivity increases with the degree of separation of the two carbonyl groups; with benzil, however, it is doubtful if the reaction proceeds in the direction of the formation of the Schiff's base. Further, it seems that only one carbonyl group reacts in the case of β -diketones, whereas both carbonyl groups of the γ -diketones react. With acetylacetone and acetonylacetone, the experimental conditions, and with the former also the results obtained, preclude the formation of heterocyclic nuclei.

Camphor reacts not at all with aniline, and menthone and carvone only slowly. As regards the cyclohexane ketones, the reaction is slowest with the ortho- and most rapid with the para-substituted compounds, cyclohexanone occupying an intermediate position. Phenanthraquinone and santonin react slowly and phenolphthalein instantaneously, the stage reached in ten minutes persisting unchanged for twenty-one hours. T. H. P.

Preparation of α -Homopiperonal from Safrole by the Action of Ozone, and Synthesis of its Derived Perfumes. I. SHŌICHIRO NAGAI (*J. Chem. Ind. Japan*, 1922, 25, 1409—1421; cf. S. Nagai, *ibid.*, 1922, 25, 631).—By passing about 36 litres per hour of air containing 2—3% of ozone into a glacial acetic acid (10—15 parts) solution of safrole (1 part) at the ordinary temperature, safrole ozonide is produced readily. The ozonide is, however, liable to decompose spontaneously even at the ordinary temperature when freed from the solvent, or when heated, and is also readily polymerised into resinous matter by the effect of heat, air, alkali, etc. If the ozonide is decomposed by adding gradually water and zinc powder to the acetic acid solution, a yield of about 60—65% of α -homopiperonal is obtained, which is further purified by conversion into the additive product with sodium hydrogen sulphite. α -Homopiperonal is a light yellow oil, b. p.

131—133°/8 mm., d_4^{15} 1.2654, n_D^{15} 1.5547, and gives an *oxime*, white needles, m. p. 119°, *semicarbazone*, white crystals, m. p. 176—177°, and *phenylhydrazone*, light yellow crystals, m. p. 176°. K. K.

Gallaldehyde. KARL W. ROSENEMUND (*Ber.*, 1923, 56, [B], 136).—In reply to the recent observations of Nierenstein (this vol., i, 91), the author maintains that the acidity of gallaldehyde is sufficiently great to prevent its isolation from sodium carbonate solution in the manner described by Nierenstein. H. W.

A New Compound from Conifer Distillates. KARL CEDERQUIST and BROR HOLMBERG (*Ber.*, 1923, 56, [B], 298—300).—The formation of a solid product, $C_{12}H_{16}O$, was observed in the condensers during the purification of wood spirit distilled without previous neutralisation from pyroligneous acid derived from a mixture of pine wood (80%) and spruce wood (20%). It forms colourless prisms, m. p. 69—70°, and is optically inactive. It appears to be either an aldehyde or a ketone, since it is convertible into a *semicarbazone*, flattened needles or thin prisms, m. p. 198—199°, and two *oximes*, long, flattened prisms, m. p. 110—113°, and hairs or needles, m. p. 85—86°. H. W.

Action of Organomagnesium Compounds on Nitriles.
Action of Magnesium Phenyl Bromide. LOUIS BARY (*Bull. Soc. chim. Belg.*, 1922, 31, 397—410).—The action of magnesium phenyl bromide on nitriles has been studied to compare it with that of magnesium methyl and ethyl bromides (cf. Bruylants, *Bull. Acad. roy. Belg.*, 1922, [v], 8, 7; Baerts, A., 1922, i, 817). In general far higher yields of ketone are obtained than is the case with the magnesium methyl and ethyl bromides, none at all, for example, being formed when these react with acetonitrile, whereas magnesium phenyl bromide gives a yield of about 45% of ketone. In the case of the aliphatic nitriles, the yield of ketone increases with increase of the length of the carbon chain.

In the case of benzonitrile, the intermediate product, diphenylketimine, CPh_2NH , was isolated in 75% yield, and is characterised by exceptional stability compared with those ketimines in which an alkyl group is united to the ketonic carbon. This is attributed to the fact that in diphenylketimine there is no possibility of tautomeric change of the type $NH:CR \cdot CH_2Me \rightleftharpoons NH_2 \cdot CR:CHMe$. The nitrile of cyclopropanecarboxylic acid also gave a good yield of *phenylcyclopropylketimine*, a liquid of pungent, disagreeable odour, b. p. 135—136°/25 mm., d_4^{20} 1.0663, n_D^{20} 1.56201. It is rapidly converted by dilute acid into phenyl cyclopropyl ketone (Perkin, T., 1885, 47, 840), a liquid of pleasant odour, b. p. 239°, d_4^{20} 1.0566, n_D^{20} 1.5565. The *semicarbazone* has m. p. 189°.

Phenylacetonitrile, acetonitrile, propionitrile, and *n*-butyronitrile yielded the ketone and condensation products, but the ketimine was not obtained. P. M.

The Formation of Ketazines, Phenylhydrazones, and Semicarbazones of Ring-substituted Acetophenones. W. J. BRUINING (*Rec. trav. chim.*, 1922, 41, [ii], 655—686).—In order to

ascertain whether acetophenone derivatives react with hydrazine, phenylhydrazine, and semicarbazide in an analogous manner to those of benzaldehyde, the author has studied the formation of ketazines, phenylhydrazones, and semicarbazones of ring-substituted acetophenones. The general conclusions drawn are (1) that glacial acetic acid is a suitable solvent for the preparation of such phenylhydrazones, (2) that the ketazines are only formed in acid solution, their preparation presenting no difficulty when hydrazine sulphate is used, whilst a boiling solution of hydrazine brings about no reaction, (3) that the nature of the ketone used is related to the speed of formation of the ketazine and conditions the state of equilibrium when formation and decomposition of ketazine are taking place at equal rates, (4) that the formation of the semicarbazones occurs more rapidly in acid than in alkaline or neutral solution, but excess of acid decomposes the semicarbazones into their constituents, and (5) that in some cases the nitro-group in the ortho-position with respect to carbonyl considerably diminishes the reactivity of the carbonyl group. The following substances are described: *p*-acetamidoacetophenoneketazine, yellow crystals, m. p. 311° ; *p*-acetamidoacetophenonephenylhydrazone, m. p. $196-200^{\circ}$; *p*-acetamidoacetophenonesemicarbazone, white crystals, decomp. 220° ; 3:5-dibromo-*p*-aminoacetophenoneketazine, yellow crystals, decomp. 297° ; 3:5-dibromo-*p*-aminoacetophenonesemicarbazone, white crystals, m. p. 255° (decomp.); 3:5-dibromo-*p*-acetamidoacetophenone, m. p. $188-189^{\circ}$, yielding a ketazine, yellow, m. p. 344° (decomp.), a phenylhydrazone, pale yellow crystals, m. p. $244-246^{\circ}$, and a semicarbazone, white crystals, decomp. 325° ; 3:5-dibromo-*p*-diacetamidoacetophenone, obtained in two modifications, (a) unstable, m. p. 67° , which passes after some days into (b) stable, m. p. 88° ; 3:5-dibromoacetophenoneketazine, m. p. 231° ; 3:5-dibromoacetophenonephenylhydrazone, light yellow needles, m. p. $109-110^{\circ}$; 3:5-dibromoacetophenonesemicarbazone, white crystals, m. p. 268° (decomp.); 3:4:5-tribromoacetophenone, white crystals, m. p. $134-135^{\circ}$, yielding a ketazine, small, yellow crystals, m. p. 300° , a phenylhydrazone, yellow crystals, m. p. $129-134^{\circ}$, and a semicarbazone, white crystals, decomp. 265° ; 3:5-dibromo-2-nitroacetophenone, pale yellow crystals, m. p. $133-144^{\circ}$, yielding a ketazine, m. p. 210° , a phenylhydrazone, m. p. $165-166^{\circ}$, and a semicarbazone, m. p. 234° (decomp.); 3:4:5-tribromo-2-nitroacetophenone, white needles, m. p. $188-189.5^{\circ}$, yielding a ketazine, yellow needles, m. p. 244° , a phenylhydrazone, red crystals, m. p. $173-174^{\circ}$, and a semicarbazone, decomp. 249° .

H. J. E.

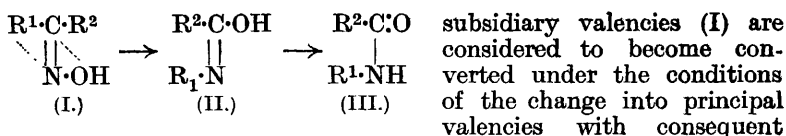
The Action of an Alcoholic Solution of Potassium Hydroxide on Ketones. VII. The Action of an Alcoholic Solution of Potassium Hydroxide on *p*-Hydroxy- and *p*-Ethoxybenzophenone and their *m*-Bromo-derivatives. P. J. MONTAGNE (*Rec. trav. chim.*, 1922, 41, 703-721; cf. A., 1920, i, 394).—The action of alcoholic potassium hydroxide on benzophenones effects the reduction of the carbonyl group to an alcoholic

group and also, in the case of halogen-substituted benzophenones, the partial replacement of halogen atoms in the ring by hydrogen. A retarding action is exerted by the ethoxyl group in the para-position; this is considerably diminished by the presence of a bromine atom in a similar position in the other ring. In the case of benzophenone itself, heating at 100° for two days completes the reduction, whilst on heating 4-ethoxybenzophenone for six days under similar conditions so little change occurs that it is found impossible to isolate the reduction product. On introducing a bromine atom into the meta-position in the ring to which the ethoxyl group is attached, the greater part of the substance is reduced after two days; a second bromine atom in the meta-position in the same ring entirely masks the retarding effect of the ethoxyl group and the substance behaves similarly to benzophenone. The author points out that the action of bromine is similar in the case of 4:4'-dibromo-3:3'-diaminobenzophenone (A., 1917, i, 143). None of the corresponding hydroxybromobenzophenones is reduced even after prolonged heating, so that the effect of the hydroxyl group in inhibiting reduction is not diminished to any appreciable extent by bromine. The products resulting from the action of alcoholic potassium hydroxide on 3:5-dibromo-4-ethoxybenzophenone are 3:5-dibromo-4-ethoxybenzhydrol, 3-bromo-4-ethoxybenzhydrol, and 3:5-dibromo-4-hydroxybenzophenone, the two last-named being formed in small quantity. Hydrolysis of the ethoxyl group thus takes place to a limited extent. The introduction of a second ethoxy-group into the other ring increases the influence of the first and reduction is then incomplete after heating for six days.

The following substances were prepared: 3'-bromo-4-hydroxybenzophenone, crystals, m. p. 171° ; 3-bromo-4-ethoxybenzophenone, rhombic bipyramidal crystals ($a:b:c=0.7935:1:0.2691$), m. p. 102.25° ; 3-bromo-4-ethoxybenzhydrol, colourless crystals, m. p. 85° ; 3:5-dibromo-4-ethoxybenzophenone, colourless, monoclinic crystals ($a:b:c=1.0901:1:0.8591$; $\beta=59^{\circ}41'$), m. p. 83.5° , b. p. $244^{\circ}/11$ mm.; 3:5-dibromo-4-ethoxybenzhydrol, small needles, m. p. 81.75° ; 3'-bromo-4-ethoxybenzophenone, colourless crystals, m. p. 79.5° , b. p. $232^{\circ}/11$ mm.; 3'-bromo-4-ethoxybenzhydrol, needles, m. p. 43° ; 3:5-dibromobenzophenone, m. p. 75° , b. p. $232^{\circ}/18$ mm.; 4:4'-diethoxybenzophenone, small, colourless plates, m. p. 132° , b. p. $258^{\circ}/15$ mm.; 4:4'-diethoxybenzhydrol, crystals, m. p. 59° . 4-Ethoxybenzophenone crystallises in the monoclinic system ($a:b:c=0.7427:1:1.6049$; $\beta=87^{\circ}58'$). H. J. E.

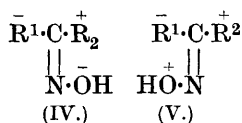
Formation and Transformation of the Naphthyl Ketoximes.

ERNST BECKMANN, OTTO LIESCHE, and ERICH CORRENS (*Ber.*, 1923, 56, [B], 341—354).—The isomerism of ketoximes has been explained by Hantzsch and Werner in accordance with the principles of ethylenic isomerism and the arbitrary but plausible assumption that the vicinal groups in these compounds exchange places during the course of the Beckmann transformation has been generally accepted until recently. Bucherer, however (*Lehrbuch der Farbenchemie*, 1914), has put forward a scheme in which the



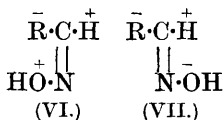
conversion of the form I into form II, from which the stable modification (III) of the transformation product is readily derived. The transformation thus consists in a change of position between the hydroxyl group and the oppositely situated radicle. Similar views have been expressed more recently by Biltz and Robl (A., 1921, i, 891) and by Meisenheimer (A., 1922, i, 152, 176). The conception has the advantage that the chemical unity of the molecule is regarded as being in a measure preserved throughout the change whereas the direct exchange of position of two neighbouring groups is scarcely possible without intermediate rupture of the molecule.

Confirmation of this view of the transformation is deduced in a somewhat different manner. In accordance with Abegg's electrochemical view of the stability of oximes, the disposition of the relatively positive and negative radicles in the alkali-stable and "acid-stable" oximes must be that shown in the annexed formulæ (IV) and (V). It is found that in the "alkali-stable" form the



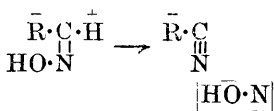
more strongly negative radicle, R^1 , wanders, whereas in the "acid-stable" variety the less strongly negative radicle, R^2 , migrates during the Beckmann change. The evidence is based on the behaviour of the phenyl naphthyl ketoximes (Betti and Becciolini, A., 1916, i, 49; Poccianti, A., 1915, i, 822) and the dinaphthyl ketoximes in which, in accordance with the dissociation constants of the corresponding carboxylic acids, the phenyl and β -naphthyl groups are considered to be about equally negative and considerably inferior in this respect to the α -naphthyl radicle.

Difficulties appear to be encountered when these views are applied to aldioximes. The varieties which readily yield nitriles



are in general favoured by the action of acids and to them the constitution VI must be ascribed, whereas the isomerides which can be successively esterified and hydrolysed without undergoing decomposition must have the configuration, VII. This, however, is

contrary to the accepted view that the water-forming groups must be obtained from vicinal positions in the compound. The



change is possibly explicable in accordance with the annexed scheme. In any case it appears to be established that in the acid-stable variety of aldioximes (*syn*-oxime) the hydrogen, as positive radicle, wanders when the change results

in the formation of a nitrile or when a normal Beckmann rearrangement occurs.

Di-β-naphthylketoxime, needles, m. p. 180—181°, is converted by phosphorus pentachloride in the presence of anhydrous ethyl ether into *β-naphtho-β-naphthylamide*, colourless, lustrous needles, m. p. 239°, the constitution of which is established by its synthesis from *β-naphthoyl chloride* and *β-naphthylamine*. *Di-α-naphthylketoxime*, small, colourless needles, m. p. 200°, is transformed similarly into *α-naphtho-α-naphthylamide*, m. p. 241°. *α-Naphthyl β-naphthyl ketone*, m. p. 135°, is prepared by the action of magnesium *α-naphthyl bromide* on *β-naphthonitrile* (the intermediate compound, $\alpha\beta\text{-(C}_{10}\text{H}_7)_2\text{C:N}\cdot\text{MgBr}$, yellow crystals, m. p. 255°, was isolated); it is converted quantitatively in acid solution at 135—140° into *α-naphthyl β-naphthyl ketoxime*, m. p. 171°, which is transformed into *α-naphtho-β-naphthylamide*, colourless needles, m. p. 200°, identical with the product obtained by the action of *α-naphthoyl chloride* on *β-naphthylamine*. H. W.

Studies in the Anthracene Series. IV. EDWARD DE BARRY BARNETT and MARCUS AURELIUS MATTHEWS (T., 1923, 123, 380—394).

Benzaurin. RICHARD MEYER and WILLY GERLOFF (*Ber.*, 1923, 56, [B], 98—104).—In a previous communication (Meyer and Fischer, A., 1913, ii, 167) it has been shown that the absorption spectrum of benzaurin is so similar to that of fuchsone that it must almost necessarily be regarded as a *p*-hydroxyfuchsone, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CPh}\cdot\text{C}_6\text{H}_4\cdot\text{O}$. Analysis of the dye, however, gives results which are in harmony with the formula $\text{OH}\cdot\text{CPh}(\text{C}_6\text{H}_4\cdot\text{OH})_2$. It is found, however, that a molecular proportion of water is readily lost when the dye is heated, and that the residue has the composition of *p*-hydroxyfuchsone. Benzaurin is therefore regarded as a hydrate of *p*-hydroxyfuchsone. This conception explains the behaviour of the substance when dissolved in alcohol or acetic acid (Meyer and Fischer, *loc. cit.*), the deepening in colour observed when the alcoholic solution is warmed and the formation of an orange-coloured solution in the cold acid being attributable to the withdrawal of water and the production of the more intensely coloured *p*-hydroxyfuchsone.

Since benzaurin obtained by Doebner's method from benzo-trichloride and phenol (*p*-hydroxybenzophenone is formed as by-product) is not crystalline and has not a definite melting point, various attempts have been made to secure a more definitely homogeneous product. The oxidation of 4 : 4'-dihydroxytriphenylmethane, m. p. 161° (acetate, m. p. 115°), or the hydrolysis of benzaurin diacetate, m. p. 119°, or *benzaurin dibenzoate*, colourless needles, m. p. 183—184°, did not lead to the desired result. More success is obtained by decomposing benzaurin perchlorate (cf. Pfeiffer, A., 1917, i, 210) with the requisite quantity of sodium hydroxide and subsequently adding dilute sulphuric acid, whereby benzaurin is caused to separate as a brilliant red precipitate. It loses one molecular proportion of water at 110—120°.

Benzaurin hydrochloride, dark red needles, is obtained by the

addition of an excess of fuming hydrochloric acid to a solution of benzaurin in glacial acetic acid. H. W.

Di- and Tri-hydroxydeoxybenzoins. ERNEST CHAPMAN and HENRY STEPHEN (T., 1923, 123, 404—409).

The Reactivity of Doubly-conjugated Unsaturated Ketones.
IV. The Effect of Substitution on the Reactivity of 4'-Dimethylamino-2-hydroxydistyryl Ketone. ISIDOR MORRIS HEILBRON and ABRAHAM BRUCE WHITWORTH (T., 1923, 123, 238—245).

The Benzilic Acid Transformation. I. G. SCHEUING (*Ber.*, 1923, 56, [B], 252—259).—It is shown that the bluish-violet dye which is produced during the preparation of benzilic acid from benzil and ethyl-alcoholic potash has no direct effect on the transformation. The attempts which have been made previously to explain the course of the benzilic acid transformation assume the rupture of one or both double bonds between the carbon and oxygen atoms of benzil by the addition of water or potassium hydroxide. Such compounds have now been isolated.

Benzil potassium hydroxide, $C_{14}H_{10}O_2.KOH$, small, indistinct, pale yellow crystals, is obtained when an intimate mixture of benzil and dry potassium hydroxide is triturated beneath a little pyridine or benzene, or by the addition of a concentrated alcoholic solution of potassium hydroxide to a cold solution of benzil in ether. It is decomposed into its components by water and into potassium hydrogen carbonate and benzil by dry carbon dioxide. It is converted slowly at 0° , in a few hours at the atmospheric temperature, and almost instantaneously at 80° , into potassium benzilate, so that it appears to be a definite intermediate product of the conversion of benzil into benzilic acid.

In a similar manner, the addition of a solution of potassium in methyl alcohol and ether to an ethereal solution of benzil leads to the separation of the compound $C_{14}H_{10}O_2.MeOK.MeOH$, small, almost colourless crystals, which is decomposed by water, alcohol, or carbon dioxide in the same manner as the product from potassium hydroxide. On the other hand, it does not undergo a similar smooth transformation, which only occurs to the extent of 15% when it is preserved beneath ether during two days at the atmospheric temperature. The product of the change is benzilic acid, whereas methyl benzilate or methoxydiphenylacetic acid would be expected. Transformation does not take place to any considerable extent when it is heated in the presence of benzene; the main products are unchanged benzil and benzoin, the latter being formed owing to the reducing action of potassium methoxide. *Benzil sodium ethoxide*, $C_{14}H_{10}O_2.EtONa$, a pale yellow, distinctly crystalline substance, is prepared by the addition of sodium ethoxide dissolved in a mixture of ethyl alcohol and xylene to a solution of benzil in the latter solvent. The formation of benzil potassium ethoxide can only be observed at a low temperature; it becomes altered in an unexplained manner at 0° . H. W.

The Beckmann Transformation in the Cases of *o*- and *p*-Quinoneoximes. ERNST BECKMANN and OTTO LIESCHE (*Ber.*, 1923, 56, [B], 1—23).—The experiments described do not establish beyond all doubt the normal course of the Beckmann transformation in the cases of *p*- and *o*-quinones. The expected enlargement of the ring appears to be proved most conclusively in the instance of anthraquinonemonoxime. The direct action of the transforming agents on dioximes does not appear to lead to the production of an eight-membered ring containing two nitrogen atoms, but this seems possible in the case of anthraquinone if the monoxime is first transformed and the product converted into its oxime and again transformed.

I. *Phenanthraquinone- and naphthaquinone-oxime* [with HERBERT DIETRICH].—The action of phosphorus pentachloride on β -naphthaquinoneoxime [2-nitroso- α -naphthol] has been studied by Borsche and Sander (*A.*, 1915, i, 299), who have isolated a product to which they ascribe the constitution $\text{COCl}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{CN}$, but for which the cyclic structure, $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{CCl}=\text{N} \\ \text{CH}\cdot\text{CH} \end{smallmatrix}\rangle\text{CO}$, appears to the authors to be equally possible. The same chloride, colourless, matted needles, m. p. 80° , is obtained by the action of phosphorus pentachloride on the oxime in the presence of light petroleum. It is converted by ammonia in the presence of anhydrous ether into the substance $\text{C}_{10}\text{H}_8\text{ON}_2$, m. p. 207° , and by boiling water into the monobasic acid, $\text{C}_{10}\text{H}_7\text{O}_2\text{N}$, m. p. 179° , the *silver, sodium, potassium, and barium* salts of which are described. It is hydrolysed by boiling aqueous sodium hydroxide solution to *o*-carboxycinnamic acid, m. p. 184° (the *silver* salt is described). The action of a saturated solution of hydrogen chloride in a mixture of glacial acetic acid and acetic anhydride or of benzenesulphonyl chloride in the presence of pyridine on β -naphthaquinoneoxime gives the acid, $\text{C}_{10}\text{H}_7\text{O}_2\text{N}$, m. p. 179° , the properties of which appear to the authors to be compatible with either the cyclic or open structure.

β -Naphthaquinonedioxime is converted by phosphorus pentachloride in the presence of light petroleum by the Beckmann mixture and by benzenesulphonyl chloride and pyridine into the anhydride, $\text{C}_{10}\text{H}_6\text{ON}_2$, m. p. 81° , the ready formation of which causes a stabilisation which inhibits the Beckmann transformation.

α -Naphthaquinonemonoxime [4-nitroso- α -naphthol] does not undergo a smooth transformation with any of the reagents investigated. With Beckmann's mixture, it yields a compound, $\text{C}_{12}\text{H}_9\text{O}_3\text{NCl}_2$, long needles, m. p. 165° after previous softening. With benzenesulphonyl chloride and pyridine, the ester, $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{C}(\text{O}\cdot\text{SO}_2\text{Ph})\cdot\text{CH} \\ \text{C}(\text{NO})=\text{CH} \end{smallmatrix}\rangle$, colourless, matted needles, m. p. 183 —

184° , is produced. α -Naphthaquinonemonoxime is not affected by boiling acetyl chloride, but is converted by the cold reagent into ill-defined compounds containing halogen. The *acetyl* derivative, $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{C}(\text{OAc})\cdot\text{CH} \\ \text{C}(\text{NO})=\text{CH} \end{smallmatrix}\rangle$, lustrous, brown needles, m. p. $132\cdot5^\circ$, is obtained readily by the action of acetic acid and acetic anhydride;

it does not yield homogeneous products when treated with the transforming agents.

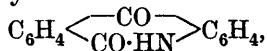
α -Naphthaquinonedioxime is converted by the Beckmann mixture into the corresponding diacetate, m. p. 164°, which is transformed by the reagent at a higher temperature into ill-defined chlorinated compounds.

II. *Benzoquinone- and Anthraquinone-oximes* [with A. PHILIPPOVICH VON PHILIPPSBERG].—*p*-Benzoquinonemonoxime is converted by benzenesulphonyl chloride in the presence of pyridine into the corresponding ester, m. p. 131°, which (without being isolated) is transformed by being further heated and subsequently treated with sulphuric acid into the compound, $\text{CO} \begin{smallmatrix} \text{CH:CH}\cdot\text{CO} \\ \text{CH:CH}\cdot\text{NH} \end{smallmatrix}$, yellowish-

brown needles, m. p. 224°. The substance dissolves in solutions of alkali hydroxides and carbonates yielding solutions from which the *cobalt, silver, molybdenum, manganese, tin, zinc, lead, and iron* salts are prepared; it gives a *benzoyl* derivative, leaflets, m. p. 189—190°.

Many attempts are described to effect the transformation of *p*-benzoquinonedioxime, but these have not been successful. Apparently the conversion only occurs if a certain minimum temperature is exceeded (below which only salt formation takes place). With the compound in question, this temperature is so high that, when augmented by the local and unavoidable heat of the reaction, it causes the extensive decomposition of the products of the change.

Anthraquinonemonoxime is converted by a mixture of phosphorus pentachloride and acetyl chloride into the compound,



short, colourless needles, m. p. 245°, which is transformed by successive treatment with boiling sodium hydroxide solution and acid into 2-*o*-aminobenzoylbenzoic acid, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, m. p. 199° (decomp.), the *silver, lead, and copper* salts of which are described. It yields a *methyl* ester, m. p. (indefinite) 168—173°. The presence of the amino-group is established by its ability to yield a diazo-compound. Anthraquinonemonoxime is converted by a mixture of phosphorus pentachloride and phosphoryl chloride into the phosphoric acid derivative, which is isolated as the *silver* salt, $\text{CO} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{C}\cdot\text{N}\cdot\text{O}\cdot\text{PO}(\text{OAg})_2$, whereas benzenesulphonyl chlor-

ide and pyridine transform it into the corresponding *ester*, $\text{C}_{20}\text{H}_{13}\text{O}_4\text{NS}$, slender, colourless needles, m. p. 154°. The transformation product, $\text{C}_{14}\text{H}_9\text{O}_2\text{N}$, is converted by further treatment with hydroxylamine hydrochloride in boiling alcoholic solution (96%) into the corresponding *oxime*, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{C}(\text{NOH}) \\ \text{CO}\cdot\text{HN} \end{smallmatrix} \text{C}_6\text{H}_4$, colourless needles, m. p. 243° (decomp.) [*benzoyl* derivative, m. p. 209°], which is converted by the Beckmann mixture at 170° into phthalyl-*o*-phenylenediamine, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO}\cdot\text{NH} \\ \text{CO}\cdot\text{NH} \end{smallmatrix} \text{C}_6\text{H}_4$, m. p. 275—

278°, identical with the product synthesised by Anderlini and Meyer (A., 1906, i, 765), for which, however, an alternative constitution has been suggested by Thiele and Falk (A., 1906, i, 750).
H. W.

Arylamine Salts of the Anthraquinonesulphonic Acids.

A. G. PERKIN and W. G. SEWELL (*J. Soc. Chem. Ind.*, 1923, 42, 27—31r).—The arylamine salts of the anthraquinonesulphonic acids are well-defined crystalline substances, sparingly soluble in water or alcohol. They are readily obtained by adding an acid solution of the arylamine hydrochloride to a solution of the sodium salt of the sulphonic acid. The salts are useful for the purification of the alkali salts of the sulphonic acids, and they can also be used for transforming one alkali or alkaline-earth salt into another, as they are easily reconverted into a metallic salt by boiling with the requisite quantity of either aqueous or alcoholic alkali or alkaline-earth hydroxide. Certain of these salts, notably the aniline salts, can be employed with fair exactitude for the analysis of anthraquinone-mono- and -di-sulphonates by titrating a suspension of the aniline salt in boiling water with standard alkali hydroxide in presence of phenolphthalein. Advantage can be taken of the sparing solubility of the methylaniline, compared with the dimethylaniline β -sulphonates, to effect a fairly complete separation of methylaniline from a mixture of the two bases, provided it is present in considerable amount. The following are among the salts described: *Aniline anthraquinone-2-sulphonate*, colourless needles, m. p. 309°; *p-toluidine anthraquinone-2-sulphonate*, colourless needles, m. p. 308°; α -*naphthylamine 2-sulphonate*, m. p. 253°; *aniline anthraquinone-1-sulphonate*, m. p. 284°; *methyl-aniline anthraquinone-2-sulphonate*, m. p. 202—203°; *dimethylaniline 2-sulphonate*, m. p. 192—194°; *1-sulphonate*, m. p. 215°; *diethyl-aniline anthraquinone-2-sulphonate*, m. p. 174—175°; the aniline salts of the following anthraquinonedisulphonic acids, 1:5-, orange-yellow crystals; 1:8-, needles; 2:6-, plates; and 2:7-, plates; none of these salts exhibited a melting point. The *methyl-aniline* salts of the 1:5-disulphonic acid, m. p. 251°, orange plates; 1:8-disulphonic acid, 2:6-disulphonic acid, needles, m. p. 205—210°, and 2:7-disulphonic acid, m. p. 230°, are described, as also are the corresponding dimethylaniline salts. *Quinoline anthraquinone-1-sulphonate* melts at 195°, and the 2-sulphonate at 225°. *Pyridine anthraquinone-1-sulphonate* forms needles, m. p. 158°.

G. F. M.

The Camphor Series. II. SHIGERU KOMATSU (*Mem. Coll. Sci. Kyoto*, 1922, 6, 55—72).—[With KITARO FUJII].—Applying Reformatzky's synthesis to *d*-camphor, using ethyl, *l*-menthyl, and *d*-bornyl esters of iodoacetic acid, esters of bornylacetic acid were obtained, all of which gave the same *l*-isobornylacetic acid on hydrolysis. *Ethyl isobornylacetate*, $C_9H_{16} \cdot C(OH) \cdot CH_2 \cdot CO_2Et$, is a viscous liquid, b. p. 108—112°/3 mm., $[\alpha]_D^{25} = -24.97^\circ$. *l*-*Menthyl isobornylacetate* was obtained as a syrup. *d*-*Bornyl isobornylacetate*, m. p. 196—197°, has $[\alpha]_D^{18} + 17.44^\circ$. *l*-*Bornylacetic acid*,

prepared from the ethyl ester, had $[\alpha]_D^{17} -20.32^\circ$, from the *d*-menthyl ester, -19.85° , and from the *d*-bornyl ester, -25.62° , all in alcohol. For the *barium* salt in water, values of $[\alpha]_D^{18}$ from 9.53° to 12.91° were observed.

[With SHOZO YAMAGUCHI.]—When *d*-camphoroxime was reduced by Forster's method in amyl alcohol with sodium, *d*-bornylamine and *l*-isobornylamine were formed in the proportions of 65.9% of the former to 34.1% of the latter. The high proportion of *l*ævo compound formed, compared with the proportion of *l*-borneol formed by the reduction of *d*-camphor, 19%, may be attributed to the influence of the more positive amino-group on the asymmetric transformation of the carbonyl carbon atom in the camphor molecule. When *d*-bornylamine was passed over thoria at 400° , it was decomposed into camphene and ammonia.

[With RISABURO NAKAI.]—When *d*-borneol was passed over thoria at 400° with ammonia gas, no bornylamine was formed, but *d*-camphene was obtained; in the same way, *l*-borneol gave *l*-camphene. It is probable that camphene was not formed directly from borneol by the Wagner rearrangement, but through the intermediate formation of bornylamine which, as shown above, decomposes into camphene and ammonia. Both *d*- and *l*-camphene gave the same *l*-isocamphane when reduced with hydrogen in presence of nickel. Some specimens of *d*-camphene were found to solidify on keeping; the crystals had m. p. 50° , $[\alpha]_D^{20} +17.61^\circ$. The question of the existence of solid and liquid forms of camphene is being further investigated.

E. H. R.

Pinene of Spanish Turpentine. A. MADINAVEITIA (*Anal. Fis. Quim.*, 1922, 20, 531—533).—By fractional distillation of different samples of Spanish turpentine, collecting the fraction $154.5\text{--}157^\circ$, yields of pinene varying from 35 to 90% are obtained. Except in the case of turpentine from *Pinus halepensis*, the pinene obtained is dextrorotatory. The differences in yield of pinene by fractional distillation are attributed to the presence of varying amounts of nopinene.

G. W. R.

Castelamarin—A Bitter Principle from *Castela Nicholsoni*. LOUIS PIERRE BOSMAN (*T.*, 1923, 123, 207—210).

Chinese Tannin. J. HERZIG (*Ber.*, 1923, 56, [B], 221—228).—The methylation of Chinese tannin by means of diazomethane has been reinvestigated and methylotannin (cf. Herzig and Tscherne, A., 1905, i, 254) has been prepared in excellent yield. As judged by the specific rotation and methoxyl content, the product must be regarded as homogeneous; if this is the case, the yields show that the parent substance of methylotannin must be present to the extent of at least about 90% in Chinese tannin. Additional evidence of the chemical individuality of Chinese tannin is thus adduced (cf. Iljin, A., 1914, i, 567; Freudenberg, A., 1922, i, 1170).

The main reason for the poor yields of methylotannin which have been encountered frequently is to be found in ester transformation, which leads to the production of methyl trimethoxy-

benzoate. In two instances, methyl pentamethyl-*m*-digallate was isolated and this appears to be the first instance in which this compound has been prepared from Chinese tannin directly. The improvement in the methylation of the tannin is brought about by the preliminary, repeated distillation of the ethereal solution of diazomethane at as low a temperature as possible, and with the help of a dephlegmator. The residue, after removal of the excess of the reagent and desiccation in a vacuum, is solid and can be powdered; occasionally it is obtained directly in pulverulent form. It is almost completely insoluble in cold methyl alcohol, after treatment with which it has a methoxyl content almost identical with that of methylotannin obtained previously. After further purification from warm methyl alcohol, it has $[\alpha]_D^{25} + 12.44^\circ$, $[\alpha]_D^{24} + 12.75^\circ$, $[\alpha]_D^{22} + 12.22^\circ$ in benzene solution (2%), whereas Herzog and Renner (A., 1909, i, 713) found $+9^\circ$ to $+11^\circ$.

H. W.

[Tannins and Similar Substances. II. Chinese Tannin.] KARL FREUDENBERG and WILHELM SZILASI (*Ber.*, 1923, 56, [B], 406).—The preparation of highly active Chinese tannin (A., 1922, i, 1169) only succeeds when the crude tannin, $[\alpha]_D + 90^\circ$, has remained for a protracted period in aqueous solution in contact with aluminium hydroxide.

H. W.

Reduction of an Indanthrene Dye by Means of Sodium Hyposulphite. JOHN H. YOE and GRAHAM EDGAR (*J. Physical Chem.*, 1923, 27, 65—73).—The reaction between an oxyindanthrene dye (Ponsol-yellow-G) and sodium hyposulphite has been investigated, and it is shown that the reduction and solution of the dye involve (a) the comparatively rapid reaction of the dye with the hyposulphite to form an insoluble crystalline reduced dye, and (b) peptisation of the latter by hydroxyl-ions, with the formation of a colloidal solution. The rate of solution and the amount of dye peptised by a given solution depend on the state of subdivision of the dye. Positive ions tend to coagulate the solution and to retard the peptisation of the reduced dye.

J. S. G. T.

Ability of Alkaloids to Form Oxides. Oxygenase of the Bach-Chodat System. OBDULIO FERNÁNDEZ and ANTONIO PIZARROSO (*Anal. Fis. Quim.*, 1922, 20, 589—594; cf. Fernandez, A., 1921, i, 485).—The ability of a number of alkaloids and other compounds containing the group $-\text{CO}\cdot\text{NH}-$ to form oxides in the presence of hydrogen peroxide is investigated. The conclusions drawn are indefinite.

G. W. R.

Aristolochic Acid. ARMAND CASTILLE (*J. Pharm. Belg.*, 1922, 4, 569—571; from *Chem. Zentr.*, 1922, iii, 1301).—Aristolochic acid from *Aristolochia clementis*, *A. longa*, and *A. rotundifolia*, is identical with Pohl's aristolochine (A., 1892, 874). It has molecular weight 343 and corresponds with the formula $\text{C}_{17}\text{H}_{11}\text{O}_7\text{N}$. It gives on reduction a substance, $\text{C}_{17}\text{H}_{13}\text{O}_4\text{N}$, which is characterised by its fluorescence in solution, and probably contains an anthraquinone nucleus.

G. W. R.

Aldehydes derived from Cinchonine, Quinine, and their Acyl Compounds. L. SEEKLES (*Rec. trav. chim.*, 1923, **42**, 69—104).—When quinine, cinchonine, or their acetyl or benzoyl derivatives are subjected to the action of ozone in cold chloroform solution, addition occurs at the double linking of the vinyl group with formation of an ozonide which, when treated with water, decomposes into formaldehyde and a new aldehyde. The terms quininal and cinchoninal are suggested for the new aldehydes from quinine and cinchonine, respectively. These and a large number of their derivatives are described. *m*-Chloropicric acid (3-chloro-2:4:6-trinitrophenol) was found useful for obtaining derivatives of the new aldehydes, since it readily precipitated them in a crystalline form and an estimation of chlorine provided a ready method of analysis. The following new salts of this acid were prepared.

Quinine+2X (X=*m*-chloropicric acid), yellow, m. p. 217° (decomp.); *cinchonine*+X, yellow, crystalline, clusters, m. p. 198°; +2X, greenish-yellow crystals, m. p. 209°; *acetylcinchonine*+X, greenish-yellow, m. p. 188°; +2X, yellow, m. p. 143—144°; *benzoylcinchonine*+X, yellow, m. p. 140—141°; +2X, yellow, m. p. 156°; *acetylquinine*+2X, m. p. 139°; *benzoylquinine*+X, greenish-yellow, m. p. 129—130°; +2X, yellow crystals, m. p. 150°.

Acetylcinchonine when pure has $[\alpha]_D^{15} +139.5^\circ$ in water containing 3 mols. HCl; it could not be crystallised. Acetylquinine under the same conditions has $[\alpha]_D^{22.9} -120.8^\circ$, m. p. 116°. It crystallises in the bisphenoidal class of the rhombic system, $a : b : c = 1.1142 : 1 : 0.6119$.

Acetylcinchonine ozonide forms a white, voluminous mass, softening at 75°, decomposing at 95—100°. *Acetylcinchoninal* was obtained as a white, amorphous substance having a marked tendency to polymerise, m. p. 106—109°; $[\alpha]_D^{21.0} +28.2^\circ$. Attempts to hydrolyse the acetyl group were unsuccessful. It forms a *mono-m-chloropicrate*, m. p. 155°, and a *di-m-chloropicrate*, m. p. 156—165°. The *phenylhydrazone* of acetylcinchoninal is an amorphous powder, m. p. 135—142°, *acetate*, amorphous, m. p. 106°; *p-bromophenylhydrazone*, yellow powder, m. p. 126°, *acetate*, yellow, m. p. 105°; *p-nitrophenylhydrazone*, yellow powder, sintering from 125°, m. p. 134°, decomp. 141°; *acetate*, yellow, m. p. 90°. When the last was recrystallised from alcohol, small, yellow crystals, m. p. 226°, were obtained, but were not identified. The phenylhydrazone forms a *m-chloropicrate*, m. p. 154—165° (decomp.). Acetylcinchoninal also forms a compound with ammonia and one with sodium hydrogen sulphite.

Benzoylcinchonine ozonide forms a white, voluminous mass decomposing at about 100°. *Benzoylcinchoninal* is a white substance, m. p. 130° (decomp.); $[\alpha]_D^{22.3} -72.4^\circ$. Its *mono-m-chloropicrate* forms greenish-yellow crystals, m. p. 165°, and the *di-m-chloropicrate*, yellow crystals, m. p. 165°. The *phenylhydrazone* is amorphous, yellow, m. p. 117—118°, *acetate*, m. p. 127°; *p-bromophenylhydrazone*, orange, amorphous, m. p. 120—122°, *acetate*, m. p. 112—114°; *p-nitrophenylhydrazone*, yellow, m. p. 126—

127° (decomp.), *acetate*, m. p. 130—131°. An aldehyde-ammonia compound is indicated.

Acetylquinine ozonide forms a very voluminous, white mass, softening at 75°, decomposing at 90—105° with evolution of gas. *Acetylquininal* is a white substance, m. p. about 120° (decomp.), $[\alpha]_D^{20} -63.5^\circ$. It forms a *mono-m-chloropicrate*, greenish-yellow, m. p. 166° (decomp.), and a *di-m-chloropicrate*, yellow, softening and decomposing from 138°. The *phenylhydrazone* is a yellow substance, m. p. about 125°, *acetate*, very hygroscopic, yellow, m. p. 65°; *p-bromophenylhydrazone*, yellow, m. p. 120°; *p-nitrophenylhydrazone*, yellow, m. p. 125°. *Acetylquininalammonia* is a white powder, m. p. 82—85°.

Benzoylquinine ozonide is a voluminous, white mass, m. p. 95—100°. *Benzoylquininal* is a white substance, m. p. 126°; $[\alpha]_D^{20} +79.4^\circ$; *mono-m-chloropicrate*, greenish-yellow, m. p. 142° (decomp.); *di-m-chloropicrate*, yellow, blackening at 155°. The *phenylhydrazone* is a yellow powder, softening from 116°, m. p. 128°, *acetate*, m. p. 118°; *p-bromophenylhydrazone*, yellow, m. p. about 125°, *acetate*, softens at 118—119° (decomp.); *p-nitrophenylhydrazone*, yellow, m. p. 122—133°, *acetate*, m. p. 112—115° (decomp.).

Benzoylquininal-ammonia is a white substance, m. p. 131—132°, containing 1 mol. of ether. When prepared in benzene solution it separates with 1 mol. of benzene, m. p. 136—139°.

Cinchonine ozonide is a white, amorphous substance, not very voluminous, decomposing at 105°. *Cinchoninal*, $C_{18}H_{20}O_2N_2$, is a white, amorphous substance, m. p. 143—145°, $[\alpha]_D^{20} +100.5^\circ$; it readily reduces Fehling's solution and silver nitrate. It forms a *mono-m-chloropicrate*, greenish-yellow crystals, decomposing slowly at 151°, and a *di-m-chloropicrate*, decomp. at 155°. The *phenylhydrazone* is amorphous, m. p. 130—135°, and decomposes violently at 140°; *p-bromophenylhydrazone*, yellow, m. p. 120°; *p-nitrophenylhydrazone*, m. p. 130—132° (decomp.). These three hydrazones do not form acetates.

Quinine ozonide is a white, amorphous substance decomposing at 109°. *Quininal*, $C_{18}H_{22}O_3N_2$, forms small colourless crystals, m. p. 160°, having strong reducing properties, $[\alpha]_D^{19} -30^\circ$. The *mono-m-chloropicrate* forms yellow crystals, m. p. 130°; *di-m-chloropicrate*, a yellow, vitreous substance, m. p. 126° (decomp.). The *phenylhydrazone* has m. p. 145—147°; *p-bromophenylhydrazone*, yellow, m. p. 125—130° (decomp.). Quininal does not form a compound with ammonia, but forms an additive compound with sodium hydrogen sulphite in alcohol, decomposed by water.

E. H. R.

The Synthesis of Ephedrine. E. FOURNEAU and J. PUYAL (*Anal. Fis. Quim.*, 1922, 20, 394—399; cf. Späth, A., 1921, i, 45; Fourneau, A., 1905, i, 57; Eberhard, A., 1915, i, 834).—Ephedrine is obtained from phenylethylcarbinol by the following reactions. Dehydration of phenylethylcarbinol gives propenylbenzene; by the action of bromine water, the corresponding bromohydrin is

obtained, b. p. 145—155°/25 mm. By heating the bromohydrin with a 10% methylamine solution in a sealed tube at 120° for three hours, phenyl- α -methylaminoethylcarbinol (ephedrine) is obtained and separated by appropriate methods. After recrystallisation, colourless prisms are obtained, m. p. 60°. The hydrochloride gives m. p. 180°, subsequently rising to 190°. The stereoisomeric ψ -ephedrine is obtained from ephedrine hydrochloride by way of acetylation of the latter compound, whereby acetyl ψ -ephedrine is obtained as colourless crystals, m. p. 176°. Acetyl ψ -ephedrine, by treatment with hydrochloric acid, gives a ψ -ephedrine hydrochloride, m. p. 175°, from which the base, m. p. 117°, is obtained.
G. W. R.

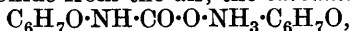
The Influence of Papaverine on the Optical Activity of Narcotine in Acid Solution. HAROLD EDWARD ANNETT (T., 1923, 123, 376—379).

[Scopoline. VI. The Constitutions of Scopolamine and Scopoline. The Hofmann Degradation of Scopoline.] J. GADAMER (*Ber.*, 1923, 56, [B], 130—131).—A criticism of the recent communication of Hess and Wahl (A., 1922, i, 854).

H. W.

Furylethylamine. YASUHIKO ASAHINA and ATSUSHI FUJITA (*J. Pharm. Soc. Japan*, 1922, 1084—1090).—According to the method of Claisen (A., 1905, i, 286), furfuraldehyde (12 g.) and ethyl chloroacetate (15 g.) were condensed in cold absolute ethereal solution by the aid of metallic sodium (3.5 g.) yielding ethyl furylglycidate, $C_4OH_3 \cdot CH < \begin{smallmatrix} O \\ CH \cdot CO_2Et \end{smallmatrix}$, b. p. 114—117°/5 mm. The

ester was saponified with alcoholic potash; the resulting potassium salt was dissolved in water, to which the calculated quantity of hydroxylamine hydrochloride was added when the resulting oxime separated as an oil (Rosenmund and Dornsafft, A., 1920, i, 56). *Furylacetaldoxime*, $C_4OH_3 \cdot CH_2 \cdot CH : N \cdot OH$, b. p. 90—92°/4 mm., is a light yellow, viscid liquid having a strongly sweet taste (about fifty times that of sucrose). When kept, the oily oxime (*anti*-form) gradually changes into the crystalline stable form (*syn*-form), m. p. 64°, the sweetness being reduced by half. By reduction with 3% sodium amalgam and 50% acetic acid in methyl-alcoholic solution, the oxime is converted into *furylethylamine*, $C_4OH_3 \cdot CH_2 \cdot CH_2 \cdot NH_2$, a colourless liquid, b. p. 155°/762 mm., d_4^{20} 1.0080, n_D^{21} 1.47994; it has a strongly amine-like odour and absorbs carbon dioxide from the air, the *carbamate*,



m. p. 87°, being formed. The *benzoate* has m. p. 81°. K. K.

Methylisopyromucic Acid and a Method of Characterising Acids of the Sugar Group. L. J. SIMON and A. J. A. GUILLAUMIN (*Compt. rend.*, 1922, 175, 1208—1211; cf. Chavanne, A., 1905, i, 77).—As *isopyromucic acid* may be prepared by dehydration of a dibasic acid derived from a hexose or of a monobasic acid

derived from a pentose, dehydration of a methyl pentose was effected, the lactone of rhamnose being used. The homologue of isopyromucic acid thus obtained, *methylisopyromucic acid*, $C_6H_6O_3$, is of yellow colour, m. p. 133° . Oxidation by the sulpho-chromic mixture shows the presence of a methyl group directly linked to carbon. The acid has a strong reducing action on silver salts and on permanganate. Its *benzoyl* derivative, m. p. 121° , may be prepared by the action of benzoyl chloride either directly or in alkaline solution. It is not a true acid, but rather a phenol, $CH \ll \begin{smallmatrix} C(OH) \cdot CO \\ CH = CMe \end{smallmatrix} > O$ (cf. Chavanne, A., 1902, i, 637, 690); the coloration with ferric chloride is bluish-green. A method of characterising the acids derived from sugars, details of which are given, depends on the fact that dibasic acids derived from hexoses and monobasic acids derived from pentoses and methyl pentoses give colours with ferric chloride whilst monobasic acids derived from hexoses do not do so. The latter give a positive result after careful oxidation.

H. J. E.

Selenium Organic Compounds. II. Synthesis of Diarylthiophens and Diarylselenophens. MARSTON TAYLOR BOGERT and PILAR PEREZ HERRERA (*J. Amer. Chem. Soc.*, 1923, 45, 238—243).—When acetophenoneanil is fused with sulphur at $220-240^\circ$, a 28% yield of pure 2:4-diphenylthiophen is obtained. The tolils may be used with equal success, and if substituted acetophenones are used the corresponding diarylthiophens are obtained. If selenium is used instead of sulphur, the products are diarylselenophens. The following new compounds are described: *acetophenone-o-tolil*, b. p. $210-220^\circ/57$ mm.; *p-methylacetophenoneanil*, b. p. $220-240^\circ/53$ mm.; 2:4-diphenylthiophen-5-mercurichloride, m. p. 223° (corr.); 2:4-diphenylselenophen, m. p. 112.3° (corr.), and its 5-mercurichloride, m. p. 224° (corr.); 2:4-di-p-tolylselenophen, m. p. 136.3° (corr.).

Acetophenonedimethylacetal was prepared by heating together at 40° for several hours methyl orthoformate, acetophenone, anhydrous methyl alcohol, and a trace of concentrated hydrochloric acid. After the mixture had stood for sixteen hours, it was made just alkaline with sodium methoxide and the methyl alcohol distilled off.

W. G.

Derivatives of Hydroxypyrrole. ERICH BENARY and RUDOLF KONRAD (*Ber.*, 1923, 56, [B], 44—52).—Previous attempts to obtain simple hydroxypyrrole derivatives from the hydroxy-esters (Benary and Silbermann, A., 1913, i, 651) by hydrolysis and subsequent removal of carbon dioxide have been unsuccessful on account of the small stability of the pyrrole ring towards alkali hydroxide. Attempts have therefore been made to increase the stability by the introduction of the phenyl group in position 1. The hydrolysis of the esters to the corresponding acids is thus rendered possible, but the subsequent removal of carbon dioxide can only be effected without extensive decomposition if the hydroxyl group is protected by methylation.

Ethyl β -anilinoacrylate is transformed by chloroacetyl chloride in the presence of anhydrous ether and pyridine into a mixture of *ethyl β -anilino- α -chloroacetylacrylate*, $\text{NPh}\cdot\text{CH}\cdot\text{C}(\text{CO}\cdot\text{CH}_2\text{Cl})\cdot\text{CO}_2\text{Et}$, needles, m. p. 83° , and *ethyl N-chloroacetyl- β -anilinoacrylate*, $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{NPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$, colourless prisms, m. p. $136\text{--}137^\circ$. The former ester is transformed by a cold alcoholic solution of potassium hydroxide into *ethyl 4-hydroxy-1-phenylpyrrole-3-carboxylate*, $\text{NPh}\left\langle\begin{array}{c} \text{CH}\cdot\text{C}\cdot\text{CO}_2\text{Et} \\ \text{CH}\cdot\text{C}\cdot\text{OH} \end{array}\right\rangle$, colourless, matted needles, m. p. 83--

84° . The corresponding *acid* crystallises in small rods, m. p. $172\text{--}174^\circ$ (decomp.), and becomes resinified when heated above its melting point in a vacuum. The hydroxy-ester is converted by amyl nitrite into *ethyl 5-oximino-4-keto-1-phenylpyrroline-3-carboxylate*, lemon-yellow, hexagonal prisms, decomp. about 185° after softening and gradually melting above 175° ; if an excess of sodium nitrite is gradually added to a solution of the ester in glacial acetic acid, an isomeric product, $\text{C}_{13}\text{H}_{12}\text{O}_4\text{N}_2$, almost colourless, coarse needles, m. p. $157\text{--}158^\circ$, is formed, the constitution of which has not been elucidated. *4-Acetoxy-1-phenylpyrrole-3-carboxylic acid*, colourless needles, m. p. $145\text{--}147^\circ$, is produced from the hydroxy-acid, acetic anhydride, and anhydrous sodium acetate; when heated at the atmospheric pressure or in a vacuum, it loses carbon dioxide and acetic acid, and leaves a black, resinous residue. *Ethyl 4-hydroxy-5-benzeneazo-1-phenylpyrrole-3-carboxylate*, orange-yellow needles, m. p. $170\text{--}172^\circ$, after previous softening, could not be hydrolysed to the corresponding *acid*, $\text{NPh}\left\langle\begin{array}{c} \text{CH}=\text{C}\cdot\text{CO}_2\text{H} \\ \text{C}(\text{N}\cdot\text{NPh})\cdot\text{C}\cdot\text{OH} \end{array}\right\rangle$,

which, however, is prepared by the action of benzenediazonium chloride on an alkaline solution of the hydroxy-acid; it crystallises in orange-coloured needles, m. p. about $185\text{--}187^\circ$ after softening at 175° . It is decomposed with loss of aniline when heated in a vacuum. *4-Methoxy-1-phenylpyrrole-3-carboxylic acid* is prepared by the action of methyl sulphate on the hydroxy-acid and subsequent hydrolysis of the *methyl* ester; it forms leaflets, m. p. $166\text{--}167^\circ$ (decomp.) [the *potassium* salt, long, colourless needles, is described]. The acid loses carbon dioxide when heated in a vacuum at $180\text{--}200^\circ$, and yields *3-methoxy-1-phenylpyrrole*, $\text{NPh}\left\langle\begin{array}{c} \text{CH}\cdot\text{CH} \\ \text{CH}\cdot\text{C}\cdot\text{OMe} \end{array}\right\rangle$, colourless needles, m. p. $33\text{--}34^\circ$, which when

molten or dissolved rapidly become brown on exposure to air. Attempts to hydrolyse the methoxyl to the hydroxyl group by aluminium chloride, hydrogen chloride, or hydrogen bromide were unsuccessful owing to the instability of the free hydroxypyrrole.

Methyl β -anilino- α -chloroacetylcrotonate is converted by potassium hydroxide in methyl alcoholic solution into *methyl 4-hydroxy-1-phenyl-2-methylpyrrole-3-carboxylate*, $\text{NPh}\left\langle\begin{array}{c} \text{CMe}\cdot\text{C}\cdot\text{CO}_2\text{Me} \\ \text{CH}=\text{C}\cdot\text{OH} \end{array}\right\rangle$, small needles, m. p. $123\text{--}124^\circ$; the corresponding *acid* crystallises in colourless needles, m. p. 145° . The hydroxy-ester is converted by amyl nitrite into *methyl 5-oximino-4-keto-2-methyl-1-phenyl-*

pyrroline-3-carboxylate, $C_{13}H_{12}O_4N_2$, pale yellow needles, m. p. 185—187° (decomp.), from which the corresponding *acid*, $C_{12}H_{10}O_4N_2$, small, pale yellow needles, m. p. 171—172° (decomp.), is obtained. Sodium nitrite converts the hydroxy-ester dissolved in glacial acetic acid into *methyl 5-nitroimino-4-keto-1-phenyl-2-methylpyrroline-3-carboxylate*, orange-coloured needles, m. p. 192—193° (decomp.) after previous softening. H. W.

The Action of Diazomethane on Dyes and certain Nitro-pyrroles. WILLIAM KÜSTER and WILHELM MAAG (*Ber.*, 1923, 56, [B], 55—69).—It has been shown previously (Küster, A., 1922, i, 885) that the action of diazomethane on bilirubin leads to the introduction of two methyl groups into the molecule and in addition a molecule of diazomethane is combined, forming a compound, $C_{36}H_{42}O_6N_6$. A further investigation of this compound and comparison of its properties with those of substances obtained by the action of diazomethane on pyrrole derivatives led the authors to the conclusion that a portion of the bilirubin molecule must contain the pyrrolenylmethanepyrrol group.

The product, $C_{36}H_{42}O_6N_6$, of the addition of diazomethane to esterified bilirubin is a red, amorphous powder which contains three methyl groups eliminable by hydriodic acid. It can be prepared in a crystalline form resembling bilirubin by the action of diazomethane on pure bilirubin and bilirubinammonia suspended in anhydrous ether; it, however, passes readily into the resinous variety.

Indigoid ethyl bis-2-methylpyrroline-3-carboxylate (Benary and Silbermann, A., 1913, i, 652) contains two carbethoxy-groups which are readily hydrolysed by hydriodic acid at 140°, whereas a further evolution of alkyl iodide is not observed below 300°; it is converted by diazomethane in the presence of ether into a red resin.

Methyl 5-3'-acetyltetronylidene-4-keto-2-methylpyrrole-3-carboxylate, $CO_2Et \cdot \overset{\overset{|}{Me}}{\underset{\underset{|}{C:NH}}{C}} \cdot CO > C:C < \overset{\overset{O}{||}}{CH_2} \text{---} C(\overset{\overset{O}{||}}{CMe \cdot OH}) \cdot CO$, yellow needles, m. p. 190° (decomp.), is prepared by the action of alcoholic potassium hydroxide solution on a mixture of acetyltetronamide and ethyl chloroacetylaminocrotonate; it is converted by diazomethane into a reddish-brown *resin*, $C_{16}H_{19}O_6N$, m. p. 75° (decomp.).

Ethyl 5:5'-bis-4-keto-2-methylpyrroline-3-carboxylate hydrate, $C_{16}H_{20}O_5N_2 \cdot H_2O$ (cf. Benary and Silbermann, *loc. cit.*), loses two ethyl groups under the action of hydriodic acid at 140°, and does not suffer further loss of alkyl iodide below 340°; it is converted by diazomethane into a yellow, brittle *resin*, $C_{18}H_{24}O_5N_2$, m. p. 73—74° (decomp.).

3-Hydroxy-4-carbethoxy-5-methylpyrrolenyl-2-furylmethane, $C_{13}H_{13}O_4N$ (Küster, A., 1922, i, 858), combines with hydrogen chloride in the presence of acetone to form a *hydrochloride*, $C_{13}H_{14}O_4NCl$, rust-brown needles, which readily lose hydrogen chloride on exposure to air. The substance is converted by diazomethane into a dark brown resin. 3-Hydroxy-4-carbethoxy-5-methyl-2-o-pyrrolenylhydroxyphenylmethane, brownish-yellow needles,

m. p. 207° (decomp.), is readily prepared from Benary's pyrrole and salicylaldehyde, and is transformed by diazomethane into a yellow resin, m. p. about 40° after previous darkening.

Ethyl 2 : 5-dimethylpyrrole-3-carboxylate is oxidised by chromic acid to *carbethoxymaleinimide*, $C_7H_7O_4N$, colourless needles, m. p. 115°.

Benary's indigoid pyrrole (*loc. cit.*) is oxidised by nitric acid (*d* 1.4) at 0° to *ethyl 5-nitro-2 : 4-dihydroxypyrrole-3-carboxylate*, colourless needles, decomp. 100°. The *potassium* salt, $C_7H_7O_6N_2K$, decomp. 167°, *barium* salt, decomp. 165°, *lead*, and *copper* salts are described. Hydrogen sulphide reduces the nitro-compound to a colourless substance, m. p. 121°. The ester is readily hydrolysed to *5-nitro-2 : 4-dihydroxypyrrole-3-carboxylic acid*, colourless needles, decomp. 124°, the *ammonium* and *silver* salts of which are described; the *methyl* ester crystallises in colourless needles, decomp. 112°. *Ethyl 5-nitro-2-hydroxy-4-methoxypyrrole-3-carboxylate*, a pale yellow liquid, b. p. 146°, which solidifies to needle-shaped crystals when cooled with ice, is readily prepared by the action of diazomethane on the corresponding dihydroxy-ester. *5-Nitro-2-hydroxy-4-methoxypyrrole-3-carboxylic acid* crystallises in colourless needles; the *ammonium* salt, *silver* salt, and the *methyl* ester, a colourless liquid, b. p. 145°, are described.

Ethyl 5-nitro-4-hydroxy-2-methylpyrrole-3-carboxylate, colourless needles, m. p. 100.5° (decomp.), is readily hydrolysed to *5-nitro-4-hydroxy-2-methylpyrrole-3-carboxylic acid*, colourless needles, decomp. 124°. It is converted by diazomethane into *ethyl 5-nitro-4-methoxy-2-methylpyrrole-3-carboxylate*.
H. W.

The Tetrachlorodipyridinoiridiates. Configurations of the Two Series of Iridiumdipyridinotetrachloro-compounds.

MARCEL DÉLÉPINE (*Compt. rend.*, 1922, 175, 1211—1213; cf. this vol., i, 135).—These are neutral un-ionised substances. *cis*- and *trans*-Isomerides exist which are derived from the orange and red salts, respectively. They are not of equal stability towards oxidising agents, and are themselves of unequal oxidising power. Both decompose iodides according to the equation $Ir(C_5H_5N)_2Cl_4 + MI \rightarrow Ir(C_5H_5N)_2Cl_4M + I$, but only the *cis*-compound decomposes bromides. This is consistent with the fact that bromine can be used only in preparing the orange salts. The author concludes that the *cis*-isomeride behaves as a halogen intermediate between chlorine and bromine, and the *trans* as intermediate between bromine and iodine. The constitution was determined by reason of the dichroism of the chloride derived from the orange salt, which is isomorphous with and confers the property of dichroism on platinum tetrachlorodipyridine, $PtCl_4(C_5H_5N)_2$. It has been shown (Werner and Fassbender, A., 1897, i, 631; Jörgensen, A., 1901, i, 163) that the latter substance has the *cis*-configuration, hence the same configuration is inferred for the orange salts. The red salts have, therefore, the *trans*-configuration.
H. J. E.

δ-Ketonic Nitriles and their Relation to Cyclic Compounds.

E. P. KOHLER and B. L. SOUTHER (*J. Amer. Chem. Soc.*, 1922, 44, 2903—2914; cf. this vol., i, 54).—Cyanoacetamide and cyano-

acetonitrile, like methyl cyanoacetate, condense with phenyl styryl ketone, but the three products, although closely related, behave differently towards most reagents. All three form cyclic compounds under the influence of halogen acids in indifferent media. The product from methyl cyanoacetate forms a tetrahydropyridine derivative, in the production of which the cyano-group is involved and molecular rearrangement occurs. The product from cyanoacetamide also forms a tetrahydropyridine derivative, but in its production the amide group is involved. Under the same conditions, the product from the dinitrile forms only a trace of a tetrahydropyridine derivative, the main product being a mixture composed of a pyridine and a hexahydropyridine derivative. This mixture is doubtless due to a series of reactions starting with the addition of halogen acid to one of the cyano-groups and ending with the spontaneous oxidation and reduction of an intermediate dihydropyridine derivative. The results confirm the view that such oxidation-reduction reactions are associated with the extraordinary activity of hydrogen which is in combination with atoms that are flanked on both sides by unsaturated groups; but they do not support the conclusion of Knoevenagel and his co-workers (cf., A., 1903, i, 785) that hydropyridine derivatives are incapable of reacting in all possible desmotropic modifications.

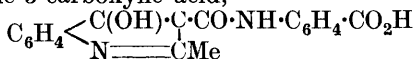
Cyanoacetamide condenses with phenyl styryl ketone under the conditions previously described (*loc. cit.*) to give α -cyano- γ -benzoyl- β -phenylbutyramide, m. p. 161—163°, and similarly cyanoacetoneitrile yields α -cyano- γ -benzoyl- β -phenylbutyronitrile, m. p. 125—126°. When dry hydrogen chloride or bromide is passed into a chloroform solution of the above amide, 2-keto-3-cyano-4:6-diphenyltetrahydropyridine, m. p. 220°, is obtained, and this on hydrolysis with concentrated sulphuric acid yields 2-keto-3-carbamyl-4:6-diphenyltetrahydropyridine, m. p. 181—182°, and when treated with nitrous acid gives 1-hydroxy-3-cyano-4:6-diphenylpyridine, m. p. 313—315°. With alcoholic ammonia, the dihydropyridine derivative undergoes spontaneous oxidation-reduction and the products are a hydroxypyridine and 2-keto-3-cyano-4:6-diphenylpiperidine, m. p. 188—189°. α -Cyano- γ -benzoyl- β -phenylbutyronitrile also reacts with halogen acids in dry chloroform solution. With hydrogen chloride, one of the products is 2-chloro-3-cyano-4:6-diphenylpyridine, m. p. 154.5°, and with hydrogen bromide 2-bromo-3-cyano-4:6-diphenylpyridine, m. p. 169—170°, is obtained. In the latter reaction a red oil was also formed from which after pouring it into a solution of sodium hydrogen carbonate 2-keto-3-carbamyl-4:6-diphenylpiperidine, m. p. 170°, was isolated, and this on treatment with hydrogen chloride in methyl alcohol gave methyl 2-keto-4:6-diphenylpiperidine-3-carboxylate, m. p. 177°.

With alkalis, the cyanoamide additive product, m. p. 161—163°, described above, is transformed into its cyclic isomeride, the only other product being a trimolecular compound. With alcoholic alkalis, the dinitrile additive product gives pyridyl ethers, of which 2-methoxy-3-cyano-4:6-diphenylpyridine, m. p. 110°, and 2-ethoxy-3-cyano-4:6-diphenylpyridine, m. p. 112°, were prepared.

The rearrangement of the cyanoacetamide additive product to cyclic compounds takes place so easily that only cyclic bromo-compounds were obtained from it, even when the bromination was carried out in the presence of potassium acetate. From the dinitrile, however, it was possible to obtain one open-chain bromo-compound by brominating it in the presence of potassium acetate. The behaviour of this substance towards halogen acids confirms the view previously expressed (*loc. cit.*) regarding the mechanism by which bromopyridine derivatives are formed when bromine acts on open-chain ketonic nitriles, since when dry hydrogen chloride is passed into a chloroform solution of the bromo-compound the product is a chloropyridine derivative. The compounds described are: α -bromodi- α -cyano- γ -benzoyl- β -phenylbutyronitrile, m. p. 126—127°, 5-bromo-2-keto-3-cyano-4 : 6-diphenyltetrahydropyridine, m. p. 165°, 5-chloro-2-keto-3-cyano-4 : 6-diphenyltetrahydropyridine, m. p. 178—181°, 3 : 5-dibromo-2-keto-3-cyano-4 : 6-diphenyltetrahydropyridine, m. p. 195° (decomp.), 5-bromo-2-hydroxy-3-cyano-4 : 6-diphenylpyridine, m. p. 303—306° (decomp.), 2-chloro-5-bromo-3-cyano-4 : 6-diphenylpyridine, m. p. 181—182°, and 2 : 5-dibromo-3-cyano-4 : 6-diphenylpyridine, m. p. 189—190°. W. G.

The Ethoxyquinaldines. W. T. K. BRAUNHOLTZ (*J. Amer. Chem. Soc.*, 1922, **44**, 2967; cf. T., 1922, **121**, 169).—In reference to a paper by Gutekunst and Gray (A., 1922, i, 950), the author directs attention to the preparation and description of the 5-, 6-, and 7-ethoxyquinaldines by himself (*loc. cit.*). W. G.

The Constitution of Dianhydrodiacetylanthranilic Acid. GUSTAV HELLER and HERBERT GRUNDMANN (*Ber.*, 1923, **56**, [B], 200—205).—The action of phosphoryl chloride on acetylanthranilic acid or its esters or on acetylanthranil has yielded a compound which Anschütz and Schmidt (A., 1903, i, 56) designate dianhydrodiacetylanthranilic acid, and to which they assign the constitution $C_6H_4 \begin{smallmatrix} <C(OH):CH \cdot CO \cdot NH \\ NH \cdot CO \cdot CH : C(OH) \end{smallmatrix} > C_6H_4$ or $C_6H_4 \begin{smallmatrix} <C(OH) \cdot CH_2 \cdot CO \cdot N \\ N \cdot CO \cdot CH_2 \cdot (HO)C \end{smallmatrix} > C_6H_4$. This compound has now been obtained incidentally by the action of acetic anhydride on benzene- or *p*-toluene-sulphonylanthranilic acid, and is shown to be the *o*-carboxyanilide of 4-hydroxy-2-methylquinoline-3-carboxylic acid,



p-Toluenesulphonylanthranilic acid is converted by boiling acetic anhydride into the mixed *anhydride* of toluene-*p*-sulphonic acid and the *o*-carboxyanilide of 4-hydroxy-2-methylquinoline-3-carboxylic acid, $C_6H_4 \begin{smallmatrix} <C(OH) \cdot C \cdot CO \cdot NH \cdot C_6H_4 \cdot CO \cdot O \cdot SO_2 \cdot C_6H_4 \cdot Me \\ N = CMe \end{smallmatrix} >$, pale yellow crystals, m. p. 214—215° (decomp.). The substance is decomposed by dilute sodium hydroxide solution into the *o*-carboxyanilide of 4-hydroxy-2-methylquinoline-3-carboxylic acid, m. p. 249—250° (decomp.), identical with the product obtained by Anschütz and Schmidt (*loc. cit.*). It is converted by glacial acetic
k*

and concentrated hydrochloric acids at 130—140° into 4-hydroxy-2-methylquinoline. A substance, $C_{31}H_{28}O_{10}N_2S$, slender needles, m. p. 133·5°, is obtained as by-product of the action of acetic anhydride on *p*-toluenesulphonylanthranilic acid. It appears to contain acetic anhydride and solvent of crystallisation; when deprived of this it has m. p. 159—160° (decomp.), but the amount of it available was insufficient for an extended examination.

Benzenesulphonylanthranilic acid is transformed by boiling acetic anhydride into the mixed *anhydride*, $C_{15}H_{13}O_5NS$, slender needles, m. p. 157—158°.

p-Toluenesulphonylanthranilic acid is transformed by glacial acetic and concentrated hydrochloric acids at 140° into *anthranilic acid toluene-p-sulphonate*, $C_{14}H_{15}O_5NS$, slender needles, m. p. 218° (decomp.). The corresponding benzenesulphonate has m. p. 230° (decomp.). H. W.

The Constitution of Naphtholisatin and its Derivatives.

C. CÂNDEA (*Bull. Acad. Sci. Roumaine*, 1922, 8, 31—39).—Colourless condensation products of isatin with α -naphthol were prepared. These differ from similar compounds obtained from phenols in that they are almost insoluble in alkaline solutions, are not oxidised to coloured substances, and do not form acetyl derivatives. The condensation probably occurs at the 3-position of the indole nucleus (cf. Dănăilă and Căndeia, A., 1916, i, 417). The derivatives obtained were: *Di- α -naphtholisatin*, $C_{28}H_{19}O_3N$, prismatic needles, m. p. above 300°. *Di- α -naphtholmonobromoisatin*, $C_{28}H_{18}O_3NBr$, prismatic needles, m. p. above 300°. *Di- α -naphtholdibromisatin*, $C_{28}H_{17}O_3NBr_2$, prismatic needles, m. p. above 300°. *Di- α -naphtholmonochlorisatin*, $C_{28}H_{18}O_3NCl$, crystals, m. p. above 300°. *Di- α -naphtholdichloroisatin*, $C_{28}H_{17}O_3NCl_2$, prismatic needles, m. p. above 300°. H. J. E.

Stereochemical Studies. VII. 2-Thion-4-methylthiazoline-3-acetic Acid.

BERTIL GROTH and BROR HOLMBERG (*Ber.*, 1923, 56, [B], 289—298).—2-Thion-4-methylthiazoline-3-acetic acid, $S < \begin{array}{c} CS-N \cdot CH_2 \cdot CO_2H \\ | \\ CH: CMe \end{array}$, pale honey-yellow, thick plates or short

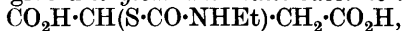
prisms, m. p. 198—199° (decomp.), is prepared in 87% yield by the action of chloroacetone on an aqueous solution of glycine hydrochloride and potassium hydroxide which has been agitated with carbon disulphide until the latter is completely dissolved; it dissolves in water to the extent of 2·06 g. per litre at the atmospheric temperature. The *sodium* salt, rectangular plates (+5H₂O), *barium* salt, rosettes of needles (+2H₂O), *methyl* ester, almost colourless needles, m. p. 96—97°, and *ethyl* ester, long, almost colourless needles, m. p. 97—98°, are described. The acid could not be resolved into its optical antipodes by treatment with *l*- or *d*-phenylethylamine in aqueous or alcoholic solution; the *salts* of the *r*-acid with the optically active bases were isolated (m. p. 161—162° and 160—162°). The acid is unusually stable towards hydrolysis by acid or alkali. It is oxidised by nitric acid (or less

conveniently by bromine water) to the inner *anhydride* of 2-keto-4-methylthiazoline-3-acetic acid, $\text{CO} < \begin{array}{c} \text{CH}_2 \cdot \text{N} \cdot \text{CMe} \\ \text{O} - \text{CH} - \text{S} \end{array} > \text{CH}$, which is isolated as the *hydrogen sulphate*, $\text{C}_6\text{H}_7\text{O}_2\text{SN}, \text{H}_2\text{SO}_4$, a colourless, crystalline, somewhat hygroscopic substance, m. p. 114—115°, to a turbid liquid. The corresponding *hydrochloride* (anhydrous and monohydrate) is described; it has m. p. above 230° (decomp.) after darkening at 200° and becoming black at 230°. The free base is a colourless, crystalline powder ($+2.5\text{H}_2\text{O}$), m. p. 110—115° (decomp.) after softening and becoming discoloured at 95°, m. p. (anhydrous) 165° (decomp.). It is stable in hot aqueous, acidic solution, but is readily decomposed in neutral or alkaline solution with the formation of ill-defined products. It was not found possible to isolate the corresponding acid, since the tendency towards dehydration is so marked that the anhydride can exist even in faintly alkaline solution. H. W.

Stereochemical Investigations of the Diketothiazolidines.

I. STEN KALLENBERG (*Ber.*, 1923, 56, [B], 316—331).—In contrast to the ψ -thiohydantoins and the rhodanines, the diketothiazolidines which have a mobile hydrogen atom attached to the asymmetric β -carbon atom, exhibit normal stereochemical relationships. They can readily be prepared in optically active forms which easily undergo racemisation in consequence of the possibility of desmotropic change.

Potassium ethylthiocarbamate, $\text{NEt} \cdot \text{CO} \cdot \text{SK}$, is prepared conveniently by the action of carbon oxysulphide on a solution of potassium hydroxide and ethylamine hydrochloride in absolute alcohol. Under certain conditions, particularly with regard to concentration, it reacts with a solution of sodium *l*-bromosuccinate in cold water to give *d*-ethylcarbamidothiolsuccinic acid,



small plates, $[\alpha]_D +103.5^\circ$ in absolute alcoholic solution. The acid is readily decomposed by concentrated ammonia with the production of *d*-thiomalic acid, by warm acids to *d*-thiomalic acid, carbon dioxide, and ethylamine, on the one hand, and to *r*-diketoethylthiazolidineacetic acid, $\begin{array}{c} \text{NEt} \cdot \text{CO} \\ \text{CO} - \text{S} \end{array} > \text{CH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, on the

other, by alkalis into *d*-thiomalic acid, carbon dioxide, and amine. *r*-Ethylcarbamidothiolsuccinic acid crystallises in colourless, thin prisms or short needles, m. p. 141—142° (decomp.).

The action of cold concentrated hydrochloric acid on *d*-ethylcarbamidothiolsuccinic acid gives a mixture of *r*-diketoethylthiazolidineacetic acid, colourless prisms, m. p. 113—115°, and the corresponding *d*-acid which, however, could not be caused to crystallise. The racemic acid can be resolved with the aid of active phenylethylamine, but the active acids are again obtained only in the form of non-crystalline syrups.

d-Methylcarbamidothiolsuccinic acid, prepared from potassium methylthiocarbamate and sodium *l*-bromosuccinate, has m. p. 114—116° (decomp.), $[\alpha]_D +99.2^\circ$ in absolute alcoholic solution.

The corresponding *r*-acid crystallises in colourless, spherical aggregates, m. p. 135—136° (decomp.). The active acid is converted by concentrated hydrochloric acid into *d*-diketomethylthiazolidineacetic acid, transparent prisms, m. p. 101—102°, $[\alpha]_D +208.0^\circ$ in absolute alcoholic solution (the success of the reaction greatly depends on the conditions of the experiment, which are described in detail in the original). It is converted in alkaline solution into *r*-methylcarbamidothiolsuccinic acid. Since *d*-methylcarbamidothiolsuccinic acid is not racemised under similar conditions, it follows that *d*-diketomethylthiazolidineacetic acid must be converted into the corresponding *r*-compound previously to fission of the thiazole ring. Preliminary measurements show that the velocity of racemisation is diminished with increasing concentration of hydrogen-ions and increased by increasing concentration of hydroxyl-ions. *r*-Diketomethylthiazolidineacetic acid crystallises in small, colourless plates, m. p. 98—99°.

d-Dimethylcarbamidothiolsuccinic acid forms colourless prisms, m. p. 138—139° (decomp.), $[\alpha]_D +81.7^\circ$ in absolute alcoholic solution. It is decomposed by hot *N*-sodium hydroxide solution to a small extent into thiomalic acid, carbon dioxide, and dimethylamine, but the greater portion is constitutionally unchanged and only slightly racemised. Similar treatment with *N*-sulphuric acid causes an almost complete fission into partly racemised thiomalic acid; concentrated hydrochloric acid at the atmospheric temperature gives the same result, except that fission is less extensive and racemisation of the products more pronounced.

H. W.

The Tautomerism of Amidines. I. 2:4- and 2:5-Diphenylglyoxalines. RICHARD BURTLES and FRANK LEE PYMAN (T., 1923, 123, 361—367).

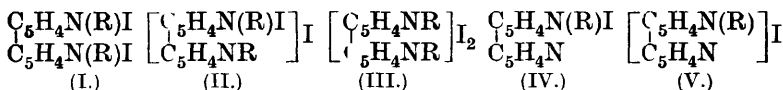
The Tautomerism of Amidines. II. The Alkylation of Open-chain Amidines. FRANK LEE PYMAN (T., 1923, 123, 367—370).

Some New Hypnotics of the Barbituric Acid Series. H. A. SHONLE and A. MOMENT (*J. Amer. Chem. Soc.*, 1923, 45, 243—249).—Various dialkyl- and alkylaryl-barbituric acids were prepared and tested for hypnotic action. The monoalkyl- and aryl-derivatives were found to be inactive in doses of 0.5 to 1 g. per kg. of body weight when injected subcutaneously in rabbits. Dimethylbarbituric acid was without any apparent action on rabbits in a dose of 0.75 g. per kg. of body weight. Then as the molecular weight increased the activity increased until a maximum was reached, after which it declined until the hypnotic activity was lost and the animal showed only muscular inco-ordination or no effect at all, as was the case with dibenzylbarbituric acid. However, the length and type of the carbon atom chains of the entering groups play an important part in modifying the activity. Branched chains are more active and less toxic than are the straight chains. Of the aliphatic compounds investigated, ethylisoamylbarbituric

acid was found to be the most active as well as to possess the lowest toxicity. The relative activities of the barbituric acid derivatives tested are tabulated. New malonic esters prepared are as follows : *ethyl-sec.-butylmalonic* ester, b. p. 155—160°/60 mm., d_{25}^{25} 0.9858, n_{25}^{25} 1.4264; *ethylisobutylmalonic* ester, b. p. 119—120°/8 mm., d_{25}^{25} 0.9682, n_{25}^{25} 1.4228; *ethylisoamylmalonic* ester, b. p. 150°/20 mm., d_{25}^{25} 0.9540, n_{25}^{25} 1.4255; *propylisopropylmalonic* ester, b. p. 143°/42 mm., d_{25}^{25} 0.9803, n_{25}^{25} 1.4239; *isopropyl-n-butylmalonic* ester, b. p. 136°/14 mm., d_{25}^{25} 0.9742, n_{25}^{25} 1.4291.

New derivatives of barbituric acid are *ethylisobutylbarbituric acid*, m. p. 174—176°, *ethylisoamylbarbituric acid*, m. p. 154—156°, *isopropyl-n-butylbarbituric acid*, m. p. 209—210°, *n-propylisopropylbarbituric acid*, m. p. 161—162°, *isopropylisoamylbarbituric acid*, m. p. 173—175°, *propylisoamylbarbituric acid*, m. p. 129—132°, *ethyl-sec.-butylbarbituric acid*, m. p. 155—157°. W. G.

The Colour of the 2 : 2'-Dipyridylum Halogenides. BRUNO EMMERT and JULIUS STAWITZ (*Ber.*, 1923, **56**, [B], 83—91).—An extensive series of 4 : 4'-dipyridylum di- and mono-alkyl halides has been examined. The various colours which they exhibit in substance and when dissolved and the failure of their solutions to observe Beer's law, are explained by the application of Hantzsch's views on the constitution of ammonium salts.



The constitution I is ascribed to the red dipyridylum di-iodides and the corresponding pseudo-form, IV, to the yellow monoiodides. The yellow hydrates of the di-iodides have the constitution II, whereby the difference between their colour and that of the anhydrous compounds and their similarity with the monoiodides is explained. In the aqueous and alcoholic solutions of the di-iodides, the three forms, I, II, and III, are present in equilibrium, the two latter being electrolytically dissociated. In a similar manner, the failure of the monoiodides to obey Beer's law in solution is explained by the equilibrium between the yellow molecules (IV) and the colourless molecules (V).

The following individual compounds are described : 4 : 4'-*Di-pyridyl dihydriodide*, red prisms, and the corresponding *mono-hydriodide* (golden-yellow prisms, +H₂O and anhydrous). The corresponding *dihydrobromide*, long, pale yellow needles, *mono-hydrobromide*, colourless, prismatic needles (+H₂O), and *mono-hydrochloride* (+H₂O). 4 : 4'-*Dipyridyl monomethiodide*, a pale yellow, crystalline powder, and the corresponding *hydriodide*. 4 : 4'-*Dipyridyl dimethobromide*, yellow prisms. 4 : 4'-*Dipyridyl diethiodide*, orange-coloured prisms, and the corresponding *mono-ethiodide*, lustrous, yellow leaflets. 4 : 4'-*Dipyridyl dipropiodide*, red crystals, which yields a *pentahydrate* on exposure to moist air, the *monopropiodide*, yellow crystals, the *dipropobromide*, greenish-yellow crystals, and the *dipropochloride*, colourless, lustrous leaflets

which deliquesce on exposure to air. 4:4'-Dipyridyl methiodide propiodide, red, oblique prisms. 4:4'-Dipyridyl monoisobutiodide, which closely resembles the monopropiodide. 4:4'-Dipyridyl monoisoamyl iodide. 4:4'-Dipyridyl di-sec.-hexyl iodide, a brownish-red substance, di-hydrate, yellow needles. 4:4'-Dipyridyl di-benzyl iodide, a red substance which gives an unstable, yellow hydrate, dibenzylbromide and the corresponding pale yellow tetrahydrate.

H. W.

Some Derivatives of Methylenediquinaldine and their Relationship to the Carbocyanines. FRANCES MARY HAMER (T., 1923, 123, 246—259).

The Colour of Di- and Tri-2-quinolylmethanes and their Derivatives. GÜNTHER SCHEIBE (*Ber.*, 1923, 56, [B], 137—148; cf. A., 1921, i, 62, 451; 1922, i, 1190).—Di- and tri-2-quinolylmethanes exist in colourless and coloured forms which yield an equilibrium mixture in solution or in the molten condition. The former varieties can be represented satisfactorily by formulæ of the type $\text{CH}_2(\text{C}_9\text{H}_6\text{N})_2$, but the coloured compounds do not possess the quinonoid structure, $\text{C}_9\text{H}_6\text{N}\cdot\text{CH}\cdot\text{C}_9\text{H}_6\text{N}\cdot\text{NH}$, since their absorption spectra differ entirely from those of the 1-alkyl derivatives. The hydrogen atom is not attached directly to the central carbon atom or to either nitrogen atom, but as it is shown by the chemical reactions of the compounds to be related to all three, it must be ascribed a position within their sphere of influence. The optical effect of this mode of union of the hydrogen appears to be similar to that of the union of the anion in the dye salts, although it is not ionisable. In this case, ionisation does not appear to have an immediate relationship to optical properties.

[With R. PFLOCK, K. SCHOLL, and E. FRIEDEL].—Di-2-quinolylmethane is prepared without particular difficulty by the process described recently (A., 1922, i, 1190); the success of the operation depends on the presence of small quantities of hydrogen chloride such as are usually retained by 2-chloroquinoline. König's failure to prepare the compound (A., 1922, i, 1188) is due to the use of too carefully purified materials.

A cold solution of di-2-quinolylmethane in alcohol is converted by four molecular proportions of nitric acid into the *dinitrate*, $\text{C}_{19}\text{H}_{14}\text{N}_2\cdot 2\text{HNO}_3$, colourless, lustrous leaflets. The salt is converted when heated by itself or in alcoholic solution into *nitro-di-2-quinolylmethane mononitrate*, $\text{NO}_2\cdot\text{CH}(\text{C}_9\text{H}_6\text{N})_2\cdot\text{HNO}_3$, yellow plates, decomp. 145° ; this is converted by sodium hydroxide into a colourless, crystalline substance, which, after desiccation in a toluene bath, gives the sodium salt of the mononitro-compound, $\text{C}_{19}\text{H}_{12}\text{O}_2\text{N}_3\text{Na}$, yellow crystals, m. p. 282° . *Nitro-di-2-quinolylmethane* crystallises in yellow needles, m. p. 200° . It appears to yield only monoacid salts even with an excess of mineral acid. It is converted by nitric acid in warm glacial acetic acid solution into *dinitro-di-2-quinolylmethane*, $\text{C}(\text{C}_9\text{H}_6\text{N})_2(\text{NO}_2)_2$, almost colourless prisms, m. p. 140° .

Tri-2-quinolylcarbinol is converted by acetic anhydride and

sodium acetate into the corresponding *acetate*, $C_{30}H_{21}O_2N_3$, colourless prisms, m. p. 190° .

Bromine and tri-2-quinolylmethane yield *tri-2-quinolylbromomethane*, $C_{28}H_{18}N_3Br$, colourless crystals, m. p. 169° . It gives a *di-picrate*, and is converted by alcoholic potassium hydroxide solution into *tri-2-quinolylmethyl ethyl ether*, colourless crystals, m. p. 179° , and a compound of high melting point which appears to be the ether derived from two molecules of the carbinol. It is smoothly reduced by phenylhydrazine in the presence of benzene to tri-2-quinolylmethane.

p-Dimethylaminobenzylidenepicoline forms pale yellow crystals, m. p. 139° , and, like the corresponding quinaldine derivative, gives coloured salts with acids, which are immediately decomposed by alkali. Nitrous acid appears to transform the compounds into nitrosoamines, but the investigation of these substances is not complete.

When molecular proportions of acetylacetoneanil, aniline, and zinc chloride are warmed with a little alcohol, the additive *compound* of the dianil with zinc chloride, $C_{17}H_{18}N_2 \cdot ZnCl_2$, colourless prisms, decomp. 256° , is obtained. This suffers decomposition into the monoanil when treated with ammonia. The *dianil monohydrochloride*, yellow prisms, m. p. 218° , is prepared from the monoanil and aniline hydrochloride, but it was not found possible to obtain the crystalline base from the salt.

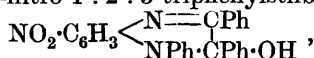
Acetylacetonecarbamide (cf. Stark, A., 1909, i, 260) which has been prepared in the light and is therefore yellow, melts at 95° to a colourless liquid which re-solidifies at about 100° , becomes yellow when further heated, and has m. p. 198° . Dibenzylideneacetylacetonecarbamide yields a *monohydrochloride*, $C_{20}H_{17}ON_2Cl$.

H. W.

Contraction of the Ring in the Cases of Quinoxaline Derivatives and a New Method of Formation of Benziminazoles. I. K. BRAND and E. WILD (*Ber.*, 1923, 56, [B], 105—119).—The condensation of the hydrochlorides of *N*-mono-substituted aromatic *o*-diamines with 1 : 2-dicarbonyl compounds leads in general to the production of quinoxaline derivatives. It is therefore remarkable that benzil and 4-nitro-2-aminophenyl-*p*-tolylamine in the presence of hydrochloric acid yield 5-nitro-2-phenyl-1-*p*-tolylbenziminazole hydrochloride in place of the expected stilbazonium chloride, the 5-membered iminazole ring being formed in place of the expected 6-membered diazine ring. A number of possibly similar instances have also been examined.

5-Nitro-2-phenyl-1-*p*-tolylbenziminazole hydrochloride, colourless, slender needles, m. p. 235° , readily separates when a solution of benzil and 4-nitro-2-amino-4'-methyldiphenylamine in alcohol is boiled with hydrochloric acid.

Benzil-5-nitro-2-anilinoanil, $COPh \cdot CPh \cdot N \cdot C_6H_3(NO_2) \cdot NHPh$, pale yellow needles, m. p. 205° , is slowly converted by sulphuric acid into the ψ -base of 6-nitro-1 : 2 : 3-triphenylstilbazonium,



m. p. 161°, which is more conveniently prepared by the action of hydrochloric acid on the anil under conditions which are described in detail in the original communication. The anil is transformed by treatment with concentrated hydrochloric acid in boiling alcoholic solution into 5-nitro-1:2-diphenylbenziminazole, m. p. 181° (cf. Walther and Kessler, A., 1906, i, 898); the latter substance is also prepared by the action of hydrochloric acid and alcohol on 6-nitro-1:2:3-triphenylstilbazonium base and from benzil and 4-nitro-2-aminodiphenylamine under somewhat similar conditions.

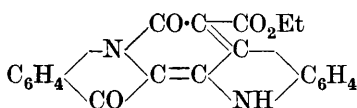
The 6-chloro-1:2:3-triphenylstilbazonium ψ -base, yellow needles, m. p. 164°, prepared by the condensation of benzil and 4-chloro-2-aminodiphenylamine in boiling alcoholic solution could not be converted into 5-chloro-1:2:3-diphenylbenziminazole by treatment with alcohol and hydrochloric acid, even after addition of nitrobenzene to the mixture.

6-Nitro-2:3-diphenylquinoxaline is unchanged when heated at 150—170° with alcohol and hydrochloric acid.

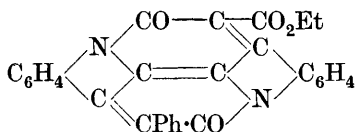
According to the conditions, particularly with respect to the amount of acid used, the action of 4-nitro-2-amino-*N*-methylaniline on benzil in the presence of alcohol and hydrochloric acid leads to the formation of benzil-5-nitro-2-methylaminomonoanil, yellow leaflets, m. p. 195°, 6-nitro-2:3-diphenylquinoxaline, 6-nitro-2:3-diphenyl-1-methylstilbazonium chloride, dark yellow needles, m. p. 168° (decomp.), and a substance, m. p. about 280°, which has not been completely investigated. More favourable conditions for the conversion of the anil into 6-nitro-2:3-diphenylquinoxaline and 6-nitro-2:3-diphenyl-1-methylstilbazonium chloride are described in detail. The ψ -base corresponding with the substance last mentioned crystallises in yellow needles, m. p. 170° (from alcohol), 176° (from benzene); repeated crystallisation from hot alcohol effects its re-conversion into the anil. H. W.

The Indigotin Group. II. A New Vat Dye Prepared from Indigotin and Ethyl Malonate. THEODOR POSNER and GOTTFRIED PYL (*Ber.*, 1923, 56, [B], 31—44; cf. Posner and Aschermann, A., 1920, i, 880).—A vat dye derived from indigotin and ethyl malonate has been patented by Posner (D.R.-P. 281998). The full investigation of the product is now described, the substance being of particular interest, since it gives violet-red shades which are quite distinct from the usual indigo colours.

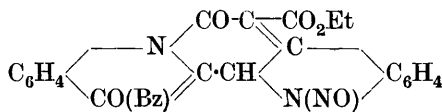
Ethyl indigotinmalonate (annexed formula), reddish-violet crystals, m. p. 296—297°, is prepared conveniently by heating a solution of indigotin in nitrobenzene with ethyl malonate and a little solid sodium hydroxide. It may also be obtained in poor yield by the protracted ebullition of a solution of indigotin in a large excess of ethyl malonate; as by-product of the latter action, a carboxylic acid, $C_{16}H_{18}O_{10}$, m. p. 129°, is formed which has not been investigated completely. It is converted by aqueous alcoholic



potassium hydroxide solution into the corresponding *potassium* salt, $C_{21}H_{14}O_4N_2.KOH$, an emerald-green powder. Hydrolysis of the carbethoxyl group could not be effected by means of acid or alkali; the protracted action of the latter appears to cause the slow loss of the whole malonyl group without, however, giving a homogeneous product. The introduction of a second malonyl complex into ethyl indigotinmalonate could not be effected, but the compound reacts with phenylacetyl chloride in the presence of boiling xylene to yield *ethyl anhydraphenylacetylindigotinmalonate* (annexed formula), m. p. above 310° . *Ethyl benzoyldihydroindigotinmalonate*, $C_{28}H_{20}O_5N_2$, colourless leaflets which become red at about 192° and decompose without melting at a higher temperature, is prepared by reduction of ethyl indigotinmalonate with



sodium hyposulphite in the presence of sodium hydroxide and addition of benzoyl chloride to the solution. The presence of the imino-group in ethyl indigotinmalonate is established by the preparation of *ethyl benzoylindigotinmalonate*, $C_{28}H_{18}O_5N_2$, orange-coloured leaflets, m. p. 240° , which is obtained in small yield by boiling the ester and benzoyl chloride, or more conveniently from these substances in the presence of pyridine. Acetyl chloride and pyridine convert ethyl indigotinmalonate into *ethyl acetylindigotinmalonate*, red crystals, m. p. 182° . *Ethyl nitrosoindigotinmalonate*, $C_{21}H_{13}O_5N_3$, tile-red crystals, decomp. $267-270^\circ$, is prepared by the action of nitrous fumes on a boiling alcoholic suspension of ethyl indigotinmalonate, into which it is re-converted by successive treatment with zinc dust and air. It is not affected by a boiling mixture of acetic anhydride and acetyl chloride, but is converted by benzoyl chloride in the presence of boiling pyridine



into *ethyl benzoylnitrosodihydroindigotinmalonate* (annexed formula), orange-yellow crystals which commence to sublime at 236° and

decompose at $245-250^\circ$; it is hydrolysed by aqueous-alcoholic potassium hydroxide solution to ethyl nitrosoindigotinmalonate.

A compound, $C_{21}H_{17}O_7N_3$, small, almost colourless needles, which become red at 210° , is formed during the preparation of ethyl indigotinmalonate. H. W.

peri-Naphthindigotin. SIKHIBHUSHAN DUTT (T., 1923, 123, 224—225).

2 : 5-Iminodihydro-1 : 2 : 3-triazole. I. Constitution of Dimroth's 5-Anilino-triazole. PAVITRA KUMAR DUTT (T., 1923, 123, 265—274).

Purines. IV. The Action of Hydrogen Peroxide on certain Phenyl-substituted Uric Acids. F. J. MOORE and ELIZABETH S. GATEWOOD (J. Amer. Chem. Soc., 1923, 45, 135—145).—It has

previously been shown (A., 1918, i, 104, 409, 410) that the action of hydrogen peroxide on uric acid may lead to two distinct series of products according to experimental conditions, but the results indicated no intermediate product between uric acid and the final products obtained. With a view to obtain information as to the relationship which may exist between the mechanism of this reaction and that of the permanganate oxidation, certain substituted uric acids have been prepared and their behaviour on oxidation by hydrogen peroxide has been studied.

9-Phenyluric acid on oxidation in alkaline solution with hydrogen peroxide gives *as*-phenylbiuret and a new phenylbiuret, m. p. 196—197.5° (cf. following abstract), together with ammonia, oxalic acid, and phenylcarbamide. 7-Methyluramil when treated in alkaline solution with phenylcarbimide yields 9-phenyl-7-methyl- ψ -uric acid, m. p. 245—250°, n_D 1.636; n_D 1.714+, from which, by boiling with hydrochloric acid, 9-phenyl-7-methyluric acid, n_D 1.887, n_D 1.674, is obtained. On oxidation with hydrogen peroxide in the presence of potassium hydroxide, this uric acid gives oxalic acid, ammonia, and *b*-phenyl-*a*-methylcarbamide. By a similar series of reactions starting with 1:3-dimethyluramil, 9-phenyl-1:3-dimethyl- ψ -uric acid, m. p. 189—190°, n_D 1.525, n_D 1.647, giving a monohydrate, and 9-phenyl-1:3-dimethyluric acid, n_D 1.155+, n_D 1.684, are obtained. The latter compound, on oxidation as above, also yields ammonia, oxalic acid, and *b*-phenyl-*a*-methylcarbamide.

9-Allyl- ψ -uric acid, m. p. 227—228° (decomp.), n_D 1.591, n_D 1.69, is also obtained from the uramil and was converted into 9-allyluric acid, n_D 1.75, n_D 1.775. The optical properties of a number of familiar compounds allied to the above were determined during the work, and the results are tabulated.

From the above results on the oxidation of substituted uric acids, it is considered that the first step in the reaction is the breaking of the bonds between the carbon atoms 2 and 3, 4 and 5, and 5 and 7, forming in the case of 9-phenyluric acid *s*-phenylbiuret, and in the cases of the other two the same phenylmethylbiuret. The phenylmethylbiuret then decomposes, giving ammonia, and phenylmethylcarbamide, while the *s*-phenylbiuret partly undergoes a similar decomposition, forming phenylcarbamide, and another portion is rearranged by the ammonia to form *as*-phenylbiuret.

W. G.

Purines. V. A Third Phenylbiuret. ELIZABETH S. GATEWOOD (*J. Amer. Chem. Soc.*, 1923, 45, 146—150; cf. preceding abstract).—The new phenylbiuret, m. p. 196—198° (decomp.), n_D 1.559; n_D 1.73, obtained during the oxidation of 9-phenyluric acid by hydrogen peroxide (*loc. cit.*) is clearly distinguished by its properties from the two isomerides already known. It can be converted into *as*-phenylbiuret by the action of ammonia and a great variety of organic bases, but not by alkalis. No method of reversing this change has been discovered. From certain theoretical considerations the author is inclined to the view that

the structure of this new biuret is that of *N*-phenylbiuret, a structure at present assigned by Schiff (A., 1907, i, 206) to the phenylbiuret prepared by Weith (A., 1878, 141). W. G.

The Upper Limit of Diazotisability in the Benzene Series. Diazo-derivatives of Mesitylene. GILBERT T. MORGAN and GLYN REES DAVIES (T., 1923, 123, 228—237).

Azopicric Acid [2 : 4 : 6 : 2' : 4' : 6'-Hexanitro-5 : 5'-dihydroxyazobenzene]. K. ELBS and FR. SCHLIEPHAKE (*J. pr. Chem.*, [ii], 1922, 104, 282—284).—The nitration of *m*-azophenol (cf. A., 1903, i, 539) by the prolonged action of an ice-cold mixture of concentrated sulphuric acid and potassium nitrate, subsequent treatment with water, and extraction with benzene, leads to the compound of 1 mol. of azopicric acid with 2 mols. of benzene, flat, deep blood-red prisms; this loses benzene gradually, more quickly on warming at 90°, giving a 60% yield of pure *azopicric acid* as a yellowish-red powder, m. p. 238—239° (decomp.), which explodes violently when quickly heated. Azopicric acid dissolves readily in benzene (giving the above-mentioned compound), and also in water, alcohol, ether, or acetone, but is insoluble in carbon disulphide or concentrated hydrochloric acid. In aqueous solution it is a fast dye to wool, and has an astringent (not bitter) taste. The potassium and barium salts are described. W. S. N.

Capacity to Form Phenylhydrazones. VI. BERNARDO ODDO and LUIGI PIATTI (*Gazzetta*, 1922, 52, ii, 333—346).—Cryoscopic investigations in anhydrous phenylhydrazine, similar to those already described (A., 1913, i, 1233; 1915, ii, 414, 415), have now been made on a number of compounds containing in the molecule either two carbonyl groups or one carbonyl together with other radicles.

Diacetyl reacts immediately with the phenylhydrazine, giving a precipitate which does not dissolve readily. After a time, however, the liquid becomes almost clear, and the depression of the freezing point gradually attains a value which is 50% of the theoretical value for the diacetyl taken, the formation of the monophenylhydrazone being thus indicated. Later, the phenylosazone is precipitated in increasing amount. Similar difficulties as regards solubility are presented by anthraquinone, with which a clear solution cannot be obtained.

With acetylacetone, the apparent molecular weight rapidly reaches a value equal to 40% of the theoretical value, and subsequently slowly falls to become constant at about one-third the calculated value, the diphenylhydrazone or, more probably, the pyrazole compound being formed: $\text{OH}\cdot\text{CMe}\cdot\text{CHAc} + \text{NH}_2\cdot\text{NHPh} = \text{OH}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CMe}\cdot\text{N}\cdot\text{NHPh} + \text{H}_2\text{O} = \begin{matrix} \text{N} \\ \parallel \\ \text{CMe} \\ | \\ \text{NPh}\cdot\text{CMe} \end{matrix} \gg \text{CH} + 2\text{H}_2\text{O}$. Similar

results are obtained with benzil, except that the initial velocity of the reaction is somewhat less. With dipyrroyl, although the phenylosazone is known, no reaction with phenylhydrazone occurs under the experimental conditions of the present investigation.

As regards terpenic ketones, camphor, bromocamphor, and

fenchone, which are bicyclic, are inert towards phenylhydrazine. The monocyclic pulegone, however, reacts completely, the molecular weight falling at approximately constant velocity to about 60% and then at gradually diminishing velocity to 52% of the theoretical value. Menthone behaves similarly to pulegone, with which, rather than with the other terpenic ketones examined, it presents structural analogies. Carvone is inactive towards phenylhydrazine, the double linking in the nucleus possibly favouring an enolic configuration. Santonin also is inactive.

The results obtained with aldehydes emphasise the promptitude with which the aldehydic function is exercised in presence of phenylhydrazine. The aldehydes investigated were dextrose, cuminaldehyde (*isopropylbenzaldehyde*), *o*-, *m*-, and *p*-nitrobenzaldehydes, phenylacetaldehyde, cinnamaldehyde, and *m*-nitrocinnamaldehyde, vanillin, *p*-dimethylaminobenzaldehyde, furfuraldehyde, and phthalaldehyde. None of these remains inert towards phenylhydrazone, and most of them quickly precipitate the phenylhydrazones. Furfuraldehyde reacts instantly, but gives no precipitate. With phenylacetaldehyde, which also yields no precipitate, the reaction is somewhat slow in its final phase, this aldehyde thus resembling the aliphatic aldehydes. Cinnamaldehyde and its *m*-nitro-derivative, on the other hand, exhibit towards phenylhydrazine the behaviour of an aromatic aldehyde, in spite of the fact that the aldehyde group lies in the side chain.

Dextrose furnishes no precipitate with phenylhydrazine, but the reaction proceeds with the regularity shown in the case of the aliphatic aldehydes, although the retarding influence of the alcoholic groups is manifest. Phthalaldehyde behaves abnormally, the value of the molecular weight in phenylhydrazine solution being only 23% of the value calculated from the amount of the aldehyde taken.

T. H. P.

The Opening of the Lactone Ring of Phthalide Derivatives by Hydrazine.

J. TEPPEMA (*Rec. trav. chim.*, 1923, 42, 30—68).—The object of this work was to study the influence on the stability of the lactone ring in phthalide of substituents both in the benzene ring and in the methylene group of the lactone ring. The stability of the ring is gauged by the ability or otherwise of hydrazine to open the ring with formation of a benzhydrazide and further by the stability of aldehydo- and keto-derivatives of the benzhydrazide. The action of hydrazine on phthalide was studied by Wedel, who concluded that the product formed was the hydrazide of *o*-hydroxymethylbenzoic acid (A., 1900, i, 363), but Blaise and Luttringer concluded that the additive compound was formed at the keto-group without rupture of the lactone ring (A., 1905, i, 329). The results of the present work do not support the latter view. A number of derivatives of *o*-hydroxymethylbenzhydrazide with aldehydes and ketones were prepared.

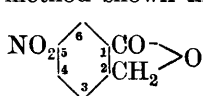
p-Methoxybenzylidene-*o*-hydroxymethylbenzhydrazide,



forms colourless needles, m. p. 165°. *isoPropylidene-o-hydroxy-*

methylbenzhydrazide forms colourless spangles, m. p. 148°. A derivative could not be obtained with acetophenone. *d-Mannose-o-hydroxymethylbenzhydrazide* crystallises in colourless needles, m. p. 106—109°; in boiling aqueous solution it is decomposed by benzaldehyde with formation of benzylidene-*o*-hydroxymethylbenzhydrazide. *d-Galactose-o-hydroxymethylbenzhydrazide* was obtained in crystals, m. p. 70—75°, but could not be recrystallised unchanged. The corresponding dextrose derivative was obtained only as a syrup; it is decomposed by benzaldehyde in hot aqueous solution. An acetyl derivative of *o*-hydroxymethylbenzhydrazide can be obtained by the action of acetic anhydride in the cold. Its decomposition in the hot, with formation of phthalide, accounts for Wedel's failure to prepare it. The acetyl compound does not react with benzaldehyde and must therefore be a *N*-acetyl derivative. *N-Acetyl-o-hydroxymethylbenzhydrazide*, $\text{OH}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}\cdot\text{NHAc}$, forms colourless spangles, m. p. 146°. No benzoyl derivative of *o*-hydroxymethylbenzhydrazide could be obtained with benzoyl chloride.

The mono-nitro-derivative obtained by nitrating phthalide either with pure nitric acid or with a nitrate and sulphuric acid is 5-nitrophthalide, m. p. 143°, not 4-nitrophthalide as stated by Hoenig (A., 1886, 242). In the literature different methods of notation are adopted by different authors; the present author adopts the method shown in the annexed formula.



5-Nitro-2-hydroxymethylbenzhydrazide forms yellow needles, m. p. 167—168°. The *isopropylidene* derivative of this forms colourless needles, m. p. 165°; the *benzylidene* derivative forms colourless spangles, m. p. 167°.

The aldehyde and ketone derivatives of nitro-*o*-hydroxymethylbenzhydrazide are not hydrolysed so readily as those of *o*-hydroxymethylbenzhydrazide, with re-formation of the phthalide, and, conversely, the presence of the nitro-group facilitates the rupture of the lactone ring. *N-Acetyl-5-nitro-2-hydroxymethylbenzhydrazide* forms colourless spangles, m. p. 171°; when boiled with acetic anhydride, it is decomposed, forming 5-nitrophthalide.

5-Aminophthalide is best prepared by reducing 5-nitrophthalide with hydrogen sulphide in ammoniacal alcoholic solution. When reduced with phosphorus and hydrogen iodide, it gives an amino-*o*-toluic acid, m. p. 196°, not 153°, as stated by Hoenig. This was identified as 4-amino-*o*-toluic acid, which establishes the constitution of the above 5-nitrophthalide. 4-Amino-*o*-toluic acid was synthesised by a new method, through the steps 4-nitro-*o*-toluidine, \rightarrow 4-nitro-2-cyanotoluene \rightarrow 4-amino-2-cyanotoluene \rightarrow 4-amino-*o*-toluic acid.

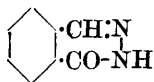
The lactone ring of 5-aminophthalide is opened by hydrazine with formation of 5-amino-2-hydroxymethylbenzhydrazide, colourless needles, m. p. 147°; *benzylidene* derivative, m. p. 161°; *isopropylidene* derivative, m. p. 170°. 5-Acetamidophthalide forms colourless needles, m. p. 222—223°. When 5-amino-2-hydroxymethylbenzhydrazide is treated with cold acetic anhydride, it forms the diacetyl derivative, 5-acetamido-2-hydroxymethylacetylbenzhydrazide,

small colourless needles, m. p. 195°; but with hot acetic anhydride, 5-acetamidophthalide is formed.

Contrary to the statement of Hoenig, 5-aminophthalide can be readily diazotised and transformed almost quantitatively into a halogen derivative by Sandmeyer's method. 5-Chlorophthalide forms colourless needles, m. p. 110°; 5-bromophthalide forms similar crystals, m. p. 98°. 5-Chloro-2-hydroxymethylbenzhydrazide forms colourless needles, m. p. 139°; benzylidene derivative, m. p. 165—166°; isopropylidene derivative, m. p. 153°; acetyl derivative, m. p. 160°. 5-Bromo-2-hydroxymethylbenzhydrazide forms colourless needles, m. p. 152°; benzylidene derivative, m. p. 171°; isopropylidene derivative, m. p. 157°; acetyl derivative, m. p. 153°.

The introduction of a single methyl, ethyl, or phenyl group into phthalide in the α -position stabilises the lactone ring to such an extent that hydrazine cannot effect the rupture. A chloro-, bromo-, or nitro-group in the 5-position of α -methylphthalide weakens the lactone ring sufficiently to permit rupture by hydrazine, but this is not the case with α -ethylphthalide or α -phenylphthalide. 5-Amino- α -ethyl- and 5-amino- α -methyl-phthalide do not react with hydrazine. The dialkyl and diphenylphthalides are extremely stable and their inactivity towards hydrazine is not affected by substituents in the 5-position.

α -Methylphthalide has n_D^{14} 1.5450, d_4^{15} 1.1601, m. p. 7°. 5-Nitro- α -methylphthalide, the principal nitration product of α -methylphthalide, is accompanied by a small quantity of an isomeride, probably the 3-nitro-compound. With hydrazine, 5-nitro- α -methylphthalide gives 5-nitro-2- α -hydroxyethylbenzhydrazide, $\text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{C}_6\text{H}_3(\text{NO}_2)\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$, forming colourless needles, m. p. 120°. The isopropylidene derivative has m. p. 127°, but when recrystallised from alcohol partly decomposes with regeneration of the lactone. A benzylidene derivative could not be obtained on account of the formation of lactone. The lactone ring in 5-nitro- α -methylphthalide is therefore more stable than that in 5-nitro-phthalide. 5-Nitro-2- α -hydroxyethyl-acetylbenzhydrazide, m. p. 126°, has similar properties to the other acetyl derivatives described. 5-Amino- α -methylphthalide does not react with hydrazine. From it were prepared 5-chloro- α -methylphthalide, colourless needles, m. p. 45°, and 5-bromo- α -methylphthalide, m. p. 59°. 5-Chloro-2- α -hydroxyethylbenzhydrazide forms colourless needles, m. p. 108°; its isopropylidene derivative has m. p. 119°. The 5-bromo-2- α -hydroxyethylbenzhydrazide has m. p. 119° and its isopropylidene derivative 135°. 5-Amino- α -ethylphthalide was obtained by reduction of the corresponding nitro-compound; it forms small, yellow needles, m. p. 140°. From this were obtained 5-chloro- α -ethylphthalide, colourless needles, m. p. 54°, and 5-bromo- α -ethylphthalide, similar crystals, m. p. 63°. By the action of hydrazine on α -amino- or α -bromo-phthalide, 1-keto-1:2-dihydrophthalazine (annexed formula) is obtained, and the same substance is formed from hydrazine and diphtalide ether, which thus behaves as the anhydride of phthalaldehydic acid. 5-Amino- α -dimethylphthalide crys-



tallises in colourless needles, m. p. 115° . With bromine, it gives 4:6-dibromo-5-amino- α -dimethylphthalide, colourless needles, m. p. 138° . 4:6-Dibromo-5-amino- α -diethylphthalide crystallises in spangles, m. p. 93° . Not one of these derivatives of a dialkylphthalide is acted on by hydrazine. The work serves to confirm and extend Hjelt's rule regarding the stability of lactone rings (A., 1891, 822). E. H. R.

The Configuration of the Doubly-linked Tervalent Nitrogen Atom. The Resolution of the Pyridylhydrazone of cyclo-Hexylene Dithiocarbonate. WILLIAM HOBSON MILLS and HANS SCHINDLER (T., 1923, 123, 312—323).

The Ionisation of Protein Chlorides. DAVID I. HITCHCOCK (*J. Gen. Physiol.*, 1923, 5, 383—394).—By the use of the silver-silver chloride electrode and the hydrogen electrode, electrometric determinations have been made of the chloride and hydrogen-ion concentrations in solutions of proteins (gelatin, egg-albumin, casein, edestin, and serum-globulin) to which varying quantities of hydrochloric acid have been added. It is concluded that the hydrochlorides of these proteins are strongly ionised, and that there is no marked repression of the ionisation by excess of hydrochloric acid. W. O. K.

Density of Albumin Solutions. M. A. RAKUSIN and G. D. FLIEHER (*Chem. Ztg.*, 1923, 47, 66).—A table is given of the density of albumin solutions at 17° up to a concentration of 15.35%, at which the solution is saturated. White of egg is a saturated solution of albumin. When freed from fat and clarified by treatment with lead acetate, albumin has a considerably lower density than the crude substance, the value for a 5% solution being d_{15}^{15} 1.01288 for the pure substance and d_{15}^{15} 1.01341 for the crude. The specific rotatory power is unchanged by the purifying process. H. C. R.

The Nature of Nucleins. S. NAKAGAWA (*Z. physiol. Chem.*, 1923, 124, 274—277).—Hydrolysis of nucleoprotein by pepsin yields no nuclein. The idea of Steudel is confirmed that nucleoproteins are loose compounds of nucleic acid and a protein base. W. O. K.

The Hydrolysis of Proteins by Strong Sulphuric Acid. E. SALKOWSKI (*Biochem. Z.*, 1922, 133, 1—20).—Horn, on complete hydrolysis by three times its weight of 73.6% sulphuric acid, gives practically no humin material. The hydrolysate reduces Fehling's solution to an extent which indicates the presence of 13% of apparent sugar. Pyruvic acid, aldehydes of the aliphatic series, and furfuraldehyde are also present. W. O. K.

Heteroalbumose. E. ZUNZ and P. GYÖRGY (*Bull. Acad. roy. Belg.*, 1914, 359—380).—An investigation of Pick's heteroalbumose (A., 1900, i, 68) by two methods: (1) Fractionation by Siegfried's method (A., 1906, i, 144) and (2) ultra-filtration, using collodion and acetic acid of three different concentrations. The authors

conclude that Pick's hetero-albumose is really a mixture. The chief constituent (insoluble in twice its bulk of 95% alcohol) is a heteroalbumose with $[\alpha]_D^{20} -72.5^\circ$, but associated with it are several protoalbumoses of low rotatory power and soluble in twice their bulk of alcohol. One of these is apparently responsible for the Adamkiewicz reaction given by some preparations of Pick's heteroalbumose. Altogether, fifteen different fractions of the latter are examined and compared with the original substance by means of elementary analysis, rotatory power, gold numbers, refractive indices, etc. E. E. T.

Bioluminescence. XV. Electro-reduction of Oxyluciferin. E. NEWTON HARVEY (*J. Gen. Physiol.*, 1923, 5, 275—284).—If a solution containing luciferin and luciferase and some sodium chloride is electrolysed, the oxyluciferin is reduced at the cathode by the nascent hydrogen, and as it is oxidised back again in the presence of the luciferase, by the oxygen dissolved in the water, with the production of light, there is immediately luminescence. Similar reduction by nascent hydrogen also takes place at the surface of metals (aluminium, manganese, zinc, and cadmium) when these are immersed in water containing oxyluciferin, although there is no actual production of molecular hydrogen. Other systems are described where electrochemical reduction of luciferin occurs. In general, the production of light by the combination oxyluciferin-luciferase is a very good test for nascent hydrogen. Molecular hydrogen does not produce luminescence. If, however, a palladiumised surface be introduced, it becomes strongly luminescent, as it activates the hydrogen.

W. O. K.

The Mechanism of the Effect of Acids and Alkalis on the Digestion of Proteins by Pepsin or Trypsin. A Correction. JOHN H. NORTHPROP (*J. Gen. Physiol.*, 1923, 5, 415; cf. this vol., i, 69).—A statement made in the previous paper (*loc. cit.*) to the effect that the amount of acid required to bring protein solution to a given P_H is independent of the nature and valency of the anion is true only of strong acids.

W. O. K.

Influence of Reaction on the Activity of Trypsin. II. W. E. RINGER (*Z. physiol. Chem.*, 1923, 124, 171—193; cf. A., 1922, i, 282).—The solution of fibrin by trypsin is inhibited by sulphates, thiocyanates, and ferrocyanides, but more strongly by multivalent kations such as calcium, which also strongly inhibit the swelling of fibrin in water. The effects, however, are not quite analogous; bile salts, for example, completely inhibit the solution of fibrin at concentrations at which the effect on the swelling is quite inappreciable. Salts with multivalent kations affect the viscosity of alkaline protein solutions (dialysed serum). The effect of these salts on the tryptic hydrolysis of such solutions is at first one of inhibition, but this very soon disappears. Experiments confirm the fact that alkaline protein solutions show a gradual increase in internal friction and that after a long time the internal friction again becomes less.

W. O. K.

Equilibrium between the so-called "Antitrypsin" of the Blood and Trypsin. RAYMOND G. HUSSEY and JOHN H. NORTHROP (*J. Gen. Physiol.*, 1923, 5, 335—351).—From a study of the inhibition of trypsin by blood plasma, it is concluded that the effect is not one of adsorption, but that it is more probably chemical in nature. It is shown that if the assumption is made that an easily dissociated compound of the trypsin and the inhibiting substance is formed, the law of mass action is obeyed according to the equation $[\text{Trypsin}][\text{inhibiting substance}]/[\text{Compound of Trypsin and inhibiting substance}] = K$. Equilibrium is attained very quickly and is reversible, and this fact opposes the view that there is an adsorption. Quantitative experiments have been carried out by the authors' method on (1) the effect of adding varying amounts of plasma to a constant amount of trypsin, (2) the effect of adding varying amounts of trypsin to a constant amount of plasma, and (3) the effect of dilution on a plasma-trypsin mixture, and the results accord with the theory that a reversible equilibrium is attained. These conclusions are in harmony with the results that have been obtained with other enzymes.

W. O. K.

Invertase. A. FODOR (*Z. physiol. Chem.*, 1923, 124, 278—281).—Criticism of the results of Willstätter, Graser, and Kuhn (A., 1922, i, 1200), pointing out the difficulty of being certain of the purity of the preparations obtained.

W. O. K.

Kinetic Researches on Saccharase. H. VON EULER and K. MYRBÄCK (*Z. physiol. Chem.*, 1923, 124, 159—170).—The unimolecular reaction constant k is determined for the inversion of sucrose by saccharase (invertase), from the expression $k = 1/t \cdot \log a/(a-x)$, where x is the amount of sucrose inverted in a time t out of the initial amount a . With increasing values of c , the initial concentration of the sucrose, the value of the product kc increases until c is about 4 g. per 100 c.c., after which it is constant until c is about 20 g. per 100 c.c., and then it decreases. If, on the assumption that a reversible equilibrium is reached between enzyme and substrate, the constant $K = [\text{Enzyme}][\text{Substrate}]/[\text{Enzyme Substrate}]$ is calculated, which is possible if it be also assumed that all the enzyme is combined with the substrate when k is maximal, it is found to vary from 0.027 to 0.0175.

W. O. K.

Influence of Amino-acid in Protecting Amylase from Inactivation by Mercury. H. C. SHERMAN and MARY L. CALDWELL (*J. Amer. Chem. Soc.*, 1922, 44, 2923—2926).—Glycine and phenylalanine and presumably other amino-acids protect against small concentrations of mercuric chloride added when testing the activity of purified pancreatic amylase and allow the latter to act almost as efficiently as if no mercury were present. The minute amounts of mercury which might conceivably have been present in the histidine and tryptophan preparations used could not, therefore, account for their entire lack of activating influence on

the amylolytic action of the enzyme as previously recorded (A., 1922, i, 283). W. G.

Influence of Lysine on the Hydrolysis of Starch by Purified Pancreatic Amylase. H. C. SHERMAN and MARY L. CALDWELL (*J. Amer. Chem. Soc.*, 1922, **44**, 2926—2930).—Lysine has no effect on the amylolytic action of pancreatic amylase, but exerts a favourable influence on its saccharogenic action. Accepting the view that the enzyme (pancreatic amylase) is essentially a protein substance which gradually becomes inactivated through hydrolysis in the aqueous medium in which it acts, and that the apparent activating influence of amino-acids is due to retardation of this hydrolysis of the enzyme, it is suggested that the lysine in the enzyme molecule is not split off until after the stage of amylolytic action has passed, but is only concerned in the later stages represented by saccharogenic activity. These observations confirm and extend the theory advanced to explain the effect of histidine and tryptophan on the same enzyme (A., 1922, i, 283). W. G.

Influence of some Organic Compounds upon the Hydrolysis of Starch by Salivary and Pancreatic Amylases. H. C. SHERMAN and NELLIE M. NAYLOR (*J. Amer. Chem. Soc.*, 1922, **44**, 2957—2966).—The authors consider that the favourable effect reported by Rockwood (A., 1917, i, 358; 1918, i, 86, 274) to be exerted by several types of organic compounds on the activity of amylolytic enzymes was due in most, if not in all, cases, other than those of natural amino-acids, to hydrogen-ion or salt effects, rather than to the organic structure of the compounds. In the presence of favourable concentrations of chloride-, phosphate-, and hydrogen-ions, no favourable effect on the activity of the enzyme was shown by methyl- and ethyl-amine hydrochlorides, aniline sulphate, benzoic acid, benzamide, anthranilic acid, or hippuric acid. Previous results as to the favourable influence of several amino-acids resulting from protein hydrolysis have been confirmed and extended. This influence may be attributed either to a direct activating effect dependent on the structural nature of these substances as α -amino-acids or to conservation of the enzyme by retarding its hydrolysis, but the results with hippuric acid fail to confirm the activation hypothesis. W. G.

Some Actions of Thorium-X on Diastases and Micro-organisms. J. P. AVERSENQ, L. JALOUSTRE, and E. MAURIN (*Compt. rend.*, 1923, **176**, 193—195).—Thorium-X, at the concentrations used, activates in a marked manner the hydrolysing and oxidising enzymes studied, the increased action in a given time being of the order of 30%. Similarly, relatively small amounts of thorium-X were capable of increasing the vitality of certain pathogenic organisms and of certain living cells. W. G.

Peroxydase. III. RICHARD WILLSTÄTTER and ADOLF POLLINGER (*Annalen*, 1923, **430**, 269—319).—In continuation of previous work (A., 1918, i, 555) on the purification of peroxydase

preparations, the authors have made a detailed study of the influence of adsorption on and subsequent elution from alumina and kaolin, and of precipitation by tannic acid, on the activity of peroxydase solutions. On the basis of these experiments, two methods of purification are worked out in detail, the results of each operation being followed by determinations of the "purpurogallin number" (*loc. cit.*). According to one method, the peroxydase in a solution having a purpurogallin number 302 is first adsorbed on alumina suspended in 50% alcohol, removed in carbonic acid solution, and then again adsorbed on alumina in dilute alcohol. One further adsorption on kaolin in 50% alcohol and three subsequent adsorptions on alumina raise the purpurogallin number to 4900, the highest value as yet observed. According to the second method, the peroxydase is subjected to four adsorptions on alumina in 50% alcohol and three on kaolin in 0.02*N*-acetic acid, and a precipitation by tannin, the final purpurogallin number being 3070.

The question as to whether iron enters into the constitution of peroxydase cannot be conclusively settled on the analytical data, because, although for a given natural source and method of purification the iron content runs roughly parallel with the purpurogallin number, a change either in the source or the process affects the proportion of iron in a way which cannot at present be simply accounted for.

C. K. I.

Reductases. II. Comparison of the Influence of Alkalis on Potato Reductase. I. A. SMORODINCEV (*Z. physiol. Chem.*, 1923, 124, 202—210; cf. A., 1922, i, 1201).—The effect of alkali on the reductase in potatoes (nitrase) is to inhibit the activity, an effect apparently independent of the kation, and due to the hydroxyl-ion concentration.

W. O. K.

Mode of Action of Vitamins. ANTONIO DE GREGORIO ROCASOLANO (*Anal. Fis. Quim.*, 1922, 20, 433—436).—Theoretical. The vitamins are held to act as colloidal catalysts.

G. W. R.

Vitamins-B and -D. CASIMIR FUNK and JULIA B. PATON (*J. Metabolic Research*, 1922, 1, 737—775).—Vitamin-B is destroyed by alkali and also by heating in an autoclave under pressure for three hours; the effect of such treatment on vitamin-D is much smaller. When grown in a solution containing both vitamins, yeast or other fungi removes the latter, which is retained tenaciously by the yeast-cells.

CHEMICAL ABSTRACTS.

An Attempt to Resolve Quaternary Phosphonium Compounds. L. G. RADCLIFFE and W. H. BRINDLEY (*Chemistry and Industry*, 1922, 42, 64—66).—In the hope of effecting a resolution of a quaternary phosphonium compound, *phenyl-p-tolylmethylallylphosphonium d-bromocamphorsulphonate* was prepared, but attempts to crystallise it failed; it was only obtained as a jelly-like mass, finally becoming resinous. The synthesis of the compound was accomplished from *p*-tolylchlorophosphine, through *phenyl-p-tolylchlorophosphine* to *phenyl-p-tolylmethylphosphine*,

which was then combined with allyl iodide. The final yield was very small. Attempts to prepare phenyl-*p*-tolylethyl-*n*-butylphosphonium iodide from phenyl-*p*-tolylethylphosphine and *n*-butyl iodide led only to the formation of an uncrystallisable oil.

E. H. R.

Additive Reactions of Phosphorus Halides. VI. The 1:2- and 1:4-Addition of Diphenylchlorophosphine. J. B. CONANT, J. B. S. BRAVERMAN, and R. E. HUSSEY (*J. Amer. Chem. Soc.*, 1923, **45**, 165—171; cf. A., 1921, i, 69).—Diphenylchlorophosphine reacts with benzaldehyde and phenyl styryl ketone in the presence of glacial acetic acid, giving, respectively, an hydroxy- and a keto-phosphine oxide. By using acetic anhydride in place of the acid, the mechanism of the reaction with the unsaturated ketone has been established. Under these conditions, an unsaturated intermediate compound, $\text{O}(\text{PPh}_2 \begin{smallmatrix} \text{O} \cdot \text{CPh} \\ \text{CHPh} \end{smallmatrix} \text{CH})_2$, is formed, but could not be isolated in a crystalline state. On treatment with water, it gives the ketophosphine oxide, and it readily combines with two equivalents of bromine to yield a dibromide without the evolution of hydrogen bromide. This dibromide, not isolated as such, on treatment with water gives a mixture of two isomeric monobromoketophosphine oxides, one of which can be obtained by direct bromination of the ketophosphine oxide itself. These two monobromo-derivatives behave differently towards alcoholic sodium hydroxide. The one with the high m. p. loses hydrogen bromide to give an unsaturated ketophosphine oxide, whilst the other is reduced to the ketophosphine oxide. On the other hand, by boiling it with potassium acetate in methyl alcohol, the bromo-compound with the high m. p. is reduced to the ketophosphine oxide.

The following compounds are described. *Diphenyl- α -hydroxybenzylphosphine oxide*, m. p. 230°, obtained from benzaldehyde and diphenylchlorophosphine. *Diphenyl- β -benzoyl- α -phenylethylphosphine oxide*, m. p. 227°, similarly obtained from phenyl styryl ketone. *Diphenyl- β -*p*-chlorobenzoyl- α -phenylethylphosphine oxide*, m. p. 225—226°. *Diphenyl- β -bromo- β -benzoyl- α -phenylethylphosphine oxide*, in two isomeric forms, m. p. 187° and 158°, respectively. *Diphenyl- β -bromo- β -*p*-chlorobenzoyl- α -phenylethylphosphine oxide*, in two isomeric forms, m. p. 196° and 187°, respectively. *Diphenyl- β -benzoyl- α -phenylvinylphosphine oxide*, m. p. 143°; and *diphenyl- β -*p*-chlorobenzoyl- α -phenylvinylphosphine oxide*, m. p. 151°.

W. G.

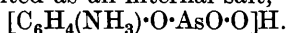
Tetraphenyldiarsine. PARRY BORGSTROM and MARGARET M. DEWAR (*J. Amer. Chem. Soc.*, 1922, **44**, 2915—2923).—An extension of previous work (A., 1920, i, 196). When tetraphenyldiarsine is prepared in a pure state, out of contact with air, its m. p. is 130—130·5° (corr.) (cf. Michaelis and Schulte, A., 1883, 187). Quantitative data are given for its oxidation in moist air and for its absorption of iodine, which latter decreases with the

age of the solution. This decrease in iodine absorption corresponds with an increase in molecular weight as determined cryoscopically in naphthalene as solvent. The specific conductivity in liquid sulphur dioxide increases with the age of the solution, changing from 13.3×10^{-6} to 100×10^{-6} mhos in nineteen days. The conductivity also increases with rise in temperature. The data indicate that the bond between the arsenic atoms of the tetraphenyldiarsine is easily broken. Bivalent arsenic of the type Ph_2As^+ may be present transitorily in solution, but it is doubtful if it is the stable form. The valency or configuration of the stable form is not known.

Tetraphenyldiarsine reacts with methyl iodide, forming dimethyldiphenylarsonium iodide (cf. Steinkopf and Schwen, A., 1921, i, 694). W. G.

Some Determinations of Molecular Weight in the Arsinic Acid Series. RICHARD LORENZ and ELISABETH BREHMER (*Ber.*, 1923, 56, [B], 174—176; cf. Lorenz and Schmidt, A., 1920, i, 777, 897; ii, 465).—The molecular weights of arsanilic, *o*-toluidino-, resorcino-, 3-nitro-4-aminophenyl-, 3-nitro-4-hydroxyphenyl-, 3-nitrophenyl-, *p*-phenylenedi-, and *o*-phenylenediamine-arsinic acids have been estimated in aqueous solution by the ebullioscopic method. They appear generally to have the simple, non-polymerised structure of the type $\left[\text{Ph} \cdot \text{AsO} \begin{smallmatrix} \text{O} \\ \diagup \diagdown \end{smallmatrix} \text{H} \right]_{\text{H}}$. *o*-Phenylenediaminearsinic acid, however, is polymerised to such an extent that it may exhibit double the normal molecular weight, but different preparations give different values.

Arsanilic acid, $(\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{AsO}_2)_2\text{H}_2$, is strictly monobasic, and is preferably represented as an internal salt,



Similar observations are recorded with *o*-toluidinoarsinic acid, *p*-dimethylaminophenylarsinic acid, and *o*-phenylenediaminearsinic acid. Resorcino-, 3-nitro-4-aminophenyl-, dichlorophenyl-, dibromophenol-, 3-nitro-4-hydroxyphenyl-, *p*-iodophenyl-arsinic acids, and 4-amino-3-carboxyphenyl-arsine oxide behave normally with regard to electrical conductivity and exhibit normal molecular weights. H. W.

Preparation of Mercury Dibenzyl. A. GARCIA BANÚS (*Anal. Fis. Quim.*, 1922, 20, 667—668).—Mercury dibenzyl is prepared by treating benzyl chloride with excess of magnesium dust and adding mercuric chloride to the liquid, after decanting from excess of magnesium. The mixture is heated with frequent shaking under a reflux apparatus. Dilute acetic acid is added, and mercury dibenzyl is obtained by crystallisation from the ethereal solution. It has m. p. 110—111°. G. W. R.

Physiological Chemistry.

The Importance of Amides in Plant Feeding-stuffs. F. HONCAMP (*Z. angew. Chem.*, 1923, 36, 45—49).—It is shown that urea may, at least partly, replace protein in feeding-stuffs without any injury to the animal. A. G. P.

The Possibility of Urea as a Source of Protein in Ruminants. The Excretory Function of the Skin. ARTHUR SCHEUNERT, WILHELM KLEIN, and MARIA STEUBER (*Biochem. Z.*, 1922, 133, 137—191).—From experiments in which urea was administered to animals as the source of nitrogen, it has been found impossible to demonstrate that it can function as a source of protein. W. O. K.

The Measurement of Buffering. GÜNTHER LEHMANN (*Biochem. Z.*, 1922, 133, 30—45).—A valuable measure of the buffering of a solution is given by $b/(P_{H_1}-P_{H_2})$ where P_{H_1} is measured before and P_{H_2} after the addition to 10 c.c. of the buffer solution of a small quantity b of hydrochloric acid (or sodium hydroxide) measured in c.c. of 0.01*N*-solution. The P_H values are conveniently determined colorimetrically. Examples are given, chiefly of liquids of physiological importance. Values above 8 indicate strong buffering, 0.5—4, weak buffering, and below 0.5 no buffering. Blood gives a value of about 11. W. O. K.

Comparative Buffering Value of American Peptones. J. BRONFENBRENNER, G. G. DE BORD, and P. F. ORR (*Proc. Soc. Exp. Biol. Med.*, 1921, 19, 16).—The p_H of the various peptone solutions was determined electrometrically before and after the addition of measured amounts of acid and alkali, respectively. The initial reactions of the different solutions varied greatly; so did their buffer actions at a given p_H , some being 5 times greater than others. The buffering effect varied at different zones of p_H , being most marked between p_H 9 and 8, and least between p_H 5 and 4. For a given peptone the buffering varied at different p_H zones; the absolute concentration of buffer salts was highest at the lowest p_H and not at neutrality or high p_H as would be most desirable in media for use in the identification of bacteria by cultural methods. CHEMICAL ABSTRACTS.

Antiketogenesis. A. I. RINGER (*Proc. Soc. Exp. Biol. Med.*, 1921, 19, 97—99).—Glyceraldehyde, dihydroxyacetone, pyruvaldehyde, and pyruvic and lactic acids, when fed to diabetic animals, are completely and directly converted into dextrose and excreted in the urine, whilst acetaldehyde and possibly ethyl alcohol possess antiketogenetic properties. CHEMICAL ABSTRACTS.

Chemical Researches on Nuclear Staining. H. STEUDEL and SHUNGO OSATO (*Z. physiol. Chem.*, 1923, 124, 227—246).—It is considered probable that, in nuclear staining, a chemical

reaction takes place of the type: clupein nucleate+hydrochloride of the dye \rightarrow nucleate of the dye+clupein hydrochloride. By measuring the crystal violet absorbed from solutions of various strengths by heads of spermatozoa, it is shown that, if this assumption be true, the reaction does not proceed to completion, but that probably an equilibrium is set up. Similar results are obtained with protamine nucleic acid, with the nuclei of goose erythrocytes, with thymus leucocytes, and with nucleohiston, and also with other dyes—methylene-blue and eosin. W. O. K.

The Nitrogenous Compounds Extracted from Testicles of the Ox. KİYOSHI MORINAKA (*Z. physiol. Chem.*, 1923, 124, 259—266).—In an extract of ox testicles the following compounds have been identified: creatine, adenine, xanthine, arginine, histidine, choline, inositol, and probably guanine and hypoxanthine. W. O. K.

The Maximal Quantity of the Glycogen Reserve in the Livers of Dogs of Different Ages. (MME) Z. GRUZEWSKA and E. FAURÉ-FRÉMIET (*Compt. rend.*, 1922, 175, 1237—1240; cf. A., 1921, i, 699).—Dogs were fed on a special diet and the liver and muscles analysed in order to determine the time during which the accumulated reserve of glycogen could remain unused in the liver. The conclusions are drawn that prolonged over-feeding was only tolerated by the liver in the case of a young and vigorous animal, and that the glycogenic function of the hepatic cell undergoes some modification either with age or with unfavourable circumstances without any apparent change in histological aspect. Further, in order to find the maximum glycogen content in the liver of a dog kept on an appropriate diet, the analysis must be carried out before the animal has attained its original weight as measured before fasting. H. J. E.

Auto-oxidation and Anti-oxygen Action. IV. CHARLES MOUREU and CHARLES DUFRAISSE (*Anal. Fis. Quím.*, 1922, 20, 383—393; cf. A., 1922, i, 250, 824).—A discussion of the general significance of auto-oxidation and anti-oxygen action in biology. The mechanism of the auto-oxidation of acetaldehyde and its inhibition by anti-oxygens is also discussed. It is supposed that acetaldehyde exists in two forms, one of which is very reactive and auto-oxidisable. The effect of an anti-oxygen is to catalyse the transformation of the reactive into the non-reactive form. G. W. R.

Isolation of the Thyroid Hormone. BENNO ROMEIS (*Biochem. Z.*, 1922, 133, 97—111).—Thyroid gland is hydrolysed by boiling with a solution of barium hydroxide for five to six days, so that the biuret test disappears. The precipitate formed on acidifying with hydrochloric or acetic acid is purified by dissolving in dilute alkali, and reprecipitating several times by acidifying. The precipitate is extracted with 90% alcohol containing acetic acid, and on evaporating the alcohol, a precipitate separates, which is again submitted to the process of extraction by alcohol

containing acetic acid and by precipitation. This is repeated several times, and the resulting material is washed with ethyl ether and with light petroleum, and then consists of a very light brown powder, with a high iodine content. This substance resembles Kendall's thyroxin, to which it appears to be closely related. It is possibly even more active physiologically. W. O. K.

Energy Exchanges in Muscle. OTTO MEYERHOF (*Pflüger's Archiv*, 1922, **195**, 22—74; from *Chem. Zentr.*, 1922, iii, 1235—1236; cf. A., 1922, i, 897).—An investigation into the origin of the approximately 400 cal. liberated in the formation of 1 g. of lactic acid from glycogen (caloric quotient of lactic acid). The heat of combustion of lactic acid, estimated by way of zinc lactate, is 325,700 cal. per mol. The average caloric quotient of lactic acid with electrical stimulation is 370 cal. With cut muscle in a phosphate solution, the value is only 200 cal.; this is in fair agreement with the value calculated from the heat of decomposition of glycogen, the heat of dilution of lactic acid, and the heat of reaction with the phosphate. The extent to which lactic acid goes into solution influences the amount of heat developed. The heat of reaction of lactic acid with substances in intact muscle is affected by hydrogen-ion concentration. The difference between the heat of reaction of lactic acid in muscle (190—200 cal.) and with buffered solutions of amino-acids (130 cal.) or protein solutions (137—140 cal.) is attributed to changes in the state of ionisation of proteins in a non-aqueous phase. The temperature coefficient of lactic acid (per 10°) in cut muscle is 2—3, in intact muscle about 4.

G. W. R.

The Influence of Cooling on the Creatine in Muscle. ALEXANDER PALLADIN and ANNA KUDRJAVZEV (*Biochem. Z.*, 1922, **133**, 89—96).—There is a marked increase of creatine in the muscles of a rabbit if it is killed several hours after its body temperature has been reduced from 39° to about 30° by immersion for some time in a cold bath. This increase, of the order of 0.1%, reaches a maximum about twelve hours after the cooling, and there follows a slow return to normal. W. O. K.

The Decomposition of Carbohydrates in Transversely Striped Muscles. III. FRITZ LAQUER and PAUL MEYER (*Z. physiol. Chem.*, 1923, **124**, 211—226; cf. A., 1922, i, 1089).—The effect of fresh frog's muscle in converting various carbohydrates into lactic acid has been investigated. The greatest activity is shown when acting on glycogen, followed by levulose, starch, dextrose, and mannose. All the other carbohydrates tested, galactose, sorbose, sucrose, maltose, diamylose, and tetramylose (obtained from starch by the action of *Bacillus macerans*), inulin and Merck's "Karamose" give insignificant yields of lactic acid. Thus if there is a reactive form of carbohydrate present in glycogen as previously suggested (*loc. cit.*), it does not appear to be any of the above. W. O. K.

The Effect of Histozyim on the Homologues of Hippuric Acid. I. A. SMORODINCEV (*Z. physiol. Chem.*, 1923, 124, 123—139).—Histozyim, which effects the hydrolysis of hippuric acid, appears in the kidneys and skeletal muscles of dogs and also markedly in the kidneys of pigs. It is also present in the spleen, lungs, heart, and skeletal muscles of dogs, but not in the liver, and is found in the liver of calves, oxen, and horses. It is almost insoluble in water and in aqueous glycerol. Besides hippuric acid, histozyim hydrolyses also *d*- α -benzamidobutyric acid and *l*-benzoyl-leucine, but not β -benzoylalanine, *dl*- β -benzamidobutyric acid, benzamidoisobutyric acid, and *l*- β -benzamidobutyric acid. Glycocholic acid and taurocholic acid are hydrolysed with the separation of cholalic acid.
W. O. K.

Faulty Diet and its Relation to the Structure of Bone. P. G. SHIPLEY (*J. Amer. Med. Assoc.*, 1922, 79, 1563).—Among the dietetic principles concerned in the growth of bone are: (1) an uncharacterised organic substance, distinct from fat-soluble vitamin-*A*, and found in certain fish liver oils and in small amounts in butter and coconut oil, (2) calcium, (3) phosphorus, (4) water-soluble vitamin-*B*, (5) fat-soluble vitamin-*A*. Water-soluble vitamin-*C* influences the structure of the bone of the guinea pig, but not of the rat. Inadequacy of fat-soluble vitamin-*A* causes perfect calcification, but a high degree of osteoporosis develops; deficiency of water-soluble vitamin-*B* causes similar results. If the organic substance so abundantly present in fish oils is freely supplied, rickets will not develop in spite of a faulty ratio of calcium to phosphorus in the food. It is found that the shorter ultra-violet rays have an important antirachitic effect.

CHEMICAL ABSTRACTS.

Decalcification of Teeth and Bones, and Regeneration of Bone through Diet. P. R. HOWE (*J. Amer. Med. Assoc.*, 1922, 79, 1565—1567).—The magnesium content of sound teeth, when estimated by Tisdall and Kramer's method (*A.*, 1921, ii, 655), was found to range from 0.554 to 0.764% (average 0.649%), whilst decayed teeth contained 0.825 to 1.585% (average 1.154%). With all the proper food factors supplied except the antiscorbutic, the animal organism appears to withdraw calcium from the teeth and from some parts of the bone.

CHEMICAL ABSTRACTS.

Tin in the Human Organism. ÉMILE MISK (*Compt. rend.*, 1923, 176, 138—141).—Tin may be estimated in human organs by two methods. In the first, 100 g. of the pulped material and 1 g. of calcined magnesias are evaporated with 30 c.c. of 30% magnesium nitrate and the residue after drying at 250° is ignited at a dull red heat to a white ash, which is then fused with 2—3 g. of potassium hydroxide. The cold mass is extracted with water, and after filtration the filtrate is evaporated and the residue treated with nitric acid and the tin weighed as stannic oxide. In the second method, 100 g. of the material are evaporated with

50 c.c. of 30% potassium hydroxide and the residue heated to fusion, the cold mass then being treated as described above.

Tin exists normally in the human organism, and the liver has highest content, being followed by the stomach, kidneys, lungs, and brain. 0.03—0.04 g. of tin in 100 g. of human viscera is not excessive in amount.

W. G.

Glycogen Content of certain Invertebrates and Fishes.

L. G. KILBORN and J. J. R. MACLEOD (*Quart. J. Exp. Physiol.*, 1920, 12, 317—330).—By Pflüger's method, the following percentages of glycogen were found in the (moist) digestive glands (hepatopancreas): Asteroidea, 0.232 to 1.52; Lamellibranchiata, 0.31 to 1.56; Crustacea, 0.05 to 1.39; Elasmobranchii, 0.0 to 0.21; Teleostomi, 0.0 to 6.5. Feeding conditions and season seem partly responsible for the varying amounts. In the (moist) muscles the following percentages of glycogen were found: Lamellibranchiata, 0.077 to 2.67 (the latter in the adductor muscles); Crustacea, trace to 0.36; Elasmobranchii, 0.0 to 0.018; Teleostomi, 0.0 to 0.29. In all cases when it was possible to obtain a sufficient amount of heart muscle, the glycogen content was found to be several times greater than that of other muscles, and sometimes greater than that of the liver; thus in the lobster 0.85—1.42% was found in the heart muscle, while the other muscle content was 0.36%. In several cases, the glycogen was found to yield a sugar fermentable by yeast after hydrolysis. In other cases, part of the reducing material seemed to consist of other substances.

CHEMICAL ABSTRACTS.

Concentration of Urea in Saliva. P. S. HENCH and MARTHA ALDRICH (*J. Amer. Med. Assoc.*, 1922, 79, 1409—1412).—The combined urea- and ammonia-nitrogen values of the saliva are normally between 6 and 13 mg. per 100 c.c. These combined values closely approximate to those of the urea-nitrogen in the blood. In urea retention, the combined urea- and ammonia-nitrogen always increase with an increase in the blood urea-nitrogen.

CHEMICAL ABSTRACTS.

Effect of Magnesium Sulphate on the Secretion of Bile. EMMETT B. FRAZER (*J. Amer. Med. Assoc.*, 1922, 79, 1594—1596).—When introduced directly into the duodenum, or into the circulation, magnesium sulphate does not cause any change in the character of the bile, although in some instances the rate of flow was retarded.

CHEMICAL ABSTRACTS.

The Solubility of Gallstones. ANNE ROSIN (*Z. physiol. Chem.*, 1923, 124, 282—286).—Cholesterol gallstones are soluble to some extent in solutions of salts of bile acids, more particularly in solutions of sodium deoxycholate.

W. O. K.

The Excretion of Uric Acid on a Diet Poor in Purines. H. STEUDEL (*Z. physiol. Chem.*, 1923, 124, 267—273).—The endogenous uric acid in the urine depends on the condition of the contents of the intestine. The urine of an individual whose faeces

showed fermenting powers was abnormally poor in uric acid, this being due apparently to destruction of the purine substances in the intestine. W. O. K.

The Rôle of the Effect of Acids in the Production of Adrenalin Hyperglycæmia. F. KORNFIELD and H. ELIAS (*Biochem. Z.*, 1922, **133**, 192—211).—After the injection of adrenalin into rabbits, dogs, or human beings, there is only a very slight lowering of the carbon dioxide tension of the blood or in the case of men of the alveolar carbon dioxide tension (sometimes even this slight lowering is absent), but nevertheless there is marked hyperglycæmia. There is therefore no reason to believe that the hyperglycæmia is in any way due to the hypokapnia. W. O. K.

The Formation of Conjugated Glycuronic Acids after Administration of Elbon. KIYOSHI MORINAKA (*Z. physiol. Chem.*, 1923, **124**, 247—252).—The urine of rabbits to which have been given by the mouth 2 g. of elbon (cinnamoyl-*p*-hydroxyphenylcarbamide) per day for a long time contains hippuric acid and also a laevorotatory substance, isolated as the potassium salt, long, colourless prisms, shown to be the *potassium* salt of *p*-hydroxyphenylcarbamideglycuronate, m. p. 231°, decomp., $[\alpha]_D^{20} -74.99^\circ$ in water. On hydrolysis with acid, glycuronic acid and *p*-aminophenol are obtained, the latter derived by the further hydrolysis of the *p*-hydroxyphenylcarbamide formed initially. W. O. K.

[Physiological Action of Dialkyl- and Alkylaryl-barbituric Acids.] H. A. SHONLE and A. MOMENT (*J. Amer. Chem. Soc.*, 1923, **45**, 243—249).—See this vol., i, 248.

Comparative Toxicity of Different Acids towards Fish (Sticklebacks). (MLLE) FRANCE GUEYLARD and MARCEL DUVAL (*Compt. rend.*, 1922, **175**, 1243—1245).—In order to study the influence of acids on aquatic animals and to ascertain whether any toxic effect could be attributed solely to hydrogen-ion concentration, sticklebacks (*Gasterosteus aculeatus* var. *leiurus*) were placed in a series of solutions of acetic, lactic, propionic, and phosphoric acids of different hydrogen-ion concentration and the time of survival was noted. A diagram is given showing the curve obtained for each acid on plotting its p_H value against survival time in hours. The latter varies considerably with the p_H value, increasing slowly at first and then very rapidly with diminution in the concentration of hydrogen-ions, but the nature of the acids exerts considerable influence. For example, when $p_H=4$, the fish live for more than eight hours in phosphoric acid, two and a half hours in lactic acid, eleven minutes in acetic acid, and less than nine minutes in propionic acid. H. J. E.

Chemistry of Vegetable Physiology and Agriculture.

Activation of Hydrogen and Carbon Dioxide Assimilation by Bacteria. W. RUHLAND (*Ber. Deut. bot. Ges.*, 1922, 40, 180—184).—The power of utilising the chemical energy of free hydrogen for carbon dioxide assimilation is widely distributed amongst bacteria. Contrary to opinions previously advanced that the carbon dioxide is first reduced by the activated hydrogen, a slow direct combustion of hydrogen occurs which furnishes the energy for the carbon dioxide reduction. This occurs, as with green plants, with the elimination of oxygen. Hidden by the hydrogen combustion, a slow exhalation of carbon dioxide occurs, involving the consumption of both free and combined oxygen. The presence of iron is essential for the assimilation, and it must be in combination as hydrogen carbonate. If carbon dioxide is excluded from the gaseous atmosphere of inorganic cultures, very little or no hydrogen is assimilated. The ratio of the volumes of hydrogen to oxygen consumed is in the youngest cultures less, but, later, greater than 2, the variation depending on the intensity of carbon dioxide exhalation. The maximum hydrogen assimilation occurs in weak alkaline solutions, and falls off rapidly on both sides to the respective limits of $p_H=5.3$ and $p_H=9.1$. The protective action of many organic substances, for example, dextrose, against hydrogen assimilation is due to the rapid formation of acids to which they give rise, which causes the disappearance of the HCO_3^- -ion, which alone can be assimilated. The utility of the hydrogen combustion expressed by the "economic quotient," Organic substance produced/Hydrogen and oxygen used, varies considerably, and is greatest in approximately neutral solution. With the same hydrogen-ion concentration and otherwise similar conditions, it is approximately proportional to the hydrogen and oxygen used up.

G. F. M.

The Microbic Metabolism of Lactic Acid and Pyruvic Acid. E. AUBEL (*Compt. rend.*, 1923, 176, 332—335).—The author has isolated an organism from the Paris water supply which, when grown on a solution of dextrose and suitable mineral salts, produces during the first few days pyruvic acid and no lactic acid, but in the following days the pyruvic acid disappears and lactic acid makes its appearance. When the culture is on a similar medium, but the sugar is replaced by sodium pyruvate, the pyruvic acid slowly disappears and there is found in the medium acetic acid, an acid soluble in ether and giving the Hopkins reaction but only present in small amount, and a crystalline acid, m. p. 152° , not identified. When in the same medium the sodium pyruvate is replaced by calcium lactate, a portion of the lactic acid is converted into acetic acid and acetaldehyde, but pyruvic acid could not be detected.

W. G.

Growth and Respiration of Sulphur-oxidising Bacteria.

SELMAN A. WAKSMAN and ROBERT L. STARKEY (*J. Gen. Physiol.*, 1923, 5, 285—310).—*Sulphomonas thio-oxidans* oxidises sulphur to sulphuric acid or sodium thiosulphate to sulphate, and at the same time absorbs atmospheric carbon dioxide as a source of carbon. The ratio between the sulphur oxidised and the carbon dioxide reduced is 31·8:1 and 64·2:1 in the cases of sulphur and thiosulphate, respectively. Excess of sulphur in the medium does not inhibit the oxidation, but nitrates have a strong inhibiting action. Dextrose is likewise innocuous, but peptone almost completely stops sulphur oxidation in 1% concentration. The injurious effect of acid becomes marked only at concentrations exceeding 0·5*N*. The optimum p_H for growth is between 2·0 and 5·5. The zone is sharply limited on the alkaline, but not on the acid side.

W. O. K.

The Action of Saponin Substances on the Plant Cell.

FRIEDRICH BOAS (*Ber. Deut. bot. Ges.*, 1922, 40, 249—253).—Cyclamin and digitonin in feeble concentration slightly increase the fermentative activity of the yeast-cell, in higher concentration they strongly retard it. This physiological action of these saponins is due to the formation of chemical compounds with the lipoids in the protoplasm, which are thereby inactivated, and the structure of the protoplasm is disturbed by the flocculation of the saponin-cholesteride. A slight modification of the lipid structure, insufficient to cause flocculation, increases the zymase activity, on the other hand, partly by increasing the permeability, and partly perhaps by removing retarding substances. Certain combinations of saponins such as quillaia saponin and digitonin are distinctly less poisonous than digitonin alone, and the combination digitonin-sodium glycine actually leads to increased zymase activity, which is to be attributed to the strong solvent action of the latter substance on lipoids, preventing the precipitation of the cholesterol and the consequent destruction of the cell-structure. No parallel could be traced between the surface activity and the chemical activity of the various saponins.

G. F. M.

The Synthesis and Degradation of Asparagine in Plants.

D. PRIANISCHNIKOV (*Ber. Deut. bot. Ges.*, 1922, 40, 242—248).—Whilst, as has already been shown, etiolated seedlings of Gramineaceous and other plants can readily synthesise asparagine from ammonia presented in the form of a dilute solution of ammonium chloride or sulphate, and certain Leguminosæ can effect the same synthesis only when calcium carbonate is also present, the yellow lupine showed under similar conditions a quite abnormal behaviour, no asparagine was formed, the normal asparagine content of the plant decreased, and the ammonia content became abnormally great, giving the cell juice an alkaline reaction. The presence of calcium carbonate only accentuated this phenomenon. This abnormal behaviour is entirely attributable to lack of carbohydrates, as on the one hand other plants were also shown to behave in this

abnormal way under an artificially created deficiency of carbohydrates, and on the other yellow lupine seedlings to which carbohydrates were supplied, either by utilising the green plants instead of etiolated plants for the experiments, or by feeding etiolated plants with dextrose solutions, behaved normally; that is to say, the asparagine-nitrogen increased, and the ammonia-nitrogen decreased. It follows, therefore, that it is not a peculiarity of the species but the conditions of nutrition which is the determining factor for the asparagine synthesis. Only when a carbohydrate or fatty carbon chain is present can the plant convert ammonia into asparagine and thence into amino-acids and proteins, otherwise ammonia accumulates, and the plants show the symptoms of ammonia poisoning. Asparagine is to be regarded as the analogue in the vegetable kingdom of carbamide in the animal kingdom. It is pointed out that the process is reversible, and in absence of carbohydrates degradation of protein to asparagine or glutamine, and finally to ammonia, occurs. G. F. M.

Incrustive Substances of Plants. III. ERICH SCHMIDT, EBERHARD GEISLER, PAUL ARNDT, and FRITZ IHLOW (*Ber.*, 1923, 56, [B], 23—31; cf. A., 1921, i, 912; 1922, i, 206).—Further examination has confirmed the previous observation that aqueous solutions of chlorine dioxide are specific reagents for the removal of botanical incrustations. The cell-membranes of the higher fungi, archegoniates, and phanerogams are thus shown to be composed of tissue containing chitin or cellulose accompanied by hemicelluloses and pentosans and incrustation containing hexosans and pentosans accompanied by those portions of the cell-membrane which are attacked by chlorine dioxide.

The concentration of the chlorine dioxide solution (about 6%) is considerably greater than that recommended previously (*loc. cit.*). Its preparation from potassium chlorate, crystalline oxalic acid, and sulphuric acid is described in detail. Like the more dilute solution, it is without action on the tissue of plants.

For the removal of incrustations, the finely divided portions of plants are treated with an approximately 6% aqueous solution of chlorine dioxide in closed bottles at the atmospheric temperature in diffused daylight during seventy-two hours with occasional agitation. The precipitate is filtered and the residue mechanically agitated with water and again filtered. The combined filtrates are well stirred in a large porcelain dish to remove chlorine dioxide, and are afterwards dialysed against running water for at least forty-eight hours; they are subsequently evaporated to dryness under diminished pressure. The original residue is treated with a hot aqueous solution of crystalline sodium sulphite (2%) and the mixture filtered. The residue is thoroughly washed and the united filtrate and wash waters are dialysed against running water for at least seventy-two hours. They are subsequently evaporated to dryness under diminished pressure and the residue is united with that obtained by the treatment with chlorine dioxide. The product is separated by means of boiling absolute alcohol into

insoluble polysaccharides which usually contain 5—10% of ash (this cannot readily be removed by dialysis, but is reduced to about 1.5%, consisting chiefly of silica, by electro-osmosis) and soluble components of the membrane which are attacked by chlorine dioxide.

The method described previously (*loc. cit.*) for the preparation of skeleton substance completely free from incrustation requires to be supplemented by a second treatment with chlorine dioxide solution (0.2%) and sodium sulphite (2%). The residue is well filtered and placed first in alcohol and then in ether for about twenty-four hours. After being dried in a desiccator, it is thus obtained as a spongy material.

The quantitative estimation of tissue and incrustation is modified and carried out in small pressure bottles according to the process outlined above. Beech wood is thus shown to contain 54.09% of tissue and 45.91% of incrustation.

H. W.

Amylase in Plants. I. The Production and Behaviour of Amylase in Living Plants. KNUT SJÖBERG (*Biochem. Z.*, 1922, 133, 218—293).—Following Euler and Svanberg (*A.*, 1919, i, 614), the author finds that the amylolytic activity of plant preparations is conveniently measured as $S = km/P$, where k is the mean value of the reaction coefficient, calculated as a unimolecular reaction, m is the maximum weight of maltose produced, and P is the weight of the preparation applied, the maltose being produced from the starch by the preparation under standard conditions as regards p_H and temperature. From measurements of the maltose at various times, k is calculated. The optimum p_H for plant diastase is from 5 to 5.4. During the ripening of seeds there occurs a very marked increase of the amylase. Various plants at various seasons have been investigated, and it is found that the amylase activity varies very greatly, being greatest in young leaves. Algæ increase in amylase when nourished in a solution containing starch, calcium lactate, or calcium tartrate, whereas a decrease occurs if the solution contains sucrose, lactose, maltose, glucose, or galactose. Generally speaking, there is no correlation between the content of a plant in amylase, and in starch, or in sugar.

W. O. K.

Amylase in Plants. II. The Sensitiveness of the Amylase of *Phaseolus vulgaris* to Temperature. KNUT SJÖBERG (*Biochem. Z.*, 1922, 133, 294—330).—An investigation of the amylase of *Phaseolus vulgaris* shows that there are two enzymes concerned in the conversion of starch into sugar. The rate of disappearance of starch has the same temperature constant, $A = \log(k_2/k_1)T_1T_2/0.4343(T_2 - T_1)$ between 20° and 40° of about 9600, follows the law of a unimolecular reaction, and, moreover, the enzyme causing the disappearance of the starch is destroyed by sodium chloride. On the other hand, the rate of formation of sugar has a temperature constant varying from 10,000 at 20°, to 6700 at 40°, its inactivation does not follow the law of a uni-

molecular reaction, and there is no inhibition by sodium chloride. For the formation of sugar, the optimum p_H is from 5 to 5.5, and for the disappearance of starch it is from 4 to 6. The amylase is most stable at p_H 6.5—7.0. The temperature at which the enzymes are wholly destroyed is 45° for both enzymes. W. O. K.

[Constituents of] Cork. P. KARRER, J. PEYER, and ZORKA ZEGA (*Helv. Chim. Acta*, 1922, **5**, 853—863).—The carbohydrates contained in cork were studied in the course of an attempt to characterise in a more satisfactory manner than heretofore the constituents of cork. After removing the alcohols by extraction with solvents and hydrolysing with alcoholic potash to remove fatty acids, a residue was left equal to about 8% of the weight of the original air-dried cork. When this was treated with acetic anhydride and anhydrous zinc chloride at 50—60°, part of it went into solution, and when the solution was poured into water a precipitate resembling cellulose acetate was thrown down. It had $[\alpha]_D -21.2^\circ$ to -22.1° and on hydrolysis gave dextrose. By repeating the process several times on the cork residue, less pure fractions with a smaller laevorotation were obtained. The total yield obtained was about 12.1 g. of acetyl product from 430 g. of original cork. From it a very small quantity of crystalline cellobiose octa-acetate was obtained. A similar yield of acetyl compound was obtained by treating unhydrolysed cork with acetic anhydride and zinc chloride. Since the residue retained all the properties of the original cork, it is concluded that the carbohydrates cannot play any important part in the structure of the cork. It has been suggested by Grün and Wittka (*A.*, 1922, **i**, 114) that cellulose esters of higher fatty acids may be constituents of cork-like substances. The properties of such substances as cellulose hexapalmitate, however, do not resemble those of cork. The following are described.

l-Glucosan tripalmitate, $C_{54}H_{100}O_8$, prepared by the action of palmityl chloride on *l*-glucosan in chloroform solution in presence of quinoline, forms fine, white needles, m. p. 68.5°, $[\alpha]_D^{25} -21.08^\circ$. *l*-Glucosan tristearate, $C_{60}H_{112}O_8$, prepared in the same way as the last, m. p. 73.4°, $[\alpha]_D^{25} -18.4^\circ$. Cellulose hexapalmitate,

$C_{12}H_{14}O_{10}(CO \cdot C_{15}H_{31})_6$, prepared in a similar way, is a white, amorphous substance, m: p. 78°, $[\alpha]_D^{25} -3.0^\circ$. E. H. R.

The Starch of Floridean Algæ. G. MANGENOT (*Compt. rend.*, 1923, **176**, 183—185).—In the main a discussion of the subject from the point of view of plant physiology. The starch of the Florideæ, both from the chemical and physiological point of view, behaves like typical starch, except that its colour with iodine in potassium iodide distinguishes it slightly. W. G.

Biochemical Study of the *Laminaria*. Variations in the Chief Constituents. Their Relationships, Dependence on External Conditions, and their Functions. P. FREUNDLER, (Mlle) LAURENT, and (Mlle) MÉNAGER (*Bull. Soc. chim.*, 1922, [iv], **31**, 1341—1347; cf. *A.*, 1922, **i**, 98).—Further examination

of certain species of *Laminaria* shows that at the end of winter they are all completely deprived of carbohydrate reserve material, which in September attained a maximum of about 40%. At this period also the perennial *Laminaria* contain little or no "fixed" iodine. The energy for the early spring growth is thought to be provided by a reserve of iodine which is stored up by means of a special pigment which is not found in the annual algæ, and is transported to the growing areas by means of the algins. A lack of sunshine, as in 1922, is accompanied by a considerable diminution of iodine in certain regions, but it is not so pronounced in places under the influence of warm ocean currents. The greater part of the iodine in the algæ is present in unstable organic combination, but it was found that the amount that could be estimated by incineration increased spontaneously on keeping. Closely associated with the iodine are a yellow pigment decolorisable by sodium hydrogen sulphite, and a red pigment found only in deep-water algæ, which is insoluble in the sulphite, but soluble in ammonia with an intense red colour. The algins appear to act as salt concentrators. They absorb, for example, 20–25% of their weight of calcium or alkali metal chlorides, giving insoluble gels (alkali alginates). The presence of hydrolysing and alcohol-forming enzymes was established.

G. F. M.

Phycoerythrin in the Myxophyceæ. N. WILLE (*Ber. Deut. bot. Ges.*, 1922, 40, 188–192).—The occurrence is recorded of a phycoerythrin in a species of Myxophyceæ, identified as *Phormidium persicinum* growing 3–4 fathoms deep off the south coasts of Norway, which gives an absorption spectrum identical with that of the phycoerythrin found in the Florideæ, and is undoubtedly identical in other respects with that substance. A phycoerythrin has already been detected by Boresch in other species of Myxophyceæ, but this was apparently different from the colouring matter of the Florideæ, as it showed only one absorption band in the green, whilst the colouring matter of *P. persicinum* shows three bands, that near the F line being particularly characteristic of the phycoerythrin of the Florideæ.

G. F. M.

The Pigment of the Alga *Palmellococcus miniatus*, Chod., var. *porphyrea*, Wille. K. BORESCH (*Ber. Deut. bot. Ges.*, 1922, 40, 288–291).—The water-soluble pigment which occurs in a species of *Palmellococcus* found growing in moist places in the Botanical Garden in Prague and identified by Wille as *P. miniatus*, Chod., var. *porphyrea*, was identified by its absorption spectrum and reactions as a mixture of phycocyanin, and the phycoerythrin characteristic of the Schizophyceæ. The identity of the pigments in such widely-separated groups of algæ points to the common chemico-physiological relationship of plants.

G. F. M.

The Occurrence of *d*-Quercitin in the Seed Kernels of *Achras sapota*, L. A. W. VAN DER HAAR (*Rec. trav. chim.*, 1922, 41, 784–786).—*d*-Quercitin together with the saponins was

extracted from the dried and powdered seeds by means of methyl alcohol and separated from the saponins by precipitation with ether followed by extraction of the precipitate with methyl alcohol. The product was shown by various tests to be identical with the *d*-quercitin obtained from acorns. The author states that the mixture of lactose and sucrose obtained by Bouchardat (A., 1871, 1915) from the sap and also from the ripe fruit of *Achras sapota* was in reality a mixture of sucrose with quercitin. H. J. E.

The Localisation of the Hydrocyanic Acid Glucosides and of Emulsin in Bitter Almonds and in Cherry-laurel Leaves.

L. ROSENTHALER and K. SEILER (*Ber. Deut. pharm. Ges.*, 1922, 32, 245—248).—A method is described for the microscopic detection of hydrocyanic acid from the glucoside and emulsin in the plant-tissues (cf. *Schweiz. Apoth. Ztg.*, 1922, 60, 477). In bitter almonds, both amygdalin and emulsin are found in all tissues except the shell. Detailed data are given of the distribution of prulaurasin and emulsin in the leaves of the cherry-laurel at the beginning of March. In general, both substances occur in the same tissues, although there are some in which prulaurasin is found without emulsin. Where the emulsin and the hydrocyanic acid glucoside are present in the same cell and yet do not react, there must be some internal separation of them within the cell.

P. M.

The Odorous Constituents of Apples. II. Evidence of the Presence of Geraniol. FREDERICK B. POWER and VICTOR K. CHESNUT (*J. Amer. Chem. Soc.*, 1922, 44, 2938—2942).—An examination of the essential oil from the parings of McIntosh apples, a particularly fragrant variety of the fruit, confirms the results of a previous investigation (A., 1920, i, 653), that the odorous constituents of apples consist chiefly of amyl esters, but in addition proof of the presence of geraniol was obtained. It is probable that geraniol either in the free state or in the form of esters is contained in varying amounts in all apples, but is more abundant in those varieties which possess its distinctive odour.

W. G.

The Constituents of the Benzene Extract of American Cotton.

ROBERT GEORGE FARGHER and MAURICE ERNEST PROBERT (*J. Text. Inst.*, 1923, 14, T., 49—65).—The material at the disposal of the authors was obtained by heating approximately two tons of American cotton with commercial “90% benzol” in a rotating kier by means of steam at 40 lb. pressure, and consisted, therefore, of the material extracted with benzene, together with that removed by the condensed steam. The crude product was dried at 100° in a vacuum, when it was left as a dark brown solid wax. On the laboratory scale, the benzene extract amounted to 0.51% of the dried cotton.

The crude wax was mixed with purified sawdust and extracted by light petroleum, ether, benzene, alcohol, and chloroform, and

the extracts were submitted to exhaustive examination, which is described in detail. The following substances were isolated. *Alcohols* :—Gossypyl alcohol is the chief constituent; montanyl alcohol occurs in smaller amount, and carnaübyl alcohol, ceryl alcohol, sitosterol, and α - and β -amyrins are also present. Sitosterolin, the glucoside, was also encountered. *Acids* :—Palmitic, stearic, and oleic acids occur in the free state; montanic, cerotic, palmitic, and stearic acids, and a new acid, occur as salts, chiefly of sodium; whilst carnaübic, palmitic, stearic, and oleic acids, and a lower homologue of oleic acid are present as esters. *Hydrocarbons* :—Triacontane and hentriacontane have been isolated, but the bulk of the hydrocarbons present are liquid.

Gossypyl alcohol, $C_{30}H_{62}O$, is the chief constituent of the benzene extract. It occurs in three forms, differing in solubility, but yielding the same derivatives. The α -form, which is the least soluble, crystallises in feathery needles, m. p. $87-88^\circ$; the β -form separates in leaflets, m. p. $85-87^\circ$; and the γ -modification forms small leaflets, m. p. $82-83^\circ$. On recovery from the acetate, the α -form appears to have changed into the β -modification. *Gossypyl acetate* forms small, silky needles, m. p. $68-69^\circ$; the *benzoate* is a felted mass of minute needles, m. p. 65° ; the *p-bromobenzoate* forms clusters of needles, m. p. $66-67^\circ$; and the *p-nitrobenzoate* crystallises in tufts of needles, m. p. 72° . The various forms of the alcohol all gave the same acid on fusion with potash-lime. *Gossypic acid*, $C_{30}H_{60}O_2$, crystallises in radiating clusters of needles, m. p. $85-86^\circ$; the *methyl* ester has m. p. $68-69^\circ$, the *ethyl* ester, m. p. $66-66.5^\circ$, the *amide*, m. p. $108-109^\circ$, and the *anilide*, m. p. 99.5° .

Montanyl alcohol, $C_{28}H_{58}O$, crystallises as a mass of minute needles, m. p. $85-86^\circ$; its *acetate* forms clusters of leaflets or needles, m. p. 69° ; the *benzoate* has m. p. $66-67^\circ$; the *p-bromobenzoate* is a mass of minute needles, m. p. $66-66.5^\circ$; and the *p-nitrobenzoate* has m. p. $70-70.5^\circ$. On fusion with potash-lime, the alcohol yielded montanic acid which was completely identified with a sample from montan wax.

Both gossypyl and montanyl alcohols obstinately retain water, even when heated for some hours at 115° in a vacuum. The anhydrous forms were obtained by saponification of the acetates. This tendency necessitated a careful examination of their derivatives, and conversion into the substituted benzoates and the corresponding acids proved to be the best means of characterising the alcohols. Furthermore, molecular-weight determinations were successfully made by saponifying the esters and titrating.

Of the acids present, carnaübic acid and the new acid are worthy of mention. The former has been definitely characterised. It crystallises in leaflets, m. p. $72-73^\circ$; the *methyl* ester has m. p. $55-56^\circ$, the *ethyl* ester, m. p. $52-53^\circ$; the *amide*, $C_{23}H_{47}\cdot CO\cdot NH_2$, m. p. 103.5° ; and the *anilide*, m. p. $94-94.5^\circ$. The new acid, $C_{34}H_{68}O_2$, is possibly identical with an acid found by Schalfef in 1876, associated with the melissic acid of beeswax; it separates in fern-like clusters, m. p. $90-91^\circ$; the *methyl* ester has m. p. $75-76^\circ$, the *amide*, m. p. $108-109^\circ$, and the *anilide*, m. p. 105° .

The liquid hydrocarbons were divided into five fractions boiling between 170° and 220°, under 28 mm., and five more with b. p. 150—210°/1 mm. All the oils were pale yellow and reacted with a solution of bromine in chloroform. Densities and refractive indices are recorded.

J. C. W.

***Stenocalix pitanga*, Berg, or *Eugenia pitanga*, Berg-Arech (Pitanga or Nangapire).** VÍCTOR COPPETTI and MATÍAS GONZÁLEZ (*Anal. Fis. Quím.*, 1922, 20, 406—419).—The leaves of *Eugenia pitanga*, a Uruguayan tree, yield an essential oil, which contains as its principal constituents citronellol, geranyl acetate, geraniol, cineol, terpinene, sesquiterpenes, and polyterpenes. A resin also occurs composed of resin acids, resens, and resinotannols. Alkaloids, glucosides, bitter principles, and other neutral substances are absent. The leaves are not toxic.

G. W. R.

Examination of Authentic Grape Juices for Methyl Anthranilate. FREDERICK B. POWER and VICTOR K. CHESNUT (*J. Agric. Res.*, 1923, 23, 47—53).—Grapes usually regarded as representing pure-bred *Vitis labrusca*, which includes the concord, the commonest variety grown in the Eastern States of America and used for edible purposes and the preparation of unfermented grape juice, all contain methyl anthranilate. With few exceptions it was also found in varying amounts in hybrids of *V. labrusca*, especially when this species predominates. On the other hand, this ester could not be detected in juices from Californian grapes which are derived from *V. vinifera*, the European cultivated species, nor from *V. rotundifolia*, the species grown in the Southern States. It is suggested that the presence or absence of methyl anthranilate may possess some diagnostic value in determining the botanical relationship of varieties of uncertain origin. In those varieties in which it occurs methyl anthranilate doubtless imparts a distinctive odour, but it does not completely account for the entire aroma, and a complete chemical examination of the odorous constituents still remains to be accomplished.

G. F. M.

The Presence of Aucubin and Melampyritol [Dulcitol] in some Species of Melampyrum. (MLLE) MARIE BRAECKE (*Compt. rend.*, 1922, 175, 990—992; cf. Bridel and Braecke, A., 1922, i, 209, 799).—Following the extraction of aucubin from *Melampyrum arvense*, an attempt was made to ascertain whether it is present in other species, and also whether dulcitol, present in *M. nemorosum* and *M. arvense*, could be found. Aucubin was obtained in pure condition from *M. cristatum*, *M. nemorosum*, and *M. pratense*; dulcitol is present in *M. cristatum*, but was not obtained from *M. pratense*.

H. J. E.

Confirmation of the Occurrence of Linalyl Esters in Peaches. FREDERICK B. POWER and VICTOR K. CHESNUT (*J. Amer. Chem. Soc.*, 1922, 44, 2966—2967; cf. A., 1922, i, 99).—In addition to the formation of citral by the oxidation of the alcohol

mixture arising from the saponification of the esters obtained from peaches the authors have now proved the presence of acetone and lævulic acid in the products of oxidation. These substances were also obtained by the oxidation of linalool itself, and thus confirmation of the presence of linalyl esters in peaches was obtained.

W. G.

The Enzymes of the Latex of the Indian Poppy (*Papaver somniferum*). HAROLD EDWARD ANNETT (*Biochem. J.*, 1922, **16**, 763—769).—The latex of the Indian opium poppy has a powerful oxidising action on guaiacum tincture, pyrogallol, benzidine, and tyrosine in the absence of hydrogen peroxide. The reaction is inhibited by the presence of this reagent. The actions on benzidine and tyrosine are particularly powerful. The dialysed latex before and after filtration also oxidises the above reagents. Opium powder stored for three years contains an oxidising enzyme which acts on benzidine. It is suggested that the loss of morphine in dry opium powder on storage may be due to the action of oxidising enzymes. Amylase, invertase, maltase, emulsin, and urease are absent from the latex, which shows, however, a weak proteolytic activity.

S. S. Z.

The Bark of *Tiliacora acuminata*, Miers. L. VAN ITALLIE and A. J. STEENHAUER (*Pharm. Weekblad*, 1922, **59**, 1381—1388).—Among the products obtained from the alcoholic extract of the dry powdered bark is a new alkaloid, *Tiliacorine*, of m. p. 260—261°, decomp., $\alpha_D +105.3^\circ$, and composition $C_{30}H_{27}O_3N(OMe)_2$. The methoxy-groups were estimated by Zeisel's method, but no other light could be obtained on the constitution. (See *J.S.C.I.*, 1923, 159A.)

S. I. L.

The Presence of Aucubin in the Seeds of *Veronica hederæfolia*, L. C. CHARAUX (*Bull. Soc. Chim. biol.*, 1922, **4**, 568—570).—A glucoside, isolated from the seeds of *Veronica hederæfolia* by extraction with alcohol in presence of calcium carbonate, has been identified as aucubin, m. p. 180°, $[\alpha]_D -163.5^\circ$. W. O. K.

The Chemical Composition of Soja Bean Oil. WALTER F. BAUGHMAN and GEORGE S. JAMIESON (*J. Amer. Chem. Soc.*, 1922, **44**, 2947—2952).—The sample of soja bean oil examined had d_{25}^{25} 0.9203; n_D^{20} 1.4736; iodine number (Hanus) 128.0; saponification number, 189.5; acid number, 0.5; acetyl number, 17.0; Reichert-Meissl number, 0.16; Polenske number, 0.26; unsaponifiable matter, 0.6%; saturated acids, 11.5%; unsaturated acids, 83.5%. Detailed analysis showed its composition to be as follows: Glycerides of linolenic acid 2.3%, of linolic acid 51.5%, of oleic acid 33.4%, of palmitic acid 6.8%, of stearic acid 4.4%, of arachidic acid 0.7%, and of lignoceric acid 0.1%, and 0.6% of unsaponifiable matter. Total 99.8%.

W. G.

The Chemical Composition of Sunflower-seed Oil. GEORGE S. JAMIESON and WALTER F. BAUGHMAN (*J. Amer. Chem. Soc.*, 1922, **44**, 2952—2957).—The sample of sunflower-seed oil from

south-eastern Missouri examined had d_{25}^{25} 0.9193; n_{20}^{20} 1.4736; iodine number (Hanus), 130.8; saponification number, 188.0; acid number, 2.3; acetyl number, 14.5; Reichert-Meissl number, 0.27; Polenske number, 0.25; unsaponifiable matter, 1.20%; saturated acids, 7.1%; unsaturated acids, 86.6%. Detailed analysis showed its composition to be as follows: Glycerides of oleic acid 33.4%, of linolic acid 57.5%, of palmitic acid 3.5%, of stearic acid 2.9%, of arachidic acid 0.6%, and of lignoceric acid 0.4%, and 1.2% of unsaponifiable matter. Total 99.5%.

W. G.

The Genesis of Carbohydrates in Wheat. Presence of Lævulosans in the Stem. H. COLIN and H. BELVAL (*Compt. rend.*, 1922, 175, 1441—1443).—Prior to the formation of the ear, the stem of the wheat plant contains only those carbohydrates coming to it from the leaf, and the ratio of reducing sugars to sucrose is much greater in it than in the leaf. From the month of June, however, as soon as the corn has shot, a change occurs. After the sugars have been extracted by alcohol from the stem a residue remains which, on hydrolysis with acid, gives a large amount of lævulose and at the time of ripening the carbohydrates of the stem consist of sucrose and lævulosans.

W. G.

Bird-lime. III. YUSHICHI NISHIZAWA (*J. Chem. Soc. Japan*, 1922, 43, 810—817; cf. A., 1921, i, 760; 1922, i, 652).—The decomposition products of white bird-lime have been studied. A mixture of powdered calcium oxide and bird-lime was subjected to dry distillation at the ordinary pressure and the product was fractionated at about 48 mm. pressure, the refractive indices of the fractions being measured. The fraction distilling at 155—160°/48 mm. had the formula $C_{14}H_{28}O$ or $C_{15}H_{30}O$; it did not give an aldehydic reaction. The fraction distilling at about 155°/48 mm. absorbed 8.3 g. of ozone; the product on decomposition with boiling water gave an oily aldehydic compound, its oxime had m. p. 76°, and the semicarbazone, colourless plates, m. p. 91°. From the fraction distilling at 200—270°/5—7 mm. crystals, m. p. 82°, were obtained which gave an oxime, m. p. 58°, and semicarbazone, m. p. 170°, and proved to be identical with palmitone obtained by the distillation of calcium palmitate.

K. K.

The Soil Solution Extracted by Lipman's Direct Pressure Method compared with 1:5 Water Extracts. PAUL S. BURGESS (*Soil Sci.*, 1922, 14, 191—216).—Analysis of 1:5 water extracts and of the soil solution shows that if all the soil moisture be assumed to act as solvent, the soil solution contains approximately as much calcium, magnesium, and nitrate as is removed in the extract, but considerably less phosphate, potash, and sulphate. On the assumption that "unfree water" exists, the amount of calcium, magnesium, nitrate, and sulphate in the extract is about twice that in the soil solution; and phosphate and potassium are in considerably larger proportions.

A. G. P.

The Relation of Soil Moisture to Physiological Salt Balance for Plants. JOHN W. SHIVE (*Soil Sci.*, 1922, **14**, 391—411).—Crop yields on soils at various moisture-contents and with the addition of various fertilising salt mixtures were examined. It was shown that the salt balance characteristic of high yields is not markedly affected by the moisture content, provided the osmotic pressure of added solutions is roughly the same. Only when the total concentration of the solutions added to the soil were widely different was there any serious alteration in the optimum salt balance. The effect of moisture conditions on crop yield is as great as that brought about by varied fertiliser treatment. Unfavourable moisture conditions cannot be corrected by any kind of fertiliser treatment. Fertilisers cannot be utilised efficiently by the plant unless the optimum soil moisture obtains. A. G. P.

The Potential Acidity of Soils. OLOF ARRHENIUS (*Soil Sci.*, 1922, **14**, 223—232).—The potential acidity or buffer action of soils was shown in many cases to be correlated with the type of titration curve and with soil fertility, a high buffer capacity being usually associated with a productive soil. The lime requirement of soils may be determined from data showing the relative changes in p_H values brought about by titration with alkali and acid. A. G. P.

The Measurement of Soil Acidity by Means of Alkaline Solutions. V. VINCENT (*Compt. rend.*, 1922, **175**, 1233—1234).—Solutions of lime-water and of calcium or sodium hydrogen carbonate give inconsistent results when used for measuring soil acidity, the latter giving a lower value as the organic matter in the soil combines more completely with the lime-water, whereas the hydrogen carbonate only measures organic acids together with the acidity due to aluminium salts. It is stated that these facts afford some explanation of the physical reaction of soils to the addition of calcium compounds and that the nature of the calcium compound conditions the alkalinity of the soil water. H. J. E.

Absorption by Colloidal and Non-colloidal Soil Constituents. M. S. ANDERSON, W. H. FRY, P. L. GILE, H. E. MIDDLETON, and W. O. ROBINSON (*U.S. Dept. Agr. Bull.*, 1922, **1122**, 1—20).—A complete separation of the colloidal matter from the finer mineral particles of the soil was not found possible and a direct determination could therefore not be made of the relative absorption in soils due to colloids and non-colloids from a fractionation of the soil into these two classes of materials. From a study of the absorptive capacities of twenty-one soil minerals powdered to definite sizes varying between 1 and 50 microns in diameter, it was calculated that except in the case of the most highly micaceous soils in which the non-colloidal absorptions might reach 10—20% of the whole soil absorption, less than 5% of the total absorption of the soil is due to the non-colloidal part. Absorption by non-colloidal constituents should therefore

not seriously affect absorptive methods for estimating the amount of colloids in soil. Minerals ground to a state of subdivision probably equal to that of the mixed soil colloids, or "ultra clays," absorb less than the average ultra clay. The average absorption of peat and synthetic inorganic gels, on the other hand, is more nearly like that of the ultra clays. The fact that soil colloids are not merely finely comminuted minerals but appear to be of quite different nature from the non-colloidal particles thus affords an explanation for the marked difference in the absorptive capacities of these two classes of soil materials. CHEMICAL ABSTRACTS.

Influence of the Calcium-Magnesium Ratio on Soils under Continuous Cultivation. H. H. HILL (*Virginia Agr. Exp. Sta., Tech. Bull.*, 1922, 24, 1—15).—Continuous cropping of a loam soil with maize was found to change the ratio of calcium to magnesium in the soil from about 1 : 1 to 1 : 2. Good results were obtained with equal proportions of magnesium and calcium, but when magnesium was in excess, crop exhaustion was manifest. When acid phosphate was used alone, the calcium : magnesium ratio was not as wide as on the plots which received mixtures of acid phosphate, potassium sulphate, and sodium nitrate; potassium sulphate and sodium nitrate when applied alone exerted no appreciable effect on the retention of calcium. CHEMICAL ABSTRACTS.

(Theoretical and Practical Principles of) Carbon Dioxide Manuring. HENRIC LUNDEGÅRDH (*Angew. Botanik*, 1922, 4, 120—151; from *Chem. Zentr.*, 1922, iii, 1387).—The intensity of carbon dioxide assimilation by the leaves of beans and potatoes in closed cylinders in full daylight is nearly proportional to the concentration of carbon dioxide in the air up to two to four times the normal amount. Assimilation is increased even when the carbon dioxide content is further increased. From analyses of the atmosphere in the vicinity of leaves of growing crops it is shown that the proportion of carbon dioxide present and available for assimilation varies with different types of manuring by about 28%. The carbon dioxide concentration is increased by artificial fertilisers as well as by farmyard manure. It is shown that the carbon dioxide concentration at the level of assimilating leaves is controlled by the production of carbon dioxide in the soil. In the layers immediately above the soil, it is only slightly affected by wind velocity. Rain and warmth increase the production of carbon dioxide by the soil and, consequently, its assimilation by plants.

G. W. R.

Organic Chemistry.

The Oxidation of Hydrocarbons, with Special Reference to the Production of Formaldehyde. II. The Action of Oxygen on Methane. T. SHERLOCK WHEELER and E. W. BLAIR (*J. Soc. Chem. Ind.*, 1923, 42, 81—86, 87—92r).—In continuation of previous work on the oxidation of ethylene (A., 1922, i, 1105), the authors have investigated the oxidation of methane, more especially as regards the effects of temperature, time of heating, catalysts, etc., on the production of formaldehyde. The results obtained indicate that a short time of heating and slow oxidation are the principal factors determining a good yield of formaldehyde. The higher the temperature the more liable formaldehyde, in a given concentration, is to decompose or oxidise. At 500°, it does not decompose rapidly if present in concentrations below 2%. At concentrations below 0.2%, formaldehyde is completely unstable at 720°. With shorter times of heating, equimolecular mixtures of methane and oxygen give the higher yields of formaldehyde; for longer times and probably also for higher temperatures, the yields are greater in the case of mixtures containing excess of hydrocarbon. In all cases, the yield of formic acid is very small. Whereas the presence of a very small amount of ammonia increases the stability of this product, no similar effect is observed with formaldehyde. The results are in agreement with the hydroxylation theory of the oxidation of methane proposed by Bone.

J. S. G. T.

The Oxidation of Paraffin by means of Atmospheric Oxygen. ADOLF GRÜN and E. ULBRICH (*Z. angew. Chem.*, 1923, 36, 125—126).—The yield of total and insoluble fatty acids in the oxidation of paraffin with air is very largely increased by increasing the rapidity of the air current. By increasing the current of air from 150 litres to 1200 litres per hour, other conditions being kept constant, the yield of insoluble fatty acids was increased from 36.5% to 61.7%. The yield is also dependent on the moisture content of the air, but the data obtained on this point are somewhat conflicting. The increase of yield caused by the more rapid air current is chiefly due to the more efficient stirring which occurs, but also partly to the increased volume of oxygen made available. Experiments carried out with air diluted with various proportions of carbon dioxide showed that gas mixtures containing as little as 1.3% by weight of oxygen exert a marked oxidising effect when passed through paraffin heated at 160°.

H. C. R.

The Reaction between Ethylenic Hydrocarbons and the Grignard Reagent. HENRY GILMAN and H. MARJORIE CRAWFORD (*J. Amer. Chem. Soc.*, 1923, 45, 554—558).—A quantitative study of the behaviour of magnesium methyl iodide towards a number of hydrocarbons having one or more ethylenic linkings in their

molecule shows that there is not an addition of the Grignard reagent to such a linking. This applies not only to the ordinary conditions but also in a case where an excess of the organo-magnesium halide was used or the ordinary ether was replaced by *n*-butyl ether as a solvent. W. G.

Preparation and Reactions of Bromopicrin. LOUIS HUNTER (T., 1923, 123, 543—549).

Unsaturated Residues in their Chemical and Pharmacological Relationship. IV. JULIUS VON BRAUN and WERNER SCHIRMACHER (*Ber.*, 1923, 56, [B], 538—548).—It has been shown previously that unsaturated hydrocarbon residues are not firmly united with halogen, oxygen, sulphur, or nitrogen if the double bond is in the $\beta\gamma$ -position with respect to these atoms. The effect of the lengthening of the hydrocarbon chain has been examined by a comparison of the stability of Δ^{β} -butenyl compounds with the corresponding allyl derivatives. Somewhat unexpectedly, the butenyl compounds are found to be less stable than the allyl compounds. Pharmacologically the butenyl resemble the allyl derivatives in their action, but are somewhat less powerful.

Δ^{β} -Butenyl bromide is considerably more readily hydrolysed by water at 18° than is allyl bromide. The transformation of Δ^{β} -butenyl bromide into *trimethyl- Δ^{β} -butenylammonium bromide*, a colourless, hygroscopic, crystalline mass, m. p. 165°, by trimethylamine dissolved in benzene takes place about two hundred times as rapidly as the conversion of *n*-butyl bromide into *trimethyl-n-butylammonium bromide*, m. p. 182°, under similar conditions. Δ^{β} -Butenyl bromide reacts very readily with magnesium, giving an octadiene, b. p. 113—114°, d_4^{19} 0.7420, n_D^{19} 1.4324. Δ^{β} -Butenyl bromide and magnesium phenyl bromide gives *Δ^{β} -butenylbenzene*, $C_6H_5 \cdot CH_2 \cdot CH : CHMe$, a colourless liquid, b. p. 61—63°/12 mm., d_4^{19} 0.9069, n_D^{19} 1.5157, the yield being 61% of that theoretically possible. Magnesium *p*-anisyl bromide and Δ^{β} -butenyl bromide yield *p- Δ^{β} -butenylanisole*, b. p. 108—109°/12 mm., $d_4^{19.5}$ 0.9715, n_D^{19} 1.5229; the double bond in this substance appears to be very resistant to displacement towards the benzene nucleus. It is readily hydrogenated in methyl-alcoholic solution in the presence of palladium to *p-n*-butylanisole, a colourless liquid, b. p. 104—105°/10 mm., d_4^{19} 0.9396, n_D^{19} 1.5045.

Phenyl Δ^{β} -butenyl ether, a liquid, b. p. 95—98°/12 mm., d_4^{19} 0.969, n_D^{19} 1.5187, is obtained in almost theoretical yield by the method recommended by Claisen and Eisleb (A., 1913, i, 1175) for the corresponding allyl compound. It is relatively more readily isomerised than the allyl derivative when heated, yielding *o- Δ^{β} -butenylphenol*, b. p. 108—112°/10.5 mm., d_4^{19} 1.0066, n_D^{19} 1.5385; the latter substance gives non-crystalline benzoyl and *p*-nitrobenzoyl compounds, and is converted by methyl sulphate into *o- Δ^{β} -butenylanisole*, b. p. 102—105°/12 mm., d_4^{19} 0.9721, n_D^{19} 1.5255. Similarly, α -naphthyl Δ^{β} -butenyl ether is partly isomerised when distilled in a vacuum to 2- *Δ^{β} -butenyl- α -naphthol*,

a yellow liquid, b. p. 177—180°/12 mm. (the corresponding *methyl ether* is a colourless liquid, b. p. 164—166°/13 mm.).

Δ^{β} -Butenyl bromide reacts very readily with ammonium thiocyanate dissolved in alcohol, but the primarily-formed Δ^{β} -*butenyl thiocyanate* becomes isomerised when distilled to the corresponding thiocarbimide, b. p. 158—159° (*phenyl- Δ^{β} -butenylthiocarbamide* crystallises in colourless needles, m. p. 110°).

Methyl- Δ^{β} -butenylaniline is a colourless liquid, b. p. 118—120°/14 mm., which yields a non-crystalline *hydrochloride* and *picrate* and a *methiodide*, m. p. 109°. It is readily converted by cyanogen bromide into the non-crystalline, *phenylmethyldibutenylammonium bromide* (the corresponding *chloroplatinate* is a pale yellow powder, decomp. 145°), and *phenylmethylcyanamide*, b. p. 139—140°/14 mm., m. p. 32°. *Allyl- Δ^{β} -butenylaniline*, prepared from Δ^{β} -butenyl bromide and allylaniline, is a colourless liquid, b. p. 127—130°/12 mm., which gives a non-crystalline *hydrochloride* and *methiodide* and a *picrate*, m. p. 120°. It is converted by cautious treatment with cyanogen bromide into the non-crystalline *phenylallyldibutenylammonium bromide* (corresponding *chloroplatinate*, decomp. 109°) and *phenylallylcyanamide*, a colourless liquid, b. p. 153—155°/12 mm., which is also obtained from allylaniline and cyanogen bromide.

Δ^{β} -*Butenylhomocholine*, $\text{CHMe}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{NMe}_2\cdot\text{Br}\cdot[\text{CH}_2]_3\cdot\text{OH}$, a colourless, very hygroscopic, crystalline mass, m. p. 52°, is readily prepared from γ -hydroxypropyldimethylamine and Δ^{β} -butenyl bromide in benzene solution.

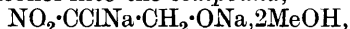
Δ^{β} -*Butenylnorcodeine* has m. p. 44° after softening at 40°. The corresponding *picrate*, m. p. 128°, and *chloroplatinate*, decomp. 198—200°, are described; the *hydrochloride* has little tendency towards crystallisation.

Ethyl di- Δ^{β} -butenylmalonate, b. p. 152—154°/17 mm., is prepared in 80% yield from butenyl bromide and ethyl malonate; the corresponding acid could not be caused to crystallise. The ester is converted by sodium ethoxide and carbamide into *di- Δ^{β} -butenylbarbituric acid*, $\text{CO}\langle\begin{smallmatrix} \text{NH}\cdot\text{CO} \\ \text{NH}\cdot\text{CO} \end{smallmatrix}\rangle\text{C}(\text{CH}_2\cdot\text{CH}\cdot\text{CHMe})_2$, leaflets, m. p. 109° (the *sodium salt* and the additive *product* with bromine, m. p. 195°, are described). H. W.

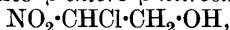
The Function of Phosphoric Oxide in the Elimination of Water from Ethyl Alcohol and Ether. D. BALAREFF (*J. pr. Chem.*, 1922, [ii], 368—377).—The dehydrating action of phosphoric oxide on ethyl alcohol vapour, the water in which exerts an appreciable partial pressure, or ethyl ether vapour (cf. Nef, A., 1901, i, 626) is partly catalytic and partly dependent on the formation of unstable additive products. At the ordinary temperature, ethyl alcohol gives, with phosphoric oxide, metaphosphoric acid, and the esters, $\text{Et}_2\text{H}_2\text{P}_2\text{O}_7$, EtH_2PO_4 , Et_2HPO_4 , and Et_3PO_4 , and perhaps other compounds; with metaphosphoric acid, EtH_2PO_4 . Phosphoric oxide dehydrates the esters EtH_2PO_4 and Et_2HPO_4 , giving a mixture of ethyl metaphosphate and pyrophosphate. W. S. N.

Aliphatic Nitro-alcohols. The Degradation of Nitrotrimethyleneglycol. RUDOLF WILKENDORF and MAX TRÉNEL (*Ber.*, 1923, 56, [B], 611—620).—It has been shown by Henry in 1895 that "nitroisobutylglycerol," $\text{NO}_2\cdot\text{C}(\text{CH}_2\cdot\text{OH})_3$, is readily obtained by the condensation of nitromethane with formaldehyde under the influence of alkali hydroxides. The removal of one molecule of formaldehyde from the compound with the formation of sodionitrotrimethylene glycol, $\text{NO}_2\cdot\text{CNa}(\text{CH}_2\cdot\text{OH})_2$, has been effected by Schmidt and Wilkendorf (A., 1919, i, 249) by means of sodium ethoxide, but the further removal of a second molecule of formaldehyde with production of β -nitroethyl alcohol could not be effected. If, however, the metallic atom in sodionitrotrimethylene glycol is replaced by halogen and the product is treated with sodium ethoxide, β -chloro- β -nitroethyl alcohol is produced in accordance with the equation $\text{NO}_2\cdot\text{CCl}(\text{CH}_2\cdot\text{OH})_2 + 2\text{NaOEt} = \text{NO}_2\cdot\text{CNaCl}\cdot\text{CH}_2\cdot\text{ONa} + 2\text{EtOH} + \text{H}\cdot\text{CHO}$. If now the chloronitroethyl alcohol is liberated by addition of acid, it immediately recondenses with the aldehyde to produce the original material. It is therefore necessary to remove the formaldehyde, which is conveniently effected by treating the sodio-compound with aqueous sodium hydroxide solution and nitromethane, whereby sodionitrotrimethylene glycol is produced. The mixture is acidified and the chloronitroethyl alcohol is separated from nitrotrimethylene glycol by distillation with steam. Catalytic reduction of the former compound in the presence of palladium and pyridine yields β -nitroethyl alcohol.

β -Chloro- β -nitropropane- $\alpha\gamma$ -diol is converted by a solution of sodium in ethyl alcohol into the *compound*,



which is transformed into β -chloro- β -nitroethyl alcohol,



b. p. $103^\circ/15$ mm. The latter substance is also obtained by the condensation of chloronitromethane with formaldehyde in the presence of saturated aqueous potassium carbonate solution. The corresponding *acetate* is a colourless, viscous liquid, b. p. 101 — $102^\circ/18$ mm. $\beta\beta$ -Dichloro- β -nitroethyl alcohol, a colourless, viscous liquid, b. p. 88 — $89^\circ/12$ mm. (*acetate*, b. p. $105^\circ/28$ mm.), is prepared by treating an ethereal suspension of the sodium compound prepared from β -chloro- β -nitropropane- $\alpha\gamma$ -diol (see above) with a slow current of dry chlorine in the absence of light.

β -Bromo- β -nitropropane- $\alpha\gamma$ -diol is converted by successive treatment with an alcoholic solution of sodium ethoxide and bromonitromethane (the latter combines with the liberated formaldehyde) into the *compound*, $\text{NO}_2\cdot\text{CNaBr}\cdot\text{CH}_2\cdot\text{ONa}$, which is transformed by oxalic acid in the presence of ether into β -bromo- β -nitroethyl alcohol, b. p. $113^\circ/15$ mm.; the corresponding *acetate* has b. p. 110 — $111^\circ/20$ mm. $\beta\beta$ -Dibromo- β -nitroethyl alcohol has b. p. $121^\circ/19$ mm., and yields an *acetate*, b. p. 105 — $106^\circ/8$ mm. Catalytic reduction of β -chloro-, $\beta\beta$ -dichloro-, or β -bromo-nitroethyl alcohol yields β -nitroethyl alcohol, b. p. $102^\circ/10$ mm. Treatment of an aqueous solution of β -nitroethyl alcohol with hydrogen in

the presence of oxalic acid and palladised barium sulphate leads to the production of β -hydroxylaminoethyl alcohol oxalate, m. p. 121—123° (decomp.) after softening at 119°; the corresponding free hydroxylamino-compound could not be caused to crystallise (cf. Kühn, *Diss.*, Berlin, 1922; Lutze, *Diss.*, Berlin, 1922).

$\beta\beta$ -Dichloro- β -nitroethyl alcohol is transformed by methyl-alcoholic sodium methoxide solution into sodium chloride, sodium nitrite, carbon monoxide, and nitrogen. H. W.

Preparation of some Esters and Glycidic Derivatives of Alkylglycerols. RAMOND DELABY (*Compt. rend.*, 1923, 176, 589—591).— $\alpha\beta$ -Dibromohydrins of alkylglycerols were obtained by the action of bromine on the corresponding alkylvinylcarbinols dissolved in twice their volume of ether. $\alpha\beta$ -Dibromobutan- γ -ol boils at 102—105°/13 mm., d_4^{20} 1·944, n_D^{23} 1·5405. $\alpha\beta$ -Dibromopentan- γ -ol boils at 112—115°/15 mm., and has d_4^{19} 1·828, n_D^{20} 1·5327. $\alpha\beta$ -Dibromohexan- γ -ol boils at 126—129°/13 mm., and has d_4^{19} 1·724, and n_D^{23} 1·5230. $\alpha\beta$ -Dibromoheptan- γ -ol boils at 132—133°/12 mm., and has d_4^{17} 1·613 and n_D^{16} 1·5191. The displacement of the hydroxyl group by a third bromine atom could only be effected by the action of phosphorus pentabromide. The resulting tribromoderivatives had the following characters: $\alpha\beta\gamma$ -tribromobutane, b. p. 110—113°/19 mm., d_4^{16} 2·190, n_D^{15} 1·5691; $\alpha\beta\gamma$ -tribromopentane, b. p. 125—128°/21 mm., d_4^{14} 2·095, n_D^{14} 1·5621; $\alpha\beta\gamma$ -tribromohexane, b. p. 137—141°/21 mm., d_4^{13} 1·896, n_D^{13} 1·5451; $\alpha\beta\gamma$ -tribromoheptane, b. p. 148—149°/27 mm., d_4^{16} 1·827, n_D^{16} 1·5394. The epibromohydrins were obtained by agitating finely powdered potassium hydroxide with an ethereal solution of the bromohydrins. The epibromohydrin of butane- $\alpha\beta\gamma$ -triol boils at 142—144°, d_4^{18} 1·468, n_D^{18} 1·4685. The epibromohydrin of heptane- $\alpha\beta\gamma$ -triol has a pleasant anise-like odour, b. p. 202—205°, and 91°/11 mm., d_4^{17} 1·246, n_D^{13} 1·4675. Butane- $\alpha\beta\gamma$ -triol and pentane- $\alpha\beta\gamma$ -triol are well characterised by their tribenzoates, melting at 79—80° and 99—100°, respectively. G. F. M.

Aluminium Trialkyl Etherates. ERICH KRAUSE and BRUNO WENDT (*Ber.*, 1923, 56, [B], 466—472).—Aluminium trialkyls have been prepared many years ago by Buckton and Odling from aluminium and mercury alkyls. In their endeavours to obtain these compounds by a more convenient process, the authors have studied the action of ethyl bromide in the presence of ethyl ether on an alloy of magnesium and aluminium containing 15·16% of the latter together with 0·24% of silicon and traces of iron and calcium under conditions similar to those usually adopted in the preparation of Grignard's reagents. When the vigorous action is completed, the ether is removed as far as possible by distillation from a water-bath and the residue is distilled under diminished pressure in an atmosphere of nitrogen, whereby the volatile aluminium compound is removed from the non-volatile magnesium derivatives. Somewhat unexpectedly, the product is found to consist of aluminium triethyl etherate, $4\text{AlEt}_3\cdot 3\text{Et}_2\text{O}$, a colourless, mobile liquid, b. p. 112°/16 mm., which can be preserved indefinitely

in a sealed tube even if exposed to light. It decomposes very rapidly on exposure to air, but does not generally become spontaneously inflamed; it reacts explosively with water. It has b. p. 216—218°/atmospheric pressure (very slight decomp.). The composition of the product is given with some reserve owing to the exceptional experimental difficulties encountered in its analysis but the presence of ethyl ether in the product is placed beyond doubt by its actual isolation by the cautious decomposition of the etherate with water vapour and by the synthesis of the etherate from ether-free aluminium triethyl (prepared from aluminium and mercury ethyl) and ether. The etherate is more conveniently prepared in considerable quantity by the action of sublimed aluminium chloride on a solution of magnesium ethyl bromide in ether; as thus prepared, it has b. p. 112°/16 mm., 110·5°/13·5 mm., $d_4^{17\cdot4}$ (vac.) 0·8200, $n_{\text{H}_a}^{17\cdot4}$ 1·43433, $n_{\text{D}}^{17\cdot4}$ 1·43700, $n_{\text{H}_\beta}^{17\cdot4}$ 1·44349, $n_{\text{H}_\gamma}^{17\cdot4}$ 1·44884.

Aluminium trimethyl etherate, $4\text{AlMe}_3\cdot 3\text{Et}_2\text{O}$, has b. p. 68°/15 mm., and, in contrast to the ether-free compound, cannot be caused to solidify. It almost invariably inflames spontaneously on exposure to air.

Aluminium tri-n-propyl etherate, $4\text{AlPr}_3\cdot 3\text{Et}_2\text{O}$, has b. p. 135°/18 mm. H. W.

Acceleration of the Hydrolysis of $\beta\beta'$ -Dichlorodiethyl Sulphide by Alkaline Colloidal Solutions. ROBERT E. WILSON, EVERETT W. FULLER, and MILTON O. SCHUR (*J. Amer. Chem. Soc.*, 1922, **44**, 2762—2783).— $\beta\beta'$ -Dichlorodiethyl sulphide may be completely hydrolysed by a colloidal solution of 3% of sulphonated maize oil and 2% of sodium carbonate in thirty-five minutes at 85°. The action consists in the acceleration of the rate of solution of the gas per unit area of interface. This process was used during the war in the field laundries to effect the rapid and complete removal of "mustard gas" from contaminated clothing. J. F. S.

Action of Methyl Sulphate and Potassium Methyl Sulphate on Monocarboxylic Acids in the Absence of Water. L. J. SIMON (*Compt. rend.*, 1923, **176**, 583—586).—Methyl sulphate and potassium methyl sulphate can in certain cases be advantageously employed for the preparation of methyl esters by direct action on the free acids themselves in absence of water according to the equations: $\text{CH}_3\cdot\text{CO}_2\text{H} + \text{Me}_2\text{SO}_4 = \text{MeHSO}_4 + \text{CH}_3\cdot\text{CO}_2\text{Me}$, and $\text{CH}_3\cdot\text{CO}_2\text{H} + \text{MeHSO}_4 = \text{H}_2\text{SO}_4 + \text{CH}_3\cdot\text{CO}_2\text{Me}$. Thus with acetic acid the first reaction occurs on heating with somewhat more than 1 mol. of methyl sulphate at 120°, and on raising the temperature to 200° when the first reaction is nearly over, the second takes place with very slight decomposition into sulphur dioxide, etc. The yield of methyl acetate exceeds 80% of the theory. Similar results were obtained with mono-, di-, and tri-chloroacetic acids, butyric acid, etc. Benzoic acid gave a smaller yield of something over 50% of the theory. The action of potassium methyl sulphate on acetic acid at about 200° gave a 70% yield of methyl acetate, and

on benzoic acid the same yield of methyl benzoate as was obtained with methyl sulphate. G. F. M.

Polynuclear Acetato- and Similar Kations of Barium and of Cerium. R. WEINLAND and ALFRED HENRICHSSEN (*Ber.*, 1923, 56, [B], 528—538).—It has been shown previously by Weinland and Stroh (*A.*, 1922, i, 981) that lead forms polynuclear kations with acetic acid. Similar salts of barium and cerium are now described, in some of which the acetato-complex is replaced by other residues. The barium acetato-compounds all appear to contain the same dibariumdiacetato-complex, $[\text{Ba} \langle \text{CH}_3 \cdot \text{CO}_2 \rangle \text{Ba}]$.

The following individual compounds are described: *Dibariumdiacetato-perchlorate acetate*, $[\text{Ba}_2(\text{OAc})_2] \text{OAc} \text{ClO}_4$, transparent, rectangular plates, obtained from barium acetate and perchloric acid or sodium perchlorate in aqueous solution (the latter mode of formation appears to indicate that the dibariumdiacetato-kation is present in barium acetate); *Dibariumdiacetato-di-perchlorate*, $[\text{Ba}_2(\text{OAc})_2](\text{ClO}_4)_2 \cdot 2\text{AcOH}$, large, transparent prisms, from barium acetate and perchloric acid in glacial acetic acid solution; *dibariumdiacetato-picrate heptahydrate*, yellow, slender rods; *dibariumdiacetato-chlorate acetate*, $[\text{Ba}_2(\text{OAc})_2] \text{OAc} \text{ClO}_3$, transparent rhombohedra, from barium acetate and sodium chlorate.

The following salts contain the analogous dibariumdiformato-kation: the *nitrate*, $[\text{Ba}_2(\text{HCO}_2)_2]_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, large, hexagonal pyramids, obtained from barium formate and nitric acid in aqueous solution; the *perchlorate formate*, $[\text{Ba}_2(\text{HCO}_2)_2] \text{ClO}_4 \text{HCO}_2 \cdot \text{H}_2\text{O}$, lustrous cubes, prepared by the spontaneous evaporation of an aqueous solution of barium formate and perchloric acid; the *picrate*, $[\text{Ba}_2(\text{HCO}_2)_2][\text{C}_6\text{H}_2(\text{NO}_2)_3\text{O}]_2 \cdot 4\text{H}_2\text{O}$, dark yellow prisms; the *ferricyanide potassium formate*, $[\text{Ba}_2(\text{HCO}_2)_2]_3[\text{Fe}(\text{CN})_6]_2 \cdot 2\text{HCO}_2\text{K} \cdot 8\text{H}_2\text{O}$, dark red crystals, from barium formate and potassium ferricyanide; the *ferricyanide*, $[\text{Ba}_2(\text{HCO}_2)_2]_3[\text{Fe}(\text{CN})_6]_2 \cdot 10\text{H}_2\text{O}$, small, dark red plates, from barium formate and sodium ferricyanide; the *cobalticyanide potassium formate*, $[\text{Ba}_2(\text{HCO}_2)_2]_3[\text{Co}(\text{CN})_6]_2 \cdot 2\text{HCO}_2\text{K} \cdot 8\text{H}_2\text{O}$, pale yellow crystals; the *nitroprusside*,

$[\text{Ba}_2(\text{HCO}_2)_2][\text{Fe}(\text{CN})_5\text{NO}] \cdot 6\text{H}_2\text{O}$, aggregates of reddish-brown leaflets.

Similar salts of cerium are described which appear to contain the triceriumtriacetato-kation. They are prepared by the action of the requisite acid on a solution of cerium acetate. Unlike the dibariumdiacetato-compounds which in certain cases can be obtained from neutral solution, the cerium compounds are only produced in a strongly acid medium. The following salts are described:

The *perchlorate acetate*, $[\text{Ce}_3(\text{OAc})_3] \text{ClO}_4 (\text{OAc})_4 \cdot 12\text{H}_2\text{O}$, long, slender, colourless rods; the *picrate acetate*, $[\text{Ce}_3(\text{OAc})_3] [\text{C}_6\text{H}_2(\text{NO}_2)_3\text{O}]_3 \cdot 3\text{H}_2\text{O}$, orange-red, rectangular plates; the *nitrate*, $[\text{Ce}_3(\text{OAc})_3](\text{NO}_3)_6 \cdot 13\text{H}_2\text{O}$,

pale pink, hexagonal plates which possibly owe their colour to traces of other rare earths; the *chromate*, $[\text{Ce}_3(\text{OAc})_3](\text{CrO}_4)_3 \cdot 6\text{H}_2\text{O}$, a yellowish-brown, microcrystalline powder; the *chloride acetate*, $2[\text{Ce}_3(\text{OAc})_3] \text{Cl}_2 \cdot \text{Ce}(\text{OAc})_3 \cdot 28\text{H}_2\text{O}$, colourless crystals. H. W.

Chloroiodoacetic Acid. HOLLAND CROMPTON and KATE MYFANWY CARTER (T., 1923, 123, 576—577).

Trifluoroacetic Acid. FRÉD. SWARTS (*Bull. Acad. roy. Belg.*, 1922, [v], 8, 343—370).—*p*-Aminobenzotrifluoride, on prolonged heating with chromic acid mixture, gives *trifluoroacetic acid* (70% of the theoretical quantity), which may be distilled over with water, and *hexa- ω -fluoro-m-azotoluene*, $\text{N}_2(\text{C}_6\text{H}_4 \cdot \text{CF}_3)_2$, orange needles, m. p. 82.3° , b. p. 282° , very volatile with steam. These two substances appear to form a compound, which is readily decomposed by sodium hydroxide. In the first stages of the oxidation (or, using permanganate), a brown, amorphous, sparingly soluble substance is formed, possibly a *quinonedianilide* of the formula $\text{CF}_3 \cdot \text{C}_6\text{H}_2\text{O}(\text{NH} \cdot \text{C}_6\text{H}_3 \cdot \text{CF}_3)_2$. Trifluoroacetic acid, obtained by distilling the sodium salt with sulphuric acid, forms rhombic plates, m. p. -15.25° to -15.28° , b. p. $72.4-72.5^\circ$, $d^{20} 1.53514$, fumes in the air, has a vesicant action, and dissolves in water with evolution of heat. It forms a constant boiling mixture with water, b. p. 105.46° , 79.4% of acid. Degrees of dissociation for $v=32$, 64, and 128 are respectively 0.943, 0.966, and 0.979, giving a dissociation constant (100 k) of about 50. The *sodium*, *potassium*, *ammonium*, *barium*, and *silver* salts are described (cf. *Mem. Acad. roy. Belg.* [8vo collection], 1894—5, 51, and A., 1921, ii, 261). Trifluoroacetates give no fluorofrom, and very little oxalic acid, when heated with sodium hydroxide (cf. A., 1906, i, 478).

Ethyl trifluoroacetate, obtained from sodium trifluoroacetate, alcohol, and sulphuric acid, has b. p. $61.7^\circ/761 \text{ mm.}$, $d^{16.7} 1.19529$, $n_D^{16.7} 1.30783$, $n_D^{16.7} 1.31237$ and $n_D^{16.7} 1.31527$.

Hexafluoroacetic anhydride, from phosphoric oxide and trifluoroacetic acid, has m. p. -65° , b. p. $39.5-40.1^\circ$; vapour non-associated. *Trifluoroacetamide*, leaflets, m. p. 74.8° , b. p. 162.5° , from the ethyl ester and ammonia, is volatile at ordinary temperatures. *Trifluoroacetonitrile*, from the amide and phosphoric oxide, boils at about -61° . Trifluoroacetic acid and aniline, when heated together at 170° give, besides *trifluoroacetanilide*, m. p. 87.64° , b. p. $220-225^\circ$, a little fluorofrom (cf. A., 1906, i, 159).

Sodium trifluoroacetate begins to decompose at 205° , giving *trifluoroacetyl fluoride*, b. p. about -59° , together with some anhydride.

The paper concludes with a useful summary of the physical properties of various fluoro-derivatives of acetic acid, as compared with those of the corresponding chloro-derivatives. E. E. T.

The Nature of Subsidiary Valency. XXVI. Complex Compounds with Sulphur Dioxide. FRITZ EPHRAIM and CLARA AELLIG (*Helv. Chim. Acta*, 1923, 6, 37—53).—The extent

to which the alkali metal salts of fatty acids will form additive compounds with sulphur dioxide was studied using lithium, sodium, potassium, rubidium, and caesium salts of the normal fatty acids from formic to valeric, and, in addition, the benzoates. Gaseous sulphur dioxide was taken up very slowly by the salts, and the most satisfactory method of investigation was to mix the anhydrous salt with liquid sulphur dioxide and allow the excess to evaporate. The lithium salts did not form compounds. Of the formates, the sodium salt formed no compound, the potassium salt took up about $\frac{1}{2}\text{SO}_2$ and the rubidium and caesium salt each about 1SO_2 . The remaining salts, including the benzoates, combined with approximately 1 mol. of sulphur dioxide. The sodium salt compounds are the least stable and gradually lose their combined sulphur dioxide in the course of a few months at the ordinary temperature. The potassium, rubidium, and caesium salts are comparatively stable up to 80° . At this temperature not merely loss of sulphur dioxide but more extensive decomposition takes place, and in the case of the formates free sulphur is formed. The additive compounds are white or faintly coloured with the exception of the formates, which are orange, resembling the compounds of alkali iodides with sulphur dioxide.

An investigation into the cause of the yellow colour of sodium hydrogen sulphite solutions showed that the colour is a characteristic property of the solution and not due to impurity. The colour was always obtained, using the purest materials, when sodium, potassium, or ammonium hydroxide solutions, or the solutions of their carbonates, sulphites, formates, and acetates were saturated with sulphur dioxide. To a less extent, the colour was obtained with solutions of calcium hydroxide and zinc acetate, but not with those of the chlorides, sulphates, and nitrates of the alkali metals nor with hydroxides of the alkaline-earth metals (except calcium), magnesium, or cadmium. The colour reaches its maximum when $5N$ -solutions of alkali hydroxides are saturated with sulphur dioxide, and is not perceptible below $0.5N$. Spectroscopically, it is very similar to a dilute chromate solution. On dilution it does not follow Beer's law, but rapidly disappears. The colour may be due to the formation of complexes of the type of KI_4SO_2 which in solution gives a colour three hundred times as intense as that of sodium hydrogen sulphite at the same concentration. There is insufficient evidence to afford a satisfactory explanation of the colour.

E. H. R.

Catalytic Decomposition of (Organic) Acids and Ketones. A. MAHLE (*Caoutchouc et Guttapercha*, 1922, 19, 473—475; from *Chem. Zentr.*, 1923, i, 38).—The decomposition of organic acids passed over a copper-aluminium catalyst at 600 — 650° is not of uniform type, since the products undergo further decomposition. Acids with six or less carbon atoms decompose almost completely with formation of gaseous products, water, and a small amount of ketones. From the higher acids liquids are produced which give on hydrogenation petroleum-like products including benzene

*m**

derivatives. Acetic acid gives carbon dioxide, carbon monoxide, methane, and hydrogen. *iso*Butyric acid gives hydrocarbons of the C_nH_{2n} and C_nH_{2n+2} series. Butyric acid gives the same products. Among the products from *isovaleric* acid is *isobutylene*. Benzene and toluene are found among the decomposition products of nonoic acid. Acetone gives carbon monoxide, methane, and hydrogen. Higher ketones give corresponding unsaturated compounds.

G. W. R.

The Configuration of the Crotonic Acids. K. VON AUWERS and H. WISSEBACH (*Ber.*, 1923, **56**, [B], 715—733).—The literature of the various attempts to elucidate the configuration of the isomeric crotonic acids is exhaustively reviewed, and the various arguments which have been brought forward are criticised in detail. Since, in spite of the large amount of physical and chemical evidence which is available, it has not been possible to establish the configuration of the acids, the authors have endeavoured to decide the question by chemical means, using as starting point substances of known composition and utilising reactions which occur under mild conditions and do not immediately involve the doubly-linked carbon atoms of the acids, thus minimising the possibility of transformations and abnormal reactions.

The possibility of converting $\gamma\gamma\gamma$ -trichlorocrotonic acid smoothly into maleic or fumaric acid has been examined. This cannot be accomplished satisfactorily by means of alkali, but fumaric acid is formed in excellent yield under the influence of sulphuric acid (60%) at 160—180°. The reaction in this state is unsuitable for configurative purposes, but, fortunately, the same change can be induced by concentrated sulphuric acid at the atmospheric temperature, although it occurs much more slowly; under these conditions, the formation of maleic acid cannot be detected. To permit valid conclusions as to the relationship of trichlorocrotonic and fumaric acids to be drawn from this result, it is, however, necessary to establish the stability of maleic acid under the experimental conditions. This acid is known to be very slightly isomerised by sulphuric acid, and in a series of experiments it is proved to be stable towards hydrogen chloride in the presence of concentrated sulphuric acid. Also, the formation of chlorosuccinic acid could not be established with certainty in any of the numerous experiments; according to the observations of previous works, it must have been produced in relatively considerable quantities if maleic acid had been formed. It is therefore regarded as established that $\gamma\gamma\gamma$ -trichlorocrotonic acid is converted directly into fumaric acid and hence has the fumaroid configuration.

The replacement of the halogen atoms of $\gamma\gamma\gamma$ -trichlorocrotonic acids by hydrogen has been investigated. This cannot be effected in the required manner by the action of sodium amalgam on the acid, of sodium or aluminium amalgam on its ethyl ester, or of sodium wire and moist ether on the amide. Zinc dust and acetic acid, however, convert the trichloro-acid or its ester into the di-

chloro-compounds, and the dichloro-acid is reducible by sodium amalgam to solid crotonic acid and a little butyric acid; the formation of *isocrotonic* acid is not observed. The possibility of molecular transformation during the reduction is discussed but is regarded as highly improbable; solid crotonic acid is therefore to be regarded as the *trans*-form and *isocrotonic* acid as the *cis*-modification.

The configurations of the monohalogenated crotonic acids can now be deduced if it is granted that electrochemical differences in the molecules of organic compounds tend to become neutralised, and that addition of halogen if occurring in the *cis*-position is followed by loss of hydrogen halide in the same position and vice versa. Each crotonic acid must then form by addition of halogen and subsequent removal of the β -halogen atom as hydrogen halide an α -halogeno-derivative of the stereoisomeric form. The configurations thus deduced are identical with those suggested by Michael and Pfeiffer from other considerations.

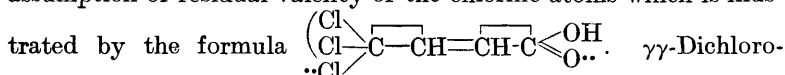
The annexed configurations (I) and (II) are ascribed to tiglic and angelic acids, respectively, since their relation to one another is very similar to that between crotonic and *isocrotonic* acids (cf. Sudborough and Davies, T., 1909, 95, 976).

The applicability of physical constants to the elucidation of the configuration of stereoisomeric compounds is discussed in detail. Melting point appears to be useful only in the cases of parent compounds since the mutual influence of substituents may completely alter the configurational relationship in the molecule. In the cases of density and refractive index, it does not invariably appear that the relative position of the groups is the decisive factor. Although a sufficiently large number of observations has not yet been made, it appears probable that the dissociation constant may be the most trustworthy physical datum. H. W.

$\gamma\gamma\gamma$ -Trichlorocrotonic Acid, $\gamma\gamma$ -Dichlorocrotonic Acid, and Maleinaldehydic Acid. K. VON AUWERS and H. WISSEBACH (*Ber.*, 1923, 56, [B], 731—741; cf. preceding abstract).— $\gamma\gamma\gamma$ -Trichloro- β -hydroxybutyric acid is obtained in approximately theoretical yield by the action of chloral hydrate on malonic acid in the presence of pyridine and is converted in the usual manner into $\gamma\gamma\gamma$ -trichlorocrotonic acid. $\gamma\gamma\gamma$ -Trichlorocrotonyl chloride, prepared conveniently by the action of thionyl chloride on the acid, is an almost colourless liquid, b. p. 75°/11 mm., (i) d_4^{20} 1.5292, d_4^{20} 1.528, $n_a^{18.8}$ 1.51414, $n_D^{18.8}$ 1.51812, $n_D^{18.8}$ 1.52890, $n_D^{18.8}$ 1.53823, n_D^{20} 1.5176; (ii) $d_4^{17.2}$ 1.5285, d_4^{20} 1.525, $n_a^{17.2}$ 1.51395, $n_D^{17.2}$ 1.51798, $n_D^{17.2}$ 1.52881, $n_D^{17.2}$ 1.53830, n_D^{20} 1.5167. $\gamma\gamma\gamma$ -Trichlorocrotonamide crystallises in lustrous leaflets, m. p. 83°. $\gamma\gamma\gamma$ -Trichlorocrotononitrile, obtained from the amide and phosphoric oxide, is a colourless liquid, b. p. 74—75°/10 mm., b. p. 91°/25 mm., $d_4^{1.2}$ 1.4319, d_4^{20} 1.420, $n_a^{11.2}$ 1.50837, $n_D^{11.2}$ 1.51225, $n_D^{11.2}$ 1.52242, $n_D^{11.2}$ 1.53138,

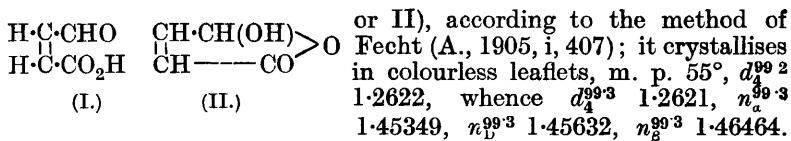
n_D^{20} 1.5083. $\gamma\gamma\gamma$ -Trichlorocrotonanilide crystallises in lustrous leaflets, m. p. 162.5—163.5°.

$\gamma\gamma$ -Dichlorocrotonic acid, long, transparent, oblique prisms, m. p. 42—43°, b. p. 130°/18 mm., 123°/13 mm., d_4^{20} 1.3331, whence d_4^{20} 1.3327, n_a^{20} 1.45680, n_D^{20} 1.45966, n_B^{20} 1.46777, n_γ^{20} 1.47565, is readily prepared by the action of zinc dust and acetic acid on an aqueous alcoholic solution of $\gamma\gamma\gamma$ -trichlorocrotonic acid; in consequence of the ready polymerisation of the dichloro-acid, the yields of the latter are somewhat variable but average about 60% of that theoretically possible; the reaction proceeds more smoothly if the esters are used. The ready mobility of one chlorine atom and the stability of the remaining two in the trichloro-acid is explained by Thiele's theory of partial valencies and by the assumption of residual valency of the chlorine atoms which is illustrated by the formula



crotonic acid is converted by concentrated sulphuric acid into succinic acid in 88% yield, an aldehyde appearing to be formed intermediately. It unites readily with bromine in chloroform solution in the presence of sunlight giving $\gamma\gamma$ -dichloro- $\alpha\beta$ -dibromobutyric acid, lustrous leaflets, m. p. 120—121°, after previous softening. Ethyl $\gamma\gamma$ -dichlorocrotonate, prepared by reduction of the corresponding trichloro-ester, has b. p. 91°/20 mm., 82°/12 mm., d_4^{16} 1.2323, d_4^{20} 1.229, n_a^{16} 1.46096, n_D^{16} 1.46347, n_B^{16} 1.47098, n_γ^{16} 1.47711, n_D^{20} 1.4619. It rapidly polymerises when preserved at the atmospheric temperature. It could not be caused to react with phenylhydrazine, semicarbazide hydrochloride, hydroxylamine sulphate, or sodium iodide dissolved in acetone. Ethyl $\gamma\gamma$ -dichloro- $\alpha\beta$ -dibromobutyrate is an almost colourless liquid, b. p. 142—144°/14 mm., 158—159°/21 mm., d_4^{22} 1.8257, d_4^{20} 1.830, n_a^{22} 1.51936, n_D^{22} 1.52233, n_B^{22} 1.53096, n_γ^{22} 1.53787, n_D^{20} 1.5235. Methyl $\gamma\gamma$ -dichlorocrotonate is a colourless, mobile liquid, b. p. 77°/14 mm., d_4^{17} 1.3050, d_4^{20} 1.302, n_a^{17} 1.46744, n_D^{17} 1.47040, n_B^{17} 1.47811, n_γ^{17} 1.48442, n_D^{20} 1.4694. Methyl $\gamma\gamma$ -dichloro- $\alpha\beta$ -dibromobutyrate crystallises in transparent, quadratic plates, m. p. 37° after previous softening, b. p. 145°/19 mm. $\gamma\gamma$ -Dichlorocrotonyl chloride is an almost colourless liquid, b. p. 66—67°/12 mm., d_4^{19} 1.4429, d_4^{20} 1.442, n_a^{19} 1.49547, n_D^{19} 1.49928, n_B^{19} 1.50818, n_γ^{19} 1.51674, n_D^{20} 1.4991. $\gamma\gamma$ -Dichlorocrotonamide, prepared by reduction of the trichloro-compound, crystallises in needles or leaflets, m. p. 82—83°; it is converted by bromine into $\gamma\gamma$ -dichloro- $\alpha\beta$ -dibromobutyramide, lustrous leaflets, decomp. 162° after shrinking at 156—157°, when moderately rapidly heated. $\gamma\gamma$ -Dichlorocrotonanilide forms long, lustrous leaflets, m. p. 83°. $\gamma\gamma$ -Dichlorocrotononitrile is a colourless liquid with an odour of almonds, b. p. 82—83°/12 mm., 93.5—93.8°/21 mm., d_4^{20} 1.3049, n_a^{20} 1.49369, n_D^{20} 1.49735, n_B^{20} 1.50714, n_γ^{20} 1.51500.

γ -Hydroxy- Δ^2 -crotonolactone is converted into maleinaldehydic acid or 2-keto-5'-hydroxy-3:4-dihydrofuran (annexed formulæ, I



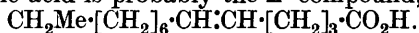
The optical data indicate that the cyclic form is mainly present in the molten substance. The corresponding *p*-nitrophenylhydrazone has m. p. 221° or (+EtOH), m. p. $211\text{--}212^\circ$. The aldehyde is decomposed by concentrated sulphuric acid without appearing to yield definite products; the formation of succinic acid could not be observed. H. W.

The Preparation and Constitution of Synthetic Fats containing a Carbohydrate Chain. HELEN S. GILCHRIST (*Rep. Brit. Assoc.*, 1922, 357).—When α -methylglucoside is heated with olive oil in the presence of sodium ethoxide, a mono-oleate of α -methylglucoside is first formed, whilst in the case of mannitol a dioleate is formed. In each case, internal dehydration follows at once, the carbohydrate chain losing one molecule of water and the fatty residues remaining intact. Anhydromethylglucoside mono-oleate and mannitan di-oleate are definite chemical individuals. On methylation, they yield unstable monomethyl derivatives. When heated with acidified alcohol, they give methyl oleate together with an alkylated sugar derivative. In both cases the anhydro-ring persists during hydrolysis. E. H. R.

Hydrogenation and Dehydrogenation of Castor Oil and its Derivatives. ANDRÉ BROCHET (*Compt. rend.*, 1923, 176, 513—515; cf. Mailhe, this vol., i, 88).—Castor oil is completely hydrogenated under a pressure of eleven atmospheres in the presence of reduced nickel at $112\text{--}114^\circ$ in ninety minutes. The hydrogenated oil has m. p. 86° and iodine number 2. When heated in an open flask, it begins to give off hydrogen at 150° , and the volume liberated increases with rise in temperature up to about 280° . The original castor oil absorbs 70 c.c. of hydrogen per gram, but the hydrogenated oil only gives off 40 c.c. per gram. Methyl ricinoleate is hydrogenated in the same manner as castor oil and absorbs the theoretical amount of hydrogen in less than an hour at $100\text{--}105^\circ$ under a pressure of twelve atmospheres. W. G.

A New Tetradecenoic Acid from Sperm and Dolphin Oils. MITSUMARU TSUJIMOTO (*Chem. Umschau*, 1923, 30, 33—36).—A tetradecenoic acid, $\text{C}_{14}\text{H}_{26}\text{O}_2$, was isolated from sperm oil by converting the glycerides into methyl esters, separating the fraction boiling up to $180^\circ/15$ mm., brominating, and refractionating the bromo-esters, whereby a fraction boiling at $132\text{--}136^\circ/5$ mm. was obtained. This was debrominated by means of zinc and acetic acid, and saponified, non-saponifiable matter was removed by extraction with ether, and the fat acid was liberated by the addition of mineral acid. It formed a colourless liquid boiling between 190° and $200^\circ/15$ mm., $d_4^{15} 0.9079$, $n_D^{15} 1.4566$, iodine value 106.8. On hydrogenation it was converted into myristic acid,

and on oxidation gave a *dihydroxymyristic acid*, $C_{14}H_{26}(OH)_2O_2$, m. p. 118—119°. The latter acid on oxidation with dichromate and sulphuric acid gave a reaction product from which nonoic acid was isolated. Only a very small amount of a substance which probably represented the corresponding scission product, glutaric acid, was obtained, but the results so far obtained indicate that the tetradecenoic acid is probably the Δ^8 -compound,



Tetradecenoic acid was also isolated from the low boiling fraction of the methylated sperm oil by the lead salt—light petroleum method, and from dolphin oil by the above bromination method. The yield from sperm oil was about 3% and from dolphin oil about 0.4%.

G. F. M.

A New Substance in Birch Tar. I. K. TRAUBENBERG (*J. Russ. Phys. Chem. Soc.*, 1918, **50**, 153—156).—*Dokozanic acid*, $C_{21}H_{42}O_2$ or $C_{22}H_{44}O_2$, lustrous leaflets, m. p. 72°, is found to the extent of 0.4% in birch tar; it is a fatty acid, similar in appearance and properties to stearic acid. The silver and sodium salts are prepared and described. The product of oxidation with nitric acid is an acidic substance, m. p. 67°, of the formula $C_{22}H_{44}O_3$, and is probably a hydroxy acid.

R. T.

Pyruvic Acid from Lactic Acid. J. G. SMULL and P. SUBKOW (*Chem. and Met. Eng.*, 1923, **28**, 357—358).—By electrolytic oxidation of lactic acid in acid, alkaline, or neutral electrolytes in a divided cell it was found that pyruvic acid was not formed when a platinum anode was used unless substances were present which removed the pyruvic acid immediately from the sphere of oxidation. Better results were obtained by the use of a lead anode and an alkaline anolyte, but the efficiency of the process is low (cf. *J.S.C.I.*, 1923, April).

A. R. P.

Inorganic Complex Salts. II. Erdmann's Salt and its Derivatives. WILLIAM THOMAS (*T.*, 1923, **123**, 617—619).

Complex Metallic Ammines. VIII. The Introduction of Di- and Tri-basic Organic Acid Radicles into the Pentamminecobaltic Complex. JAMES COOPER DUFF (*T.*, 1923, **123**, 560—575).

isoPropylmalonic Acid Derivatives and Steric Hindrance. E. PREISWERK (*Helv. Chim. Acta*, 1923, **6**, 192—198).—The effect of the isopropyl group on the reactivity of substituents in its proximity is often attributed to steric hindrance, but a study of the influence of the group in three compounds, ethyl isopropylmalonate, ethyl isopropylcyanoacetate [ethyl α -cyano- β -methylbutyrate], and isopropylbarbituric acid, proves that this explanation does not always hold. In each of these cases the carbon atom to which the isopropyl group is attached carries a reactive hydrogen atom, which can, in general, be substituted by an alkyl group. Ethyl isopropylmalonate cannot be alkylated at all,

although the corresponding ethylmalonate and *n*-propylmalonate can be alkylated. In the case of the derivatives of ethyl cyanoacetate, the *isopropyl* derivative can be alkylated as readily as any other alkyl derivative. More remarkable than this is the observation that *isopropylbarbituric acid* can be alkylated more readily than either ethyl- or *n*-propyl-barbituric acid.

The ease with which these substances can be alkylated may be taken to depend on their acidity. Barbituric acid is a comparatively strong acid, stronger than acetic, and is not easily alkylated, on account of the stability of its alkali salts. The *C*-alkylated barbituric acids are less strongly acidic, especially the *isopropyl* derivative, which is weaker than acetic acid. By weakening the acidic properties, the alkyl groups facilitate alkylation.

In the case of ethyl cyanoacetate, the weakening of acidity due to the introduction of alkyl groups is unimportant. Ethyl malonate is the most feebly acidic of the substances under consideration and in its alkyl derivatives the acidity becomes so weak that the labile hydrogen atom loses its reactivity altogether. This explains why ethyl *isopropylmalonate* cannot be alkylated.

Methylisopropylbarbituric acid, obtained by methylating *isopropylbarbituric acid* in sodium hydroxide solution with methyl iodide, forms colourless crystals, m. p. 186—187°. *isopropylallylbarbituric acid* forms colourless crystals, m. p. 137—138°. *Diisopropylbarbituric acid* forms colourless crystals, m. p. 230° (decomp.).
E. H. R.

Effect of Molybdic Acid and of Molybdates on the Rotatory Power of Malic Acid. E. DARMOIS (*J. Phys. Radium*, 1923, 4, 49—70).—A historical résumé is given of the work of Gernez and others on the effect of alkali molybdates and tungstates on the rotatory powers of malic and tartaric acids. The author has investigated more especially the effect of ammonium and sodium molybdates on the rotatory power of malic acid. Solutions were prepared by adding ammonia or sodium hydroxide to aqueous solutions containing *n* gram-molecules of molybdic acid and 1 gram-molecule of malic acid, *n* ranging from 0 to 5, and the rotatory powers for $\lambda\lambda$ 5780, 5460, and 4360 Å. measured. Curves showing the relation of the rotatory power to *n*, for various concentrations of sodium hydroxide or ammonium, all possess respective maxima. The largest dextrorotatory power measured in each case corresponded with *n*=2, and characterised solutions containing 2 gram molecules of either ammonia or sodium hydroxide to 1 of malic acid. The results of Gernez indicating the existence of solutions having maxima of *lævo*- and *dextro*-rotations and the results of the present investigation are explicable on the assumption of the existence of definite compounds, the dimolybdomalates, *e.g.*, $2\text{MoO}_3 \cdot \text{C}_4\text{H}_6\text{O}_5 \cdot 2\text{NaOH}$, and $2\text{MoO}_3 \cdot \text{C}_4\text{H}_6\text{O}_5 \cdot 2\text{NH}_3$, and of molybdomalates, *e.g.*, $\text{MoO}_3 \cdot 2\text{C}_4\text{H}_6\text{O}_5 \cdot 2\text{NaOH}$. Crystals of sodium dimolybdomalate are monoclinic and exist as hemihedral enantiomorphs [$a : b : c = 1.442 : 1 : 1.939$, $\beta = 97^\circ 46'$]. Barium dimolybdo-

malate has been prepared in the form of well defined crystals. Values of the respective rotatory and dispersive powers are given.

J. S. G. T.

***d*-Malic Acid and the Utilisation of Ammonium Molybdomalate for the Decomposition of *r*-Malic Acid.** E. DARMOIS and J. PÉRIN (*Compt. rend.*, 1923, 176, 391—394).—*r*-Ammonium molybdomalate is not deposited from its solution as such, but gives a mixture of crystals of the *d*- and *l*-salts, which may be separated mechanically. The optical rotation of these salts is of such a magnitude, $[\alpha]_{578} \pm 220^\circ$, that it is possible very readily to determine the purity of the resulting isomerides. The active molybdomalates may readily be converted into the active malic acids by decomposition with hydrogen sulphide in the presence of nitric acid, the malic acid being precipitated as its lead salt after filtering off the molybdenum sulphide. The lead salt is then decomposed by hydrogen sulphide. The preparation of *d*-malic acid from the natural *l*-acid by the Walden inversion gives a mixture of 75% of the *d*-acid and 25% of the *l*-acid, partial racemisation occurring during the inversion.

W. G.

The Formation of Derivatives of Oxalacetic Acid from Tartaric Acid. FREDERICK DANIEL CHATTAWAY and GEORGE DAVID PARKES (*T.*, 1923, 123, 663—669).

Complex Aluminium Salts of Aliphatic Hydroxy-acids. OSKAR GOLDMAN (*Biochem. Z.*, 1922, 133, 459—468).—The following salts of aluminium and an organic acid have been obtained: aluminium hydrogen tartrate, $\text{Al}(\text{C}_4\text{H}_5\text{O}_6)_3$; ammonium hydrogen aluminotartrate, $\text{C}_8\text{H}_{15}\text{O}_{12}\text{N}_2\text{Al}$; aluminotartaric acid, potassium aluminotartrate, $\text{C}_8\text{H}_7\text{O}_{12}\text{K}_2\text{Al}$; sodium aluminotartrate, $\text{C}_{12}\text{H}_9\text{O}_{18}\text{Na}_6\text{Al}$; an aluminium mucate, $\text{C}_6\text{H}_7\text{O}_8\text{Al}$; ammonium aluminomucate, $\text{C}_6\text{H}_{13}\text{O}_8\text{N}_2\text{Al}$; sodium aluminomucate, $\text{C}_6\text{H}_5\text{O}_8\text{Na}_2\text{Al}$. Constitutional formulæ are suggested. W. O. K.

Preparation of Formaldehyde. P. BOBROV (*J. Russ. Phys. Chem. Soc.*, 1918, 50, 130—136).—The yields of formaldehyde obtained by passing a mixture of methyl alcohol vapour and air through a heated tube containing copper gauze spirals as catalyst are usually 37—42% of theory. By using instead of spirals copper gauze disks packed perpendicularly to the axis of the tube, the yields were increased to 67.6—71.6% of theory. The presence of acetone up to 4% in the spirit does not materially affect the reaction. The use of copper, gold, and silver finely distributed on asbestos, as catalysts, in conjunction with the copper disks, is tried, using spirit mixed with acetone, the amount of the latter being gradually increased to 11%. Under these conditions, copper catalyst gives yields of 70.04—72.4%, gold gives 72.79%, and silver 77.73% of the theoretical. Variations in the temperature of the alcohol vapour affect the yields less than when copper disks alone are used. On the other hand, gold and silver soon lose their catalytic power, probably owing to their relative volatility in these circumstances, which gives rise, eventually, to the formation of a

metallic mirror in the tube. Pure methyl alcohol with silver catalyst gives yields of 89.5%. The formaldehyde thus obtained, however, almost immediately polymerises to a hard, white solid, which condenses in the cooler parts of the tube, blocking it, so that the process cannot continue to the end.

R. T.

Catalysis in the Preparation of Acetal. HOMER ADKINS and BRYNJULV H. NISSEN (*J. Amer. Chem. Soc.*, 1922, 44, 2749—2755).—Calcium, lithium, magnesium, cerium, ammonium, manganese, and zinc chlorides, calcium nitrate, calcium bromide, copper sulphate, sodium and lithium iodides act as true catalysts and not merely as dehydrating agents in the preparation of acetal from alcohol and acetaldehyde. Acetal is best prepared by placing 200 g. of anhydrous calcium chloride and 1050 g. of 95% alcohol in a 4-litre bottle and cooling to 8° or less. Five hundred g. of cold acetaldehyde are poured slowly down the inside wall of the bottle to form a layer on the alcohol. The bottle is closed and shaken intermittently for twelve hours. After settling, the clear upper layer is separated and washed three times with water, allowed to settle, dried, fractionated, etc. Following the procedure fully detailed in the paper, a total yield of 64% can be obtained. The equilibrium point of the equation $\text{CH}_3\cdot\text{CHO} + 2\text{EtOH} \rightleftharpoons \text{CH}_3\cdot\text{CH}(\text{OEt})_2 + \text{H}_2\text{O}$ in the presence of calcium chloride lies at 76% of acetal. Acetal has d_4^{20} 0.8254, d_{15}^{25} 0.8334; n_D^{25} 1.3682. Its vapour pressure and solubility in water and alcohol have been determined over a wide range of temperature. The following values of the vapour pressure are recorded: 33°, 52 mm.; 52.8°, 121 mm.; 62°, 178 mm.; 71°, 244 mm.; 81.7°, 365 mm.; 90.5°, 499 mm.; 95.1°, 586 mm.; 101.2°, 720 mm.; 103°, 745 mm., and 104.2°, 760 mm.

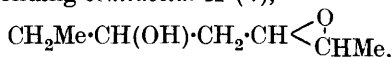
J. F. S.

Synthesis of $\alpha\gamma$ -Dihydroxyhexaldehyde and its Methyl Semiactal. BURCKHARDT HELFERICH and ARNO RUSSE (*Ber.*, 1923, 56, [B], 759—766).—The synthesis of the aldehyde is described. The main interest of the work lies in the observation that the presence of two hydroxy-groups in the α - and γ -positions of an aldehyde is sufficient for the production of two isomeric semi-actets; under the same or similar conditions, this does not appear to be the case with γ -hydroxyaldehydes.

$\alpha\gamma$ -Diketohexaldehydediethylacetal, $\text{CH}_3\text{Me}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}(\text{OEt})_2$, is prepared by the action of sodium ethoxide on a mixture of diethoxyacetic ester and methyl ethyl ketone. It is a colourless, mobile liquid, b. p. 110—116°/10 mm., d_4^{18} 1.0102, $n_D^{18.5}$ 1.4505; the copper salt, $\text{C}_{20}\text{H}_{34}\text{O}_8\text{Cu}$, m. p. 115°, is described. When reduced by sodium amalgam, the aldehyde combines with only one molecular proportion of water, yielding *hydroxyketo-n-hexaldehydediethylacetal*, a viscous, pale yellow liquid, b. p. 110—120°/3.5 mm., $d_4^{18.5}$ 1.0040, $n_D^{18.4}$ 1.4401.

Methyl dimethoxyacetate, a mobile, colourless liquid, b. p. 61—64°/12 mm., d_4^{18} 1.0962, $n_D^{18.2}$ 1.4045, is prepared by the action of methyl-alcoholic sodium methoxide on potassium dichloroacetate

followed by esterification of the product with methyl-alcoholic hydrogen chloride. It condenses with methyl ethyl ketone in the presence of sodium methoxide to give $\alpha\gamma$ -diketo-n-hexaldehydedimethylacetal, a colourless, mobile liquid, b. p. 100—106°/11 mm., d_4^{27} 1.0660, n_D^{18} 1.4574, which yields a dark blue monohydrated copper salt, m. p. 72°, and a dark green, anhydrous copper compound, m. p. 78°. It is reduced by sodium amalgam in alkaline solution in the presence of ammonium chloride to $\alpha\gamma$ -dihydroxy-n-hexaldehydedimethylacetal, $\text{CH}_2\text{Me}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OMe})_2$, a pale yellow, viscous liquid, b. p. 112—120°/3 mm., d_4^{21} 1.0407, n_D^{18} 1.4460, which is hydrolysed by *N*/10-sulphuric acid at the atmospheric temperature to $\alpha\gamma$ -dihydroxy-n-hexaldehyde, a pale yellow, moderately mobile liquid, b. p. 95—107.5°/0.5 mm., $d_4^{20.5}$ 1.0927, $n_D^{18.8}$ 1.4564; the aldehyde yields amorphous products with phenylhydrazine or its *p*-nitro-derivative. The di-methylacetal is transformed by well-cooled, methyl-alcoholic hydrogen chloride (1%) into the corresponding *semiacetal A* (?),



a colourless, mobile liquid, b. p. 103—109.5°/12 mm., $d_4^{22.5}$ 1.0510, $n_D^{20.7}$ 1.4375, and by methyl-alcoholic hydrogen chloride (0.25%)

at 100° into the *semiacetal B* (?), $\text{CH}_2\text{Me}\cdot\text{CH} < \begin{array}{c} \text{O}-\text{CH}\cdot\text{OMe} \\ \text{CH}_2\cdot\text{CH}\cdot\text{OH} \end{array}$, a

mobile, colourless liquid, b. p. 102—115°/13—15 mm., d_4^{20} 1.0246, $n_D^{20.6}$ 1.4379. The isomerides differ from one another to some extent in odour, taste, and solubility in water, but mainly in the differing rate of hydrolysis by *N*/100-sulphuric acid. They are not hydrolysed by α -glucosidase from yeast or by emulsin. H. W.

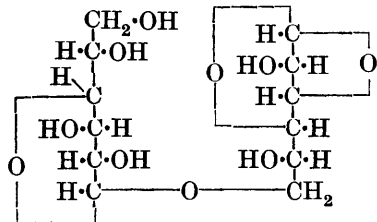
The Hydration of Dialkylethinylcarbinols and the Preparation of α -Hydroxymethyl Ketones. RENÉ LOCQUIN and SUNG WOUSENG (*Compt. rend.*, 1923, 176, 516—518).—The method of preparing methyl α -hydroxyisopropyl ketone from methylbutinenol by the action of mercuric sulphate in dilute sulphuric acid (cf. Scheibler and Fischer, A., 1922, i, 1108), is generally applicable for the preparation of such methyl α -hydroxyalkyl ketones from dialkylethinylcarbinols. The following new ketones have been prepared in this way. γ -Ethylpentane- γ -ol- β -one, $\text{OH}\cdot\text{C}(\text{Et})_2\cdot\text{COMe}$, b. p. 56—57°/13 mm., and 163—165°, d_4^{21} 0.9353, n_D^{21} 1.4303, giving an *oxime*, b. p. 116—118°, a *semicarbazone*, m. p. 155—156°, and an *acetate*, b. p. 87—90°, the *semicarbazone* of which has m. p. 145—146°. γ -Propylhexane- γ -ol- β -one, $\text{OH}\cdot\text{CPr}_2\cdot\text{COMe}$, b. p. 86—88°/14 mm., and 195°, d_4^{21} 0.9124, n_D^{21} 1.4343, giving an *oxime*, b. p. 134—135°/11 mm., m. p. 67°, a *semicarbazone*, m. p. 163°, and an *acetate*, b. p. 107—109°/13 mm. $\beta\beta$ -Trimethylpentane- γ -ol- δ -one, $\text{CMe}_3\cdot\text{CMe}(\text{OH})\cdot\text{COMe}$, b. p. 70—72°/14 mm., and 177°, d_4^{21} 0.9388, n_D^{21} 1.4442, giving an *oxime*, b. p. 124°/12 mm., m. p. 67—68°, and a *semicarbazone*, m. p. 193—194°. γ -Nonylbutane- γ -ol- β -one, $\text{C}_9\text{H}_{19}\cdot\text{CMe}(\text{OH})\cdot\text{COMe}$, b. p. 146—147°/12 mm., d_4^{21} 0.8941, n_D^{21} 1.4472, giving a *semicarbazone*, m. p. 131—132°. 1-Acetylcyclohexan-1-ol, b. p. 91°/11 mm., d_4^{21} 1.1033,

n_D^{20} 1.4726, giving an *oxime*, b. p. 146—147°/11 mm., m. p. 94—95°, and a *semicarbazone*, m. p. 217°. W. G.

Researches on Residual Affinity and Co-ordination. XV. Interactions of Acetylpropionylmethane and the Tetra-chlorides of Selenium and Tellurium. GILBERT T. MORGAN and HARRY GORDON REEVES (T., 1923, 123, 444—452).

The Influence of Dextrins on the Crystallisation of Maltose. L. DE HOOP and M. J. VAN TUSSENBROCK (*Biochem. Z.*, 1923, 135, 217—223).—In the commercial diastatic hydrolysis of starch, a maltose syrup is obtained which cannot be caused to crystallise directly. The authors have sought to discover the cause by determining the influence exerted by various substances, such as dextrins, proteins, peptones, and amino-acids on the crystallisation of pure maltose. It is found premature to attribute the lack of crystallising power of maltose syrup to dextrins. H. K.

Maltosan. AMÉ PICTET and ANDRÉ MARFORT (*Helv. Chim. Acta*, 1923, 6, 129—133).—When maltose is slowly heated to 160° under reduced pressure (15 mm.) it is converted into an anhydride, *maltosan*, $C_{12}H_{20}O_{10}$, forming a brown, amorphous powder which cannot be crystallised. It has no sharp m. p. but becomes viscous at 120° and liquid at 145—150°; $[\alpha]_D^{20} +75.6^\circ$. It cannot be distilled, and is not hydrated to maltose when boiled for a prolonged period with water. It reduces Fehling's solution at the boiling temperature, its reducing power being equal to that of maltose, and with phenylhydrazine it forms maltosazone. It reduces cold neutral potassium permanganate and is fermented by brewer's yeast. It forms a *hexa-acetyl* derivative, $C_{24}H_{32}O_{18}$, amorphous, m. p. 95°. It dissolves in concentrated hydrochloric acid to form *maltosyl chloride*, a pale yellow, hygroscopic substance, which reacts with sodium methoxide to form the known β -methylmaltoside. The above properties show a strong resemblance to those of glucosan, although the anhydride ring of maltosan is more stable. It can be regarded as a glucosylanhydro-



glucose of the formula shown. Maltosan remains unchanged under conditions which cause polymerisation of the hexosans, such as heating with zinc chloride. E. H. R.

The Preparation of Xylose from Maize Cobs. ARTHUR ROBERT LING and DINSHAW RATTONJI NANJI (T., 1923, 123, 620—621).

Swelling of Starch and the Coagulation of Albuminoids by Heat. W. W. LEPESCHKIN (*Kolloid Z.*, 1923, 32, 42—44).—The swelling of starch is shown to be due to hydration with the formation of amylopectin. Every variety of starch has not its

own swelling temperature; this process is a chemical reaction and as such is dependent on the temperature. The temperature coefficient is extraordinarily high, and is estimated at 57×10^6 — 83.9×10^6 . Similarly the coagulation of proteins is a chemical reaction and consists in the withdrawal of water from the molecule. This process is also dependent on the temperature and has a temperature coefficient of 58×10^3 — 95.4×10^3 . These very high temperature coefficients are explained as due to the cumulative effects of the acceleration of the rate of diffusion, increased solubility, and increased velocity of the actual reactions. J. F. S.

The Starch-Iodine Complex. II. L. BERCZELLER (*Biochem. Z.*, 1922, **133**, 502—508; cf. A., 1918, i, 101).—The compound formed between iodine and starch is considered to be an adsorption compound. Less iodine is taken up from alcohol than from water, and none from benzene or carbon tetrachloride, and this agrees with experimental results obtained with adsorbing charcoal. Measurements made of the adsorption of iodine by starch solution, by determination of the partition coefficient (between the starch solution and tetrachloroethane), or by dialysis, show that less is adsorbed than by solid starch. W. O. K.

The Limiting Dextrin formed by the Diastatic Degradation of Starch. C. J. LINTNER and MAX KIRSCHNER (*Z. angew. Chem.*, 1923, **36**, 119—122).—Achroodextrin II (cf. Lintner and Düll, A., 1895, i, 409), formed together with maltose by the action of diastase on starch, forms a dibenzoate and a diacetate and is attacked by neither emulsin nor *Saccharomyces Pombé*, but is converted quantitatively into dextrose by taka-diastase and completely fermented by the simultaneous action of diastase and yeast. Compounds intermediate between maltose and achroodextrin II, such as maltodextrins (cf. Brown and Millar, T., 1899, 286, 315), are not formed by the purely diastatic degradation of starch, and where they occur, as in beer, they must result from the action of maltase (cf. *J.S.C.I.*, 1923, April). T. H. P.

The Constitution of Polysaccharides. The Molecular Structure of Cotton Cellulose. JAMES COLQUHOUN IRVINE and EDMUND LANGLEY HIRST (T., 1923, **123**, 518—532).

The Absorption of Sodium Hydroxide Solutions by Cotton. HUBERT FRANK COWARD and LEO SPENCER (*J. Text. Inst.*, 1923, **14**, T. 32—45).—In order to throw some light on the question whether mercerisation is a chemical or physical phenomenon, the authors have determined the composition of the solid phase when purified cotton is immersed in sodium hydroxide solutions of various concentrations, and when cotton so treated is subsequently washed in more dilute solutions of alkali or in water. The measurements made were the weight of the dried cotton (steam oven), the weight of the centrifuged mass (seven and a half minutes at 7000 revolutions per minute; see following abstract), and the weight of sodium hydroxide absorbed, as determined by titration. The temperature was 15—18°. The curves obtained for sodium

hydroxide absorbed, over the whole range of solubility of the alkali, are complex and give no indication of the formation of definite chemical compounds, neither are they of the form commonly found for simple adsorption. However, the ratio of alkali absorbed to water absorbed is greater than the ratio of alkali to water in the original solution, and this preferential absorption is approximately proportional to the concentration of the solution in contact with the cotton. The shape of the curves in this case also does not give direct evidence of the formation of definite compounds, but it is not inconsistent with the view that a series of compounds, $(C_6H_{10}O_5)_m.(NaOH)_n$, is formed.

The volume of the absorbed solution has also been taken as a measure of the swelling of the hairs. It appears that swelling increases up to a limiting concentration of about 14.3% sodium hydroxide, when it remains constant, the hair having become about three times its original size. This limitation is imposed by the cuticle of the hair, since the contents are capable of even twelve-fold expansion. In the case of fabrics, the maximum swelling is much less, because of the mechanical constraints, and this, and similar phenomena connected with swelling, are discussed in the light of their practical significance in mercerising and dyeing.

J. C. W.

The Efficacy of a Centrifuge for Removing Surface Liquids from Cotton Hairs. HUBERT FRANK COWARD and LEO SPENCER (*J. Text. Inst.*, 1923, **14**, T. 29—32).—The centrifuge employed could be driven at 8000 revolutions per minute, or with an acceleration 2900 times that of gravity. Comparing the rates of removal of various liquids from cotton and glass wool, it is found that a few minutes' centrifuging, with an acceleration about 2000 times that of gravity, suffices to remove interfibrillar liquid down to 5 or 10% of the weight of the dry fibres, except in the case of very viscous liquids such as castor oil. Since, however, cotton retains water of the order of 50% of its weight, and sodium hydroxide solutions up to nearly 300%, under the above conditions, it follows that these liquids are held within the body of the cotton hairs to substantially the amount left after centrifuging as described. This is supported by the fact that cotton hairs swell considerably when immersed in water or sodium hydroxide solutions, but scarcely alter in liquids like alcohol or xylene.

J. C. W.

Theory of the Solvent Action of Aqueous Solutions of Neutral Salts on Cellulose. HERBERT E. WILLIAMS (*Mem. Manchester Phil. Soc.*, 1921, **65**, No. 12, 1—13).—The solution of cellulose in an aqueous solution of a neutral salt is independent of the chemical nature of the salt, but it is largely dependent on the physical properties of the salt solution. For such a solution to dissolve cellulose it must contain a hydrate, that is, an associated molecular complex of the salt and water. But this complex must be of such an order that it has a viscosity above a certain minimum, and a positive heat of dilution between well-defined limits. These limiting conditions will vary according to the nature of the cellulose

and the treatment which it has undergone; but for any particular cellulose the limits will be constant for all salt solutions in water.

J. F. S.

The Action of Acetyl Bromide on Cellulose. LÁSZLÓ ZECHMEISTER (*Ber.*, 1923, 56, [B], 573—578; cf. Bergmann and Beck, A., 1921, i, 649; Hess, A., 1922, i, 12; Karrer, A., 1921, i, 311, 766, 768; Zechmeister, *Diss.*, Zürich, 1913).—It does not appear to be possible to convert intact or nearly intact cellulose by means of acetyl bromide into acetylbromo-derivatives. The material behaves indifferently towards the reagent, acetylation or introduction of the bromine atom only occurring to a marked extent as it passes into solution, becoming thereby considerably degraded. Hydrogen bromide and acetic acid which are invariably present in technical acetyl bromide have a very important accelerating action on the acetolysis of cellulose. If the reagent is purified by being distilled over bright calcium turnings, its attack is very greatly delayed.

By the cautious addition of water to acetyl bromide, it is possible to hydrolyse it to any desired extent; it is found that with increasing hydrolysis its action becomes increasingly energetic. The course of the change is followed by analysis of the products which can be precipitated with water, since the undissolved fibres are not appreciably affected and the soluble products are difficult to determine. In the initial stages of the change, fission of the cellulose molecule appears to be initiated by hydrogen bromide, after which the disengaged hydroxyl groups become acetylated. Hydrogen bromide is thereby liberated which further hastens the general degradation. Hand in hand with the step-wise conversion into derivatives of simpler carbohydrates there occurs a partial displacement of the acetyl groups by the bromine atom, which resembles the conversion of dextrose penta-acetate into acetylbromoglucose.

Starch is converted by technical acetyl bromide into aceto-bromoglucose; the yields are, however, poor, and the conversion is effected more readily by acetyl bromide and a large excess of hydrogen bromide (cf. Bergmann and Beck, *loc. cit.*). It is remarkable that pine wood is soluble without residue in technical acetyl bromide (cf. Karrer and Widmer, A., 1921, i, 771). H. W.

[Cellulose Copper Compounds.] KURT HESS and ERNST MESSMER (*Ber.*, 1923, 56, [B], 587—591; cf. A., 1921, i, 401; 1922, i, 988).—A reply to the recent criticisms of Traube (this vol., i, 186). H. W.*

Nature of the Swelling Process. VII. Molecular Processes during Swelling and the Heat of Swelling. E. KNOEVENAGEL and E. VOLZ (*Koll. Chem. Beihefte*, 1923, 17, 51—71; cf. A., 1921, i, 420, 709, 710, 771; this vol., i, 17).—A continuation of previously published work. The swelling of cellulose acetate in binary mixtures of alcohol, nitrobenzene, and benzene has been investigated for a large number of binary mixtures of

various compositions. The results show that the liquid is adsorbed by the cellulose acetate in molecular proportions. The number of molecules of alcohol, benzene, or water adsorbed bears a constant relationship to the number of molecules of cellulose acetate, and where binary liquid mixtures of varying composition are used the sum of the number of molecules of each liquid taken up in the swelling is constant. The heat change occasioned by the swelling of cellulose acetate in the same binary mixtures has also been determined. The results although complicated by the nature of the process clearly indicate that the heat change has a molecular relationship.

J. F. S.

Graphic Representation of the Decomposition of Mono-, Di-, and Tri-methylamine Gas Mixtures. RUDOLF MICHEL (*Chem. Ztg.*, 1923, 47, 173—174).—A method is developed for the graphic representation of the thermal decomposition of the methylamines into hydrogen cyanide, ammonia, methane, hydrogen, and carbon. All the possible ways in which this may occur are summed up in the three following fundamental equations: (1) $\text{NH}_2\text{Me}=\text{NH}_3+\text{H}_2+\text{C}$; (2) $\text{N}(\text{CH}_3)_2=\text{HCN}+2\text{CH}_4$, and (3) $\text{N}(\text{CH}_3)_3=\text{HCN}+4\text{H}_2+2\text{C}$, and the gas mixtures formed are represented each by a corner of a Gibbs triangle, every point within the triangle thus representing one of the possible mixtures of gases which may arise from the decomposition of a methylamine mixture. The thermochemical relationships are also expressed by means of a Gibbs triangle in a similar way.

G. F. M.

Researches on Pseudo-bases. IV. A New Synthesis of Tertiary Amines of the Form $\text{R}\cdot\text{CH}_2\cdot\text{NR}^1\text{R}^2$. GERTRUDE MAUD ROBINSON and ROBERT ROBINSON (*T.*, 1923, 123, 532—543).

Perhalides of Quaternary Ammonium Salts. FREDERICK DANIEL CHATTAWAY and GEORGE HOYLE (*T.*, 1923, 123, 654—662).

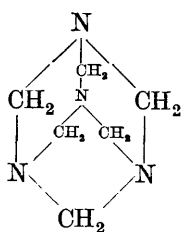
The Complex Ions formed by Silver Salts and Ethylenediamine in Aqueous Solution. P. JOB (*Compt. rend.*, 1923, 176, 442—445).—The silver-ion forms with ethylenediamine, in a dilute aqueous solution of the silver salt, two complex ions of the types Ag en_2 and Ag en , where en represents a molecule of ethylenediamine. The second complex only exists in any appreciable quantity when the concentration of the diamine is very small. The equilibrium constants of the two ions are $K=6.8\times 10^7$ and $k=10^5$, respectively, at 16° . The affinities of the silver-ion for ethylenediamine are in normal solution given by

$\text{Ag}^+ + \text{en} = (\text{Ag en})^+ + 6700 \text{ cal. (approx.)}$,
and $\text{Ag}^+ + 2 \text{en} = (\text{Ag en}_2)^+ + 10300 \text{ cal. (approx.)}$.

The second value coincides almost exactly with the value calculated by Bodländer (*A.*, 1904, ii, 122) for the affinity of silver for ammonia.

W. G.

Crystal Structure of Hexamethylenetetramine. ROSCOE G. DICKINSON and ALBERT L. RAYMOND (*J. Amer. Chem. Soc.*, 1923, 45, 22—29).—Crystals of hexamethylenetetramine have been examined by X-ray methods, using spectral photographs and Laue photographs. The data thus obtained have been accounted for by a structure with tetrahedral symmetry which may be regarded as built up of like molecules of $C_6H_{12}N_4$ in parallel orientation and on a body-centred cubic lattice of edge 7.02 Å. Both the carbon



atoms and the nitrogen atoms are equivalent among themselves. This fact is not shown by any of the structural formulæ hitherto put forward for this substance, but is in keeping with the annexed formula. Two nitrogen atoms are at a distance of about 1.44 Å. from each carbon atom, and at least approximately in the direction of two vertices of a tetrahedron, which is in agreement with the accepted view of the tetrahedral nature of the carbon atom. J. F. S.

Compounds of Normal Salts with Amino-acids and Polypeptides. PAUL PFEIFFER (*Z. angew. Chem.*, 1923, 36, 137—138).—Compounds of the types $MeX, 1A$; $MeX, 2A$; $MeX, 4A$; $MeX_2, 1A$; $MeX_2, 2A$; $MeX_2, 3A$; $MeX_2, 4A$; and $MeX_3, 3A$ such as $NaBr, NH_2 \cdot CH_2 \cdot CO_2H, H_2O$; $NaI, 2NH_2 \cdot CH_2 \cdot CO_2H, H_2O$;

$KBr, 4NHMe \cdot CH_2 \cdot CO_2H, 4H_2O$; $CaCl_2, NH_2 \cdot CH_2 \cdot CO_2H, 3H_2O$; and $CaBr_2, 3NH_2 \cdot CH_2 \cdot CO_2H$ have been prepared in crystalline form and they yield clear neutral aqueous solutions. From a consideration of their solubility, optical activity, and depression of the freezing point in aqueous solution, it is concluded that these complex compounds exist even in solution. Hence it is suggested that the adsorption of salts by the more complex colloids, such as albumin, is partly due to chemical combination, and the fact that such adsorption does not occur in definite constant proportions is ascribed to the inability of the normal salt to penetrate completely into the complex albumin molecules. This chemical theory of adsorption is also considered to hold good in industrial processes such as dyeing, weighting of silk, and tanning. A. J. H.

Synthesis of Two New Leucines. K. KURONO (*Biochem. Z.*, 1922, 134, 434—436).— α -Amino- α -methylvaleric acid and α -amino- β -dimethylpropionic acid have been prepared by the method of Zelinsky and Stadnikoff. The former melts in a sealed tube at 295° and forms a deep blue copper salt, readily soluble in water and in spirit. α -Naphthylcarbamido- α -methylvaleric acid melts at 191°. The second acid melts in a sealed tube at 293° and forms a deep blue copper salt, easily soluble in water. H. K.

A New Type of Nitrogenous Sugar Derivative. JOHN PRYDE (*Rep. Brit. Assoc.*, 1922, 357—358).—Tetramethylglucose was oxidised to tetramethylgluconic acid, which was isolated as the lactone. When this was treated with dry ammonia in alcoholic solution, a crystalline compound was obtained which appeared to

be, not the acid amide, but an amino-lactone. When this was treated with cold alkaline hypochlorite, a crystalline substance was obtained having the composition of the expected intermediate carbimide, but also having, from its behaviour, the constitution of an internal urethane, $\text{OMe}\cdot\text{CH}<\begin{smallmatrix} \text{CH(OMe)} \\ \text{CH}\cdot\text{O}\cdot\text{CO} \end{smallmatrix}>\text{NH}$. The formation of this substance shows the stabilising effect of methyl groups in the sugar chain and is an interesting example of the conversion of a carbohydrate into a derivative in which nitrogen is present in a stable cyclic substituent.

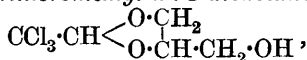
E. H. R.

A Remarkable Occurrence of Carbamide. EDMUND O. VON LIPPMANN (*Ber.*, 1923, 56, [B], 566—567).—A deposit observed in the blind end of a tube connected with the main steam supply of a beet-sugar factory was found to consist of nearly pure carbamide. The ammoniacal liquor of the evaporating plant was used as feed water for the boilers, and was apparently unusually rich in ammonia. Ammonium carbamate appears to have been the precursor of carbamide.

H. W.

Urethanes from Chlorine-substituted Secondary and Tertiary Alcohols. LESTER YODER (*J. Amer. Chem. Soc.*, 1923, 45, 475—479).—The carbamates of chlorine-substituted secondary and tertiary alcohols containing a trichloromethyl group were prepared by treating the sodium or the magnesium bromide derivative in benzene or ethereal solution with carbonyl chloride and then adding ammonia to the acid chloride thus formed. In this way were prepared *dimethyltrichloromethylcarbinyl carbamate*, m. p. 102°, *phenyltrichloromethylcarbinyl carbamate*, m. p. 127°, *dimethyltrichloromethylcarbinyl carbanilate*, m. p. 118°, *dimethyldichloromethylcarbinyl carbamate*, m. p. 122°, and *methyltrichloromethylcarbinyl carbamate*, m. p. 125°.

Chloral hydrate condenses with glycerol in the presence of zinc chloride to give 2-trichloromethyl-1:3-dioxolane-4-carbinol,

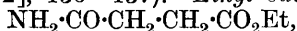


b. p. 125—128°/10 mm., which yielded a *urethane*, m. p. 114°.

The new alkyltrichloromethyl carbamates are tasteless and odourless. Methyl- and dimethyl-trichloromethyl carbamates have quite a strong hypnotic action. The dioxolane has a marked and fleeting hypnotic effect but its urethane has practically no hypnotic effect.

W. G.

Ethyl Succinamate. P. P. RUBCOV (*J. Russ. Phys. Chem. Soc.*, 1918, 50, [1—2], 136—137).—*Ethyl succinamate*,



m. p. 74—75°, b. p. 230—240°, is obtained by heating the silver salt of the corresponding acid in a sealed tube for two hours at 60—65° with ethyl iodide.

R. T.

Decomposition and Formation of Calcium Cyanamide. VICTOR EHRLICH (*Z. Elektrochem.*, 1922, 28, 529—542).—The con-

ditions under which the decomposition and formation of calcium cyanamide occur have been experimentally investigated. It is shown that the decomposition of calcium cyanamide, which commences above 1100° , is not determined solely by the temperature. Above 1200° , calcium cyanamide sublimates, but at 1300° a re-formation of calcium carbide can be deduced from the separation of lime and carbon in the nitrolime reaction. The carbon monoxide thus produced decomposes the pure sublimed calcium cyanamide partly with the formation of lime and carbon and partly with the formation of calcium carbide. Pure calcium cyanamide sublimates at 1300° without previously melting; the addition of approximately 10% of lime reduces the melting point to 1200° , and an addition of 15% of calcium chloride reduces it to $850\text{--}900^{\circ}$. Calcium cyanamide, free from carbon, decomposes above 1000° with the liberation of nitrogen according to the equation $\text{CaC} + \text{N}_2 \rightleftharpoons \text{CaCN}_2$. Dissociation pressure measurements have been made for various temperatures; the following values are recorded: 1000° , 2.5 mm., 1100° , 14 mm., 1140° , 32 mm., and 1190° , 73 mm. The addition of other materials to calcium cyanamide has little effect on the dissociation pressure at temperatures below 1200° , but above this temperature, due to the rapid sublimation of the calcium cyanamide and consequent reduction of the concentration, the dissociation pressure is strongly reduced. The decomposition of calcium cyanamide takes place with a much smaller nitrogen pressure than is the case with nitrolime under the same temperature conditions. The presence of carbon, therefore, raises the dissociation pressure, very probably under the influence of the reaction $\text{CaC}_2 \rightleftharpoons \text{CaC} + \text{C}$ which takes place from left to right below 1100° and in the opposite sense above this temperature. The process is a heterogeneous one, the course of which is determined by the constitution of the surface and the velocity of diffusion. The nitrolime reaction represented by the equation $\text{CaC}_2 + \text{N}_2 = \text{CaCN}_2 + \text{C}$ can be regarded as made up of the two reactions indicated by equations, above. A primary formation of cyanide is unlikely. The heat change of the formation of calcium cyanamide has been calculated on the basis of the Nernst heat theorem, and the value 61400 cal. obtained. It is likely that the heat change in the formation of nitrolime does not differ much from this value but is possibly a little higher.

J. F. S.

Action of Organometallic Derivatives of Magnesium on Nitriles. P. BRUYLANTS (*Bull. Acad. roy. Belg.*, 1922, [v], 8, 7—23).—Acetonitrile (1 mol.) reacts with ethereal magnesium methyl (ethyl) bromide (1 mol.) to give methane (ethane) (1 mol.), and, according to conditions, either diacetonitrile, or one of its condensation products (3-cyano-6-hydroxy-2:4-dimethylpyridine [cf. Moir, T., 1902, 81, 100] or 6-amino-3-cyano-2:4-dimethylpyridine [cf. von Meyer, A., 1908, i, 909]). The initial course of the reaction is to be represented thus: $\text{CH}_3\cdot\text{CN} \rightleftharpoons \text{CH}_2\cdot\text{C}\cdot\text{NH} \rightarrow \text{CH}_2\cdot\text{C}\cdot\text{NMgBr} \rightarrow \text{NH}\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{CN}$. No acetone is formed, and special care is necessary if diacetonitrile itself is required. Two

other substances are formed: (1) a solid substance, $C_6H_7N_3$ (?), m. p. 198—200°, converted by boiling water into ammonia and a substance of m. p. 135°; and (2) a base, $C_7H_7N_2$ (?), m. p. 123°, giving a chloroaurate, m. p. 103°. E. E. T.

Action of Organometallic Derivatives of Magnesium on Nitriles. OMER DE BOOSERÉ (*Bull. Soc. chim. Belg.*, 1923, 32, 26—51).—An investigation affording further evidence that nitriles do not always behave normally with the Grignard reagent. γ -Chlorobutyronitrile, when treated with an equimolecular proportion of magnesium ethyl bromide, is converted into four substances, as follows: (1) *cyclo*Propyl ethyl ketone (23—25%) (cf. A., 1909, i, 226). (2) *Ethyl γ -chloropropyl ketone* (14—17%), colourless liquid, b. p. 182—183°/761 mm., or 77·5—78·5°/15 mm., n_D^{20} 1·4411, d_4^{20} 1·0269; gives a semicarbazone, m. p. 98—99°; with solid potassium hydroxide gives *cyclo*propyl ethyl ketone (cf. A., 1889, 843), the latter giving the chloro-ketone when treated with hydrochloric acid. This fraction (2) also contains *cyclo*propyl ethyl ketimine, liquid, b. p. 127—128°/759 mm. (*hydrochloride*, solid, b. p. 160—170°/14—16 mm.) (cf. A., 1920, i, 485). (3) Ethyl amyl ketone (?). (4) Polymerides of *cyclo*propane carboxylonitrile. When, in the above reaction, two molecular proportions of Grignard reagent are used, the yields of fractions (1) and (2) become, respectively, 28—30% and 27—31%.

The interaction of magnesium ethyl bromide and ethyl γ -chloropropyl ketone affords as primary product the expected *diethyl- γ -chloropropylcarbinol*, but the latter on distillation, even under diminished pressure, decomposes to give (1) β -ethylhexylene β - ζ -oxide, b. p. 145—150°, n_D^{20} 1·4317, d_4^{20} 0·8703, (2) ζ -chloro- γ -ethyl- Δ -hexene, b. p. 173°, n_D^{20} 1·4524, d_4^{20} 0·9102, and (3) an inseparable mixture (b. p. 90—105°/15 mm.), probably containing *diethyl- γ -chloropropylcarbinol* and γ - ζ -dichloro- γ -ethylhexane (cf. A., 1909, i, 79). The product of the interaction of magnesium ethyl bromide and ethyl γ -chlorobutyrate, evidently the above carbinol, decomposes, even on distillation under diminished pressure, more of the chlorohexene being produced in this case.

β -Chlorobutyronitrile (1 mol.) and magnesium ethyl bromide (1 mol.) give rise to a mixture containing (1) the two isomeric crotononitriles (cf. A., 1922, i, 817), (2), the *trimeride* of one of these, white needles, m. p. 173—174°, b. p. 215—240°/13 mm., and (3) a small quantity of a mixture of two ketones. When 2 mols. of Grignard reagent are used, the main product is the trimeric crotononitrile.

α -Chlorobutyryl chloride, when added to aqueous ammonia at 0°, is converted into α -chlorobutyramide, which also is formed when methyl α -chlorobutyrate is digested for several hours with concentrated aqueous ammonia. The author notes that the chlorination of a mixture of butyric acid and butyryl chloride gives, besides α -chlorobutyryl chloride, the *anhydride*, b. p. 125—130°/15 mm.

α -Chlorobutyramide, white needles, m. p. 81°, gives α -chlorobutyronitrile with thionyl chloride. This nitrile, with one mole-

cular proportion of magnesium ethyl bromide, is converted into a mixture containing (1) a small quantity of an unsaturated hydrocarbon (?), b. p. 76—85°, (2) the two crotononitriles, and (3) unidentified products of higher b. p. When two molecular proportions of Grignard reagent are used, no hydrocarbon is formed and very little crotononitrile, the main product being an amine, which the author believes to be $\gamma\delta$ -imino- γ -ethylhexane, $\begin{matrix} \text{CEt}_2 \\ \text{CHEt} \end{matrix} > \text{NH}$.

The latter boils at 157—158°, combines with calcium chloride, forms a *hydrochloride* (white needles, m. p. 185—186°), gives a yellow crystalline *chloroplatinate* and reacts with bromine to give a *N*-bromo-derivative. A secondary product of the above reaction, of unknown constitution, boils at 118—123°/15 mm. E. E. T.

Solubility of Prussian Blue. MORITZ KOHN (*Monatsh.*, 1923, 43, 373—376).—Prussian Blue dissolves in solutions of the neutral oxalates of potassium, sodium, and ammonium to give greenish solutions. The interaction of ferric chloride and potassium ferrocyanide, even if an excess of one of these substances is present, does not lead to a precipitate of Prussian blue in presence of these neutral oxalates. The above green solutions, unlike those of Prussian blue in aqueous oxalic acid, are true solutions.

E. E. T.

The Formation of Hydroxamic Acids from Keten. CHARLES DE WITT HURD and PAUL B. COCHRAN (*J. Amer. Chem. Soc.*, 1923, 45, 515—521).—Keten will react readily with a monohydroxamic acid to form, not only a monoacetyl ester, but also a diacetyl ester. In this way, from pyromucylhydroxamic acid the authors obtained, not only the monoacetate, m. p. 94—96°, but also the *diacetate*, m. p. 54—55°. Similar results were obtained with diphenylacetylhydroxamic acid and benzhydroxamic acid.

An improved apparatus is described for preparing keten by the method of Schmidlin and Bergman (A., 1910, i, 816), the undecomposed acetone issuing from the reaction tube being removed from contact with the keten almost as soon as it leaves the tube.

The similarity of the behaviour of keten and of phenylthiocarbimide towards monohydroxamic acids is discussed. W. G.

Mercury Propyl and Mercury isoPropyl. MARCEL GORET (*Bull. Sci. Pharmacol.*, 1922, 29, 297—305; from *Chem. Zentr.*, 1922, iii, 1371).—*Mercury dipropyl* is prepared by the action of sodium amalgam on propyl bromide in the presence of ethyl acetate. It is separated from the products of reaction by distillation in steam and subsequent fractionation; it has d^{20}_4 2.046; b. p. 189°/760 mm., 82—86°/25 mm. From the residue after steam distillation *mercury propyl* is obtained after crystallisation from ethyl alcohol in leaflets, m. p. 135°. *Mercury propyl chloride* is obtained by the action of mercuric chloride on mercury propyl in alcoholic solutions; it forms white scales, m. p. 143°. *Mercury propyl bromide*, from the action of bromine on mercury propyl, forms leaflets, m. p. 135°. *Mercury propyl iodide* is crystalline, m. p. 113°. *Mercury propyl acetate*, from the action of acetic anhydride on mercury dipropyl or of

acetic acid on the corresponding hydroxide, is crystalline, m. p. 57—58°. *Mercury diisopropyl* has b. p. 75—77°/25 mm., d^{20}_4 2.05. *Mercury isopropyl hydroxide* is prepared by the action of moist silver oxide on one of the halides. It gives with the corresponding acids, *mercury isopropyl sulphide*, m. p. 60°; *mercury isopropyl cyanide*, m. p. 85°; *mercury isopropyl acetate*, m. p. 95°; *mercury isopropyl chloride*, needles, m. p. 97°. *Mercury isopropyl bromide* forms needles, m. p. 98°; *mercury isopropyl iodide*, leaflets, m. p. 125°. G. W. R.

Low Temperature Coal Tar and the Products of its Superheating. FRANZ FISCHER (*Ber.*, 1923, 56, [B], 601—603).—In a recent communication, Schütz (this vol., i, 195) has described a low temperature tar which differs greatly from that obtained previously by the author and his co-workers (A., 1917, i, 258; 1920, i, 277), in that it contains very considerable amounts of benzene and phenol. The differences cannot be attributed solely to the differing types of coal employed; it appears that the product examined by Schütz was a superheated low-temperature tar. The temperature employed (500—600°) is considerably higher than that which is actually necessary, and the structure of Schütz's retorts is such that the volatile products are necessarily exposed to the highest temperature of the furnace. Under these conditions, it has been shown previously that hydroaromatic hydrocarbons are dehydrogenated to benzene, and phenols with a long side chain are transformed into phenol and olefinic hydrocarbons. The volume of gas obtained by Schütz from each ton of coal is much greater than that usually observed in low-temperature work, and affords additional evidence of secondary decomposition. H. W.

The Benzene Theory. C. W. A. LELY (*Chem. Weekblad*, 1923, 20, 82—83).—An answer to criticisms by Olivier, by Prins, and by Schoutissen (this vol., i, 195, 196) of the triangular formula suggested by the author (this vol., i, 99). S. I. L.

Is Kekulé's Benzene Theory Tenable? C. W. A. LELY (*Chem. Weekblad*, 1923, 20, 90—96).—The triangular formula and the theory of synchronous rotation put forward for benzene (this vol., i, 99) are developed and extended to pyridine, thiophen, pyrrole, quinoline, pyrazole, glyoxaline, etc. S. I. L.

Solubility of cycloHexane in Liquid Sulphur Dioxide. W. F. SEYER and V. DUNBAR (*Trans. Roy. Soc. Canada*, 1922, 16, III, 307—310).—A determination of the equilibrium diagram of the system liquid sulphur dioxide-cyclohexane indicates the existence of a transition point at -17.0°, corresponding with the maximum solubility of sulphur dioxide in cyclohexane, and of a eutectic point at -72.5°, at which temperature the solubility of cyclohexane in liquid sulphur dioxide is very small. Above 13.6°, the liquids are miscible in all proportions. No evidence of the formation of compounds of the two substances, as suggested by Moore, Morrell, and Egloff (A., 1918, i, 285), was obtained.

J. S. G. T.

Trifluoromethylcyclohexane. FRÉD. SWARTS (*Bull. Acad. roy. Belg.*, 1922, [v], 8, 505—530; *Bull. Soc. chim. Belg.*, 1923, 32, 70—79.—A continuation of previous work (A., 1921, i, 656). The m. p. of trifluoromethylcyclohexane is -103.4° to -103.5° . The group $\cdot\text{CF}_3$ is even more resistant to reagents in this case than in the case of benzotrifluoride. Trifluoromethylcyclohexane is hydrolysed to cyclohexanecarboxylic acid only to the extent of 3%, when heated at 180° with aqueous hydrobromic acid (d 1.783) for eighty hours, in presence of silicon dioxide. Neither sodium hydroxide nor sodium amalgam affects the fluoro-compound in alcoholic solution. Bromine (1 mol.), at 130° under pressure, affords the bromo-derivative, a colourless liquid, b. p. $177-178^{\circ}$, d^{16} 1.561, together with the dibromo-derivative (the main product), b. p. $218-220^{\circ}$ (slight decomp.), or $120-122^{\circ}/30$ mm., d^{17} 1.912, and a little tribromo-derivative, b. p. $260-265^{\circ}$ (slight decomp.). The introduction of a bromine atom into the cyclohexane ring in this case facilitates further substitution. An excess of bromine (under pressure, at 170°) converts the original fluoro-compound into a mixture of 3:4- and 2:5-dibromobenzoic acids and another substance not identified. Dilute permanganate solutions have little effect on the fluoro-compound at water-bath temperatures; no toluene derivatives are formed, the change that does occur resulting in complete oxidation of the molecule.

In an attempt to prepare the hexanol from trifluoromethylbromocyclohexane, the latter was heated under pressure with an aqueous suspension of mercuric oxide, and gave rise, instead, to trifluoromethylcyclohexene, a mobile liquid, b. p. $104.5-105.5^{\circ}$, d^{16} 1.127; dibromide (?), b. p. $219-220^{\circ}$.

Zinc and ethyl alcohol converted trifluoromethyldibromocyclohexane into what is probably the same hexene. The product boils at $104.7-104.9^{\circ}/762$ mm., and has d^{20} 1.1368 and d^{16} 1.1194. It forms a constant boiling mixture with alcohol (b. p. 74.4° ; 57.5% of the hexene).

In the dibromo-derivative, one bromine atom is in position 3 ($\cdot\text{CF}_3$ in 1), and the other in position 2 or 4.

Nitric acid (d 1.15) at 130° converts trifluoromethylcyclohexane into a mononitro-derivative, but a large amount of decomposition occurs (see below). The nitro-derivative is a viscous liquid, b. p. $224-225^{\circ}$ or $124.5^{\circ}/30$ mm., d^{16} 1.3154. The sodium derivative is very soluble in alcohol. Among the products of decomposition referred to were isolated trifluoroacetic, succinic, and trifluoromethyladipic acids (?); other products probably were fluoro-derivatives of C_6 and C_7 carboxylic acids. Similar decomposition products were obtained by heating the nitrocyclohexane with nitric acid.

E. E. T.

The Isomeric Trinitrotoluenes. H. BRUNSWIG (*Z. angew. Chem.*, 1923, 36, 75—76).—A short review of the work to date on the preparation of the six isomeric trinitrotoluenes. The results of an investigation on the stability of these compounds towards heat, either alone or mixed with one-fifth of their weight of sodium

hydroxide, and on their behaviour towards sodium carbonate and lead oxide in boiling alcohol are given in tabular form with a view to supply a method for their identification, and also for their detection in the manufactured product. Their detonation temperatures, when heated alone, are all in the neighbourhood of 300° and are too close to one another to be of service. The remaining tests applied resulted as follows— α -Trinitrotoluene [2:4:6] (a) m. p. 80.5° . (b) Crystallises from methyl alcohol in needles. (c) With sodium carbonate in boiling alcohol, coloured dark reddish-brown without transformation into dinitrocresol; on continued boiling is converted into another dark salt. (d) With lead oxide in boiling alcohol, unaltered. (e) Detonation temperature mixed with sodium hydroxide, 230 – 233° . β -Trinitrotoluene [2:3:4] (a) m. p. 112° . (b) Needles. (c) Forms sodium dinitrotyloxide readily. (d) Gives the readily detonated lead dinitrotyloxide. (e) 208 – 215° . γ -Trinitrotoluene [3:4:6] (a) m. p. 104° . (b) Granulates. (c) and (d) As with β -compound. (e) 193 – 198° . δ -Trinitrotoluene [3:4:5] (a) m. p. 137.5 (134°). (b), (c), and (d) As with γ -compound. (e) 252° . ϵ -Trinitrotoluene [2:3:6] (a) m. p. 111° . (b) Needles. (c) Some sodium dinitrotyloxide very slowly formed. (d) Almost unattacked. (e) 249 – 250° . ζ -Trinitrotoluene [2:3:5] (a) 97° . (b) Granulates. (c) and (d) As with β -compound. (e) 268 – 271° .
T. S. W.

Solubility of 2:4:6-Trinitrotoluene in Organic Solvents.

C. A. TAYLOR and WM. H. RINKENBACH (*J. Amer. Chem. Soc.*, 1923, **45**, 44–59).—The solubility of 2:4:6-trinitrotoluene has been determined at a series of temperatures in water, aniline, pyridine, toluene, acetone, benzene, carbon tetrachloride, 95% ethyl alcohol, chloroform, carbon disulphide, and diethyl ether. An equimolecular compound is formed in pyridine solution which exists at temperatures below 40° and melts at 40 – 42° . The following data are recorded, in grams per 100 g. of solvent: water, 0.3° , 0.0110; 5.9° , 0.0113; 20.0° , 0.0120; 33.1° , 0.0203; 44.2° , 0.0340; 45° , 0.0370; 53.0° , 0.0534; 57.15° , 0.0614; 73.25° , 0.0963; 94.4° , 0.1375, and 99.5° , 0.1467; ether, 0.3° , 1.75; 5.9° , 2.13; 20.3° , 3.33; 26.0° , 3.92, and 33.0° , 5.15; 95% alcohol, 0.3° , 0.70; 32.0° , 1.99; 40.1° , 2.98; 45.0° , 3.70; 50.0° , 4.61; 55.0° , 6.08; 59.8° , 8.14; 65.0° , 11.40, and 74.0° , 18.58; carbon disulphide, 0.3° , 0.158; 5.6° , 0.20; 11.1° , 0.27; 24.5° , 0.62; 30.1° , 0.84; 35.0° , 1.12; 40.0° , 1.53; 45.0° , 2.02, and 46.3° , 2.20; carbon tetrachloride, 0.3° , 0.22; 5.6° , 0.28; 11.1° , 0.37; 24.5° , 0.76; 35.0° , 1.32; 45.0° , 2.37; 57.0° , 5.33; 61.7° , 8.14; 67.0° , 13.68; 72.5° , 20.72, and 78.2° , 29.76; chloroform, 0.3° , 6.33; 32.0° , 37.7; 40.1° , 66.6; 45.0° , 101; 50.0° , 150; 55° , 218; 59.8° , 296, and 65.0° , 442. The other solvents mentioned above dissolve very large quantities of trinitrotoluene, and in these cases the solubility was determined by the cooling-curve method. The whole of the values are recalculated to grams per 100 g. of solvent and tabulated, giving the solubility for temperatures in 5° intervals over the whole range examined.
J. F. S.

Preparation of Salts of 1 : 3-Dinitro-4 : 5-dinitrosobenzene.

HANS RATHSBURG (Brit. Pat. 190844).—Sparingly soluble salts of 1 : 3-dinitro-4 : 5-dinitrosobenzene are obtained by heating picryl chloride (25 kg.) in aqueous suspension with a solution of sodium azide (7 kg.) in 300 litres of water for one hour at 80—90°, and for three hours at 90—100°, whereby the picryl azide first formed is transformed with loss of nitrogen into 1 : 3-dinitro-4 : 5-dinitrosobenzene, which is separated from the mother-liquors, converted into its sodium salt by treatment with sodium hydroxide, and this in the moist state is allowed to react with the acetate or chloride of the metal of which the dinitrodinitrosobenzene salt is required.

G. F. M.

Sulphinic Acids. JULIUS VON BRAUN and WILHELM KAISER (*Ber.*, 1923, 56, [B], 549—553).—The action of aromatic sulphonyl chlorides on dithiocarbamates takes place unexpectedly in accordance with the scheme $2\text{NR}_2 \cdot \text{CS} \cdot \text{SH} \cdot \text{NHR}_2 + \text{Cl} \cdot \text{SO}_2 \cdot \text{R}^1 = \text{NR}_2 \cdot \text{CS} \cdot \text{S} \cdot \text{S} \cdot \text{CS} \cdot \text{NR}_2 + \text{NHR}_2 \cdot \text{HCl} + \text{SO}_2 \cdot \text{H} \cdot \text{R}^1 \cdot \text{NHR}_2$, and thus affords a ready method of preparing sulphinic acids. The conversion of the latter into amides has not been effected previously (cf. Knoevenagel and Polak, A., 1908, i, 971; Hilditch and Smiles, A., 1909, i, 18). It is now shown that the transformation occurs normally in the presence of an indifferent solvent, but that the new amides are much more readily decomposed than the analogous carboxylamides; they are unable to yield derivatives of the amide-chloride and imide-chloride types.

Dimethylamine, carbon disulphide, and benzenesulphonyl chloride give tetramethylthiuram disulphide, m. p. 150—154°, (?) benzenesulphondimethylamide, and benzenesulphinic acid, m. p. 83°, which is conveniently isolated through its ferric salt (cf. Thomas, T., 1909, 95, 342). Piperidine, carbon disulphide, and benzenesulphonyl chloride give *dipiperidylthiuram disulphide*, m. p. 128°, and benzenesulphinic acid. *p*-Toluenesulphinic acid, m. p. 84°, is prepared from piperidine, carbon disulphide, and *p*-toluenesulphonyl chloride, whilst tetrahydronaphthalene- β -sulphonyl chloride gives *dipiperidylthiuram disulphide*, *tetrahydronaphthalene- β -sulphonylpiperidide*, $\text{C}_{10}\text{H}_{11} \cdot \text{SO}_2 \cdot \text{C}_5\text{NH}_{10}$, m. p. 98—100°, and *tetrahydronaphthalene- β -sulphinic acid*, colourless needles, m. p. 87—88°.

Benzenesulphinanilide, $\text{SOPh} \cdot \text{NHPH}$, m. p. 112—114°, is prepared by the action of benzenesulphonyl chloride on two molecular proportions of aniline dissolved in ether at 0°. It is extensively decomposed by boiling acids without appearing to undergo a smooth fission into benzenesulphinic acid and aniline, which can, however, be brought about by cold, aqueous-alcoholic alkali hydroxide solutions. *Benzenesulphinpiperidide* has m. p. 83° after softening at 80°; it is energetically attacked by phosphorus pentachloride even in the presence of chloroform, and gives chlorinated compounds, the reaction appearing to occur in a direction different from that of benzoylpiperidine. *Benzenesulphindimethylamide*, $\text{SOPh} \cdot \text{NMe}_2$, is a yellow liquid, b. p. 90°/2—3 mm. *Benzenesulphinamide* has m. p. 121°. *Toluene-p-sulphonyl chloride*, b. p.

115—120°/4 mm., is converted in a similar manner into the corresponding *anilide*, m. p. 138°, and *amide*, colourless needles, m. p. 120° after softening at 117°. H. W.

Alkylamides of Aromatic Sulphonic Acids. W. BADER and D. A. NIGHTENGAL (U.S. Pat. 1433925).—When xylene-sulphonyl chloride and methylamine hydrochloride are heated with sodium carbonate at 80—100° in presence of moisture not exceeding 5%, xylenesulphonmethylamide is produced and may be recovered by extraction with benzene. The instance quoted is an example of a reaction of more general application. Benzene or other diluents may be present. CHEMICAL ABSTRACTS.

Preparation of Aromatic Sulphones. G. FOUQUE and J. LACROIX (*Bull. Soc. chim.*, 1923, [iv], 33, 180—183).—By the prolonged action of sulphuric acid on aromatic hydrocarbons or their derivatives under such conditions that the water formed during the reaction and condensing in the reflux condenser is not allowed to run back into the reaction mixture, aromatic sulphones were obtained in good yield. Their formation may be due to the action of a further quantity of hydrocarbon on the sulphonic acid first produced, as, for example, with benzene, $\text{PhSO}_3\text{H} + \text{C}_6\text{H}_6 = \text{SO}_2\text{Ph}_2 + \text{H}_2\text{O}$, or more probably by reason of the decomposition of the sulphonic acid under the influence of heat and in the absence of water, thus: $2\text{PhSO}_3\text{H} = \text{SO}_2\text{Ph}_2 + \text{H}_2\text{SO}_4$. The conditions required for the reaction were obtained by interposing between the reflux condenser and the reaction vessel a flask with a side tubulure in the bulb, a tube bent at right angles passing through this tubulure and connecting with the neck of the reaction flask. By this means the water and the hydrocarbon condensing in the reflux condenser flow back into the tubulated flask and separate into two layers, and consequently only the lighter hydrocarbon flows back through the tubulure into the reaction flask. When the substance to be sulphonated is heavier than water, the connecting tube is bent downwards to the bottom of the tubulated flask, so that the lower layer passes back into the reaction flask instead of the upper aqueous layer; a small orifice on the upper side of the tube just before the bend serves for the passage of the vapours from the reaction flask. By means of this apparatus diphenylsulphone, m. p. 128°, *di-p-chlorodiphenylsulphone*, m. p. 146°, *di-p-bromodiphenylsulphone*, m. p. 171°, and *di-p-hydroxydiphenylsulphone*, m. p. 240°, were prepared. G. F. M.

Doubly Refractive Naphthalene. W. KIRBY (*J. Soc. Chem. Ind.*, 1923, 42, 58T).—When naphthalene, m. p. 80·7°, d_{40}^{20} 1·185, is melted in a suitable vessel and allowed to cool, the substance in contact with the sides of the vessel solidifies to form a clear, transparent mass which is doubly refractive; the resolving power is more than 30% greater than that of Iceland spar. W. P. S.

Some Fluoro-derivatives of Diphenyl. THÉO VAN HOVE (*Bull. Acad. roy. Belg.*, 1922, [v], 8, 505—530; *Bull. Soc. chim. Belg.*, 1923, 32, 52—70).—Diphenyl (500 g.) is nitrated in the cold

with an acetic acid solution containing 2 mols. of nitric acid (*d* 1.5). After a time, most of the 4-nitrodiphenyl separates, and from the mother-liquor, by precipitation with water, etc., and distillation under diminished pressure, 2-nitrodiphenyl (195 g.) is obtained, b. p. 200—205°/30 mm., together with more 4-nitrodiphenyl (350 g. in all).

In the reduction of 4-nitrodiphenyl by means of tin and hydrochloric acid, the sparingly soluble chlorostannate is best separated by filtration. 4-Aminodiphenyl boils at 210—212°/25 mm. 2-Aminodiphenyl forms a soluble chlorostannate, and boils at 189—191°/30 mm.

4-Fluorodiphenyl, obtained by diazotising 4-aminodiphenyl in hydrofluoric acid solution, and subsequently heating at 60°, forms colourless plates, m. p. 74.2°, b. p. 253°, and is volatile in steam. 2-Fluorodiphenyl, obtained similarly, colourless prisms, m. p. 73.5°, b. p. 248°, is also volatile in steam.

The nitration of 4-fluorodiphenyl in acetic acid solution, using nitric acid (*d* 1.5), gave three products: (a) 4-fluoro-4'-nitrodiphenyl, needles, m. p. 123°, giving *p*-nitrobenzoic acid on oxidation; (b) an approximately equal weight of 4-fluoro-2'-nitrodiphenyl, needles, m. p. 59—60°, giving, on oxidation, *p*-fluorobenzoic acid, and (c) a very small quantity of 4-fluoro-2-nitrodiphenyl, prisms, m. p. 53—54°, giving, on oxidation, 4-fluoro-2-nitrobenzoic acid, m. p. 130°. In the first experiment, but never subsequently, the author obtained pale yellow prisms, m. p. 43—43.5°, which, on keeping, became opaque, and then melted at 58°. This is apparently a case of dimorphism.

4-Fluoro-4'-aminodiphenyl, obtained by the reduction of the corresponding nitro-compound, forms colourless leaflets, m. p. 120°; hydrochloride, sparingly soluble leaflets; sulphate and oxalate, very sparingly soluble leaflets; acetyl derivative, m. p. 205—205.5°.

4-Fluoro-2'-aminodiphenyl, colourless crystals, m. p. 42—42.5°, b. p. 186—187°/40 mm., forms a hydrochloride, m. p. about 210°, and a sulphate, which are much more soluble than the corresponding salts of the 4'-derivative. The amine, on oxidation, gives *p*-fluorobenzoic acid and yields an acetyl derivative, m. p. 120°.

4-Fluoro-2-nitrodiphenyl, on reduction, gives an amine, the acetyl derivative of which melts at 98°.

2-Fluorodiphenyl gives rise to three isomeric nitro-derivatives: (a) a small quantity of colourless needles, m. p. 81°, probably 2-fluoro-4-nitrodiphenyl, since the acetyl derivative (colourless prisms, m. p. 155°) of the amine obtained by reduction gives, on oxidation, benzoic acid, (b) 2-fluoro-4'-nitrodiphenyl, yellow needles, m. p. 74.5°, giving, on oxidation, *p*-nitrobenzoic acid, and (c) 2-fluoro-2'-nitrodiphenyl, prisms, m. p. 71.5°, giving *o*-nitrobenzoic acid on oxidation.

2-Fluoro-2'-aminodiphenyl, colourless crystals, m. p. 91°, gives a very soluble hydrochloride, m. p. about 205°, a soluble sulphate, and an acetyl derivative, colourless needles, m. p. 102°. 2-Fluoro-4'-aminodiphenyl, m. p. 36°, b. p. 199—201°/25 mm., gives a sparingly soluble hydrochloride, m. p. above 250°, a sparingly soluble sulphate, and an acetyl derivative, m. p. 147—148°.

In the nitration of diphenyl, small quantities of a yellow, crystalline solid, m. p. 202° , probably 3 : 5 : 4'-trinitro-4-hydroxydiphenyl, are formed. 4-Fluorodiphenyl, similarly, gives rise to a small quantity of a solid, $C_{12}H_7O_5N_2F$ (?), probably a fluorodinitro-hydroxydiphenyl.
E. E. T.

The Products of the Bromination of *as*-Diphenylethylene.
P. LIPP (*Ber.*, 1923, 56, [B], 567—571).—The author's experiences in the bromination of camphene has led him to examine the behaviour of other asymmetrically substituted ethylenes, and for this purpose *as*-diphenylethylene, $CPh_2:CH_2$, has been selected. Under certain conditions, the normal dibromide can be isolated, but it passes somewhat readily into diphenylvinyl bromide. Under drastic treatment, the latter substance suffers rearrangement of the diphenylvinyl residue, whereas under milder conditions the radicle remains intact.

[In part with W. LÜDICKE.]— $\alpha\beta$ -Dibromo- $\alpha\alpha$ -diphenylethane, $CPh_2Br\cdot CH_2Br$, is obtained by the gradual addition of a solution of dry bromine in carbon disulphide to *as*-diphenylethylene dissolved in the same medium at a temperature not exceeding 0° and subsequent removal of the solvent in a vacuum at the atmospheric temperature; it crystallises in coarse plates or prisms, decomp. 63 — 64° (corr.). When pure, it may be preserved unchanged for weeks, but rapidly passes when heated into diphenylvinyl bromide, m. p. 41 — 42° . It is converted by methyl-alcoholic potassium hydroxide solution into β -bromo- α -methoxy- $\alpha\alpha$ -diphenylethane, $OMe\cdot CPh_2\cdot CH_2Br$, short prisms or plates, m. p. 73 — 74.5° (corr.), which is unaffected by boiling dimethylaniline or aqueous potassium hydroxide solution; molten potassium hydroxide converts it into tolane, $CPh: CPh$. β -Bromo- α -ethoxy- $\alpha\alpha$ -diphenylethane crystallises in long prisms, m. p. 98 — 99° (corr.).

Diphenylvinyl bromide is transformed by molten potassium hydroxide into tolane, b. p. 158 — $160^{\circ}/10.5$ mm., m. p. 60° (corr.) [dibromide, m. p. 211° (corr.)]. It reacts with activated magnesium in the presence of ether, and the product after treatment with carbon dioxide yields $\beta\beta$ -diphenylacrylic acid, $CPh_2:CH\cdot CO_2H$, m. p. 162° (the sodium salt is relatively sparingly soluble in water), and $\alpha\alpha\delta\delta$ -tetraphenyl- Δ^a -butadiene, colourless, thin prisms, m. p. 205 — 206° (corr.).
H. W.

Crystalline Form of 4-Chloro-2-bromo-3-nitroacetanilide.
MARIA DE ANGELIS (*Atti R. Accad. Lincei*, 1922, [v], 31, ii, 450—453, 524—529; cf. A., 1920, i, 608, 834).—This compound is dimorphous. The metastable α -modification, d 1.857, forms crystals belonging to the prismatic class of the monoclinic system, $a : b : c = 1.2985 : 1 : 0.5728$, $\beta = 86^{\circ} 43'$. The stable β -modification, d 1.891, was not obtained in crystals capable of being measured accurately, but appears to be isomorphous with 2 : 4-dibromo-3-nitroacetanilide (A., 1920, i, 834).

A mixture of 4-chloro-2-bromo-3-nitroacetanilide (1 mol.) with the dibromo-analogue (1 mol.) yields triclinic crystals isomorphous with those of the dibromo-compound (*loc. cit.*, 834). A similar

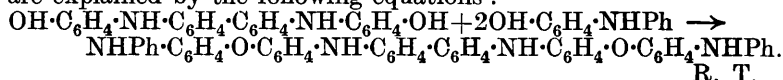
mixture of 4-chloro-2-bromo-3-nitroacetanilide with the dichloro-compound yields tabular, monoclinic crystals isomorphous with the β -form of the dichloro-derivative (*loc. cit.*, 608), or, less readily, metastable, prismatic crystals of the monoclinic system, isomorphous with those of the metastable modification of 4-chloro-2-bromo-3-nitroacetanilide. T. H. P.

Solubility of Trinitrophenylmethylnitroamine (Tetryl) in Organic Solvents. C. A. TAYLOR and WM. H. RINKENBACH (*J. Amer. Chem. Soc.*, 1923, 45, 104—107).—The solubility of tetryl has been determined in water, ether, 95% alcohol, carbon disulphide, chloroform, and carbon tetrachloride at a large number of temperatures. The following solubilities in grams of tetryl per hundred grams of solvent are recorded: Water, 0.5°, 0.0051; 9.6°, 0.0069; 14.8°, 0.0071; 20.5°, 0.0074; 30°, 0.0084; 35°, 0.0094; 40°, 0.0107; 45°, 0.0135; 50.0°, 0.0200; 60.05°, 0.0350; 65.05°, 0.0443; 69.5°, 0.0531; 84.2°, 0.0952; 96.7°, 0.1619, and 98.55°, 0.1755; ether, 0.4°, 0.1918; 9.6°, 0.3174; 20.5°, 0.4219; 29.05°, 0.4680, and 30.0°, 0.4713; 95% alcohol, 0.5°, 0.324; 25.0°, 0.648; 33.0°, 0.843; 39.0°, 1.08; 45.1°, 1.39; 51.0°, 1.81; 61.0°, 2.76; 70.05°, 4.23, and 77.1°, 5.80; carbon disulphide, 0.4°, 0.0094; 15.0°, 0.0177; 28.0°, 0.0277; 37°, 0.0437; 40°, 0.0557, and 46.1°, 0.1048; chloroform, 0.4°, 0.282; 15°, 0.473; 28.0°, 0.740; 32.2°, 0.856; 40.0°, 1.209; 50.0°, 1.780, and 58.8°, 2.53; carbon tetrachloride, 0.4°, 0.0073; 25.0°, 0.0304; 33.0°, 0.0449; 39.0°, 0.0566; 45.1°, 0.0733; 51.0°, 0.0997; 61.0°, 0.1597; 70.05°, 0.2419, and 73.25°, 0.2773. A table is drawn up giving the interpolated values for every 5° for each solvent over the range investigated. J. F. S.

Chloroacetyl-*p*-anisidine and its Nitro-derivatives. FRÉDÉRIC REVERDIN (*Helv. Chim. Acta*, 1923, 6, 87—93).—Chloroacetyl-*p*-anisidine is much more resistant to hydrolysis by acids than the corresponding acetyl, benzoyl, and toluenesulphonyl compounds. It has also to be nitrated under conditions unlike those which give the best results in the case of other acyl-derivatives of *p*-anisidine. The mono-nitro-derivative was obtained by dissolving the chloroacetyl-*p*-anisidine (12 g.) in glacial acetic acid (120 c.c.) and running in the nitric acid gradually at 10° (15 c.c., *d* 1.52). The principal product, 3-nitrochloroacetyl-*p*-anisidine, yield 80—82% of theory, forms yellow needles, m. p. 104°. A small amount of 2-nitrochloroacetyl-*p*-anisidine, yellow needles, m. p. 153°, was also obtained. Like the parent substance, the nitro-derivatives are unusually resistant to acid hydrolysis, but are rapidly hydrolysed to nitroanisidine by 4% potassium hydroxide solution. 2:3-Dinitrochloroacetyl-*p*-anisidine was obtained by nitrating 3-nitrochloroacetyl-*p*-anisidine with nitric acid, *d* 1.52, at the ordinary temperature, finishing at 45°; it forms white, prismatic needles, m. p. 172°. A small amount of 2:5-dinitrochloroacetyl-*p*-anisidine was formed at the same time, yellow needles, m. p. 126°. 2:3:5-Trinitrochloroacetyl-*p*-anisidine could only be obtained by nitrating the dinitro-compound with mixed

nitric and concentrated sulphuric acids, and the best yield obtained was only 40% of theory. It forms white needles, m. p. 245—246°. The nitro-compounds do not appear to form additive compounds with bases. With aniline, however, 3-nitrochloroacetyl-*p*-anisidine forms a compound which appears to be 3-nitroanilinoacetyl-*p*-anisidine, $\text{OMe}\cdot\text{C}_6\text{H}_4(\text{NO}_2)\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{NHPh}$, yellow spangles, m. p. 143°. 2:3-Dinitrochloroacetyl-*p*-anisidine forms with aniline a compound, orange needles, m. p. 153°, containing no chlorine; the trinitro-derivative gives a similar compound, m. p. 172—173°. E. H. R.

The Products of the Oxidation of Diphenylamine with Hydrogen Peroxide. P. P. ROUBCOV (*J. Russ. Phys. Chem. Soc.*, 1918, 50, 137—139).—Uschakov (A., 1906, i, 159; 1907, i, 361) isolated two substances, $\text{C}_{24}\text{H}_{20}\text{O}_2\text{N}_2$, and $\text{C}_{60}\text{H}_{49}\text{O}_2\text{N}_5$, from the products of the oxidation of diphenylamine with hydrogen peroxide. The first of these he showed to have the structure $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, and to be formed by the condensation of two molecules of hydroxydiphenylamine. The structure of the second was not determined. It is now suggested that its empirical formula should be $\text{C}_{48}\text{H}_{38}\text{O}_2\text{N}_4$, and that the presence of traces of diphenylamine (about 0.15%) could have caused the discrepancy in analysis. Its formation and structure are explained by the following equations:



Action of the Oxides and the Oxy-acids of Nitrogen on Diphenylurethane. HUGH RYAN and ANNE DONNELLAN (*Proc. Roy. Dublin Soc.*, 1923, 17, 113—118).—It has already been shown (A., 1919, i, 481, 482) that diphenylnitrosoamine can be nitrated more readily than diphenylamine; this is ascribed to the protective influence of the nitroso-group. The nitration of diphenylurethane has now been systematically investigated (cf. Hager, A., 1886, 59).

Nitric acid at the ordinary temperature and at low concentrations in acetic acid solution has apparently no action; under similar conditions in carbon tetrachloride solution, 4:4'-dinitrodiphenylurethane, 2:4'-dinitrodiphenylurethane (cf. Hager, *loc. cit.*), and 4-nitrodiphenylurethane, colourless prisms, m. p. 68°, are formed. Cold concentrated nitric acid (*d* 1.42) converts the urethane into its 4-nitro-derivative, whilst cold fuming nitric acid gives the 4:4'- and the 2:4'-dinitro-derivatives. Diphenylurethane, or its 4-nitro-derivative, is converted by a mixture of concentrated nitric and sulphuric acids into 2:4:2':4'-tetranitrodiphenylurethane, yellowish-white, flat prisms, m. p. 184—185°, which reacts further with the hot mixed nitrating acids to give 2:4:6:2':4':6'-hexanitrodiphenylamine. Diphenylurethane reacts in carbon tetrachloride solution with nitrogen peroxide, giving the 4:4'- and the 2:4'-dinitro-derivatives.

Notwithstanding the similarity in structure between diphenyl-

urethane and diphenylnitrosoamine, the former is less readily nitrated than the latter, the nitration at low temperatures and concentrations stopping at the dinitro-stage.

Attempts to synthesise the nitrodiphenylurethanes from ethyl chloroformate and the relevant nitrodiphenylamines were unsuccessful; their constitutions have, however, been proved by hydrolysis to the corresponding nitro-derivatives of diphenylamine.

W. S. N.

Action of the Oxides and the Oxy-acids of Nitrogen on Ethyl-*o*-tolylurethane. HUGH RYAN and NICHOLAS CULLINANE (*Proc. Roy. Dublin Soc.*, 1923, **17**, 119—124; cf. preceding abstract).—*Ethyl-*o*-tolylurethane*, a colourless oil, b. p. 225°, is less readily nitrated than diphenylamine; moreover, the ethyl group is slowly eliminated, and the nitro-products are in all cases derived from *o*-tolylurethane.

Nitrogen peroxide (vapour) converts the urethane into oxalic acid and 5-nitro-*o*-tolylurethane, m. p. 137° (Vittenet, A., 1899, i, 756, gives 127°), identical with the product formed by the action of ethyl chloroformate on 5-nitro-*o*-toluidine. In carbon tetrachloride solution, fuming nitric acid converts ethyl-*o*-tolylurethane into 3:5-dinitro-*o*-tolylurethane, slender, white needles, m. p. 159—160°, which could not be further nitrated, and is also produced by the nitration of 5-nitro- or 3-nitro-*o*-tolylurethane; the synthesis of the latter, almost colourless prisms, m. p. 131°, and of 4-nitro-*o*-tolylurethane, by the action of ethyl chloroformate on 3-nitro-*o*-toluidine or 4-nitro-*o*-toluidine, respectively, are described.

4-Nitro-*o*-tolylurethane, m. p. 137° (Vittenet, *loc. cit.*, gives 129°), is converted by heating with fuming nitric acid into slender, white needles, m. p. 193—194° (decomp.), probably 4:5-dinitro-*o*-tolylurethane.

W. S. N.

Action of the Oxides and the Oxy-acids of Nitrogen on Phenylethylurethane. HUGH RYAN and ANNA CONNOLLY (*Proc. Roy. Dublin Soc.*, 1923, **17**, 125—130; cf. preceding abstracts).—Like other urethanes, phenylethylurethane nitrates with difficulty. Unlike *o*-tolylethylurethane, it yields nitro-derivatives of the tertiary urethane when nitrated at a low temperature, although at moderately high temperatures derivatives of phenylurethane are produced.

Nitrogen peroxide in carbon tetrachloride solution converts the urethane into 4-nitrophenylethylurethane, large, colourless rhombohedra, m. p. 55—56°, and into a dinitro-compound, colourless, rhombic prisms, m. p. 88—89°, probably 2:4-dinitrophenylethylurethane; the former is converted by boiling with alcoholic potash into *p*-nitroethylaniline, but the conversion of the dinitro-compound into 2:4-dinitroethylaniline has not yet been accomplished.

The same two nitro-derivatives are obtained by the action of cold fuming nitric acid on phenylethylurethane, but when the temperature is allowed to rise during the reaction, the chief products are 4-nitrophenylurethane and 2:4-dinitrophenylurethane. A mixture of concentrated nitric and sulphuric acids converts

phenylethylurethane into 2 : 4-dinitro- and 2 : 4 : 6-trinitro-phenylurethanes.

At low concentrations in acetic acid solution and at the ordinary temperature, the urethane is converted very slowly and incompletely by nitric acid into its mononitro- and dinitro-derivatives; but in carbon tetrachloride solution the substances react more readily, with formation of 4-nitrophenylethylurethane.

W. S. N.

Action of the Oxides and the Oxy-acids of Nitrogen on Phenylbenzylurethane. HUGH RYAN and JAMES L. O'DONOVAN (*Proc. Roy. Dublin Soc.*, 1923, 17, 131—137; cf. preceding abstracts).—Like other tertiary aromatic urethanes, *phenylbenzylurethane*, a colourless oil, is difficult to nitrate. The benzyl radicle can, however, be nitrated, as well as the phenyl radicle, without decomposition of the urethane.

Nitrogen peroxide converts the urethane into *p*-nitrophenylbenzylurethane, almost colourless plates, m. p. 70—71°, and a trinitro-(2 : 4 : 4'- or 2 : 2' : 4'-)-phenylbenzylurethane, long, rhombic crystals, m. p. 110—111°; a little oxalic acid is also formed. The use of cold dilute nitric acid leads to the above mononitro-compound and oxalic acid; at higher concentrations of the acid, the trinitro-derivative is produced. Warm concentrated nitric acid converts the urethane into a tetranitro-derivative, colourless plates, m. p. 126—127°, probably 2 : 4 : 2' : 4'-tetranitrophenylbenzylurethane, and a compound, yellowish-white, silky needles, m. p. 274° (decomp.), probably 2 : 4 : 6 : 2' : 4'-pentanitrophenylbenzylamine. Secondary reactions also occur leading to *p*-nitrobenzoic acid, 2 : 4-dinitrophenylurethane, and a compound, yellow, felted needles, m. p. 264° (decomp.), either pentanitrophenylbenzylurethane or trinitrophenylbenzylamine.

The mononitro-derivative (above) is converted on being boiled with alcoholic potash into *p*-nitrophenylbenzylamine; its constitution is thereby established. It is, moreover, different from *phenyl-p*-nitrobenzylurethane, rhombic plates, m. p. 68—69°, which is formed by the condensation of ethyl chloroformate with phenyl-*p*-nitrobenzylamine.

W. S. N.

Preparation of Arylthiocarbimides. F. B. DAINS, R. Q. BREWSTER, and C. P. OLANDER (*Univ. Kansas Sci. Bull.*, 1922, 13, 1—14; cf. Hofmann, *Ber.*, 1882, 15, 986; Werner, T., 1891, 59, 400; Dains, A., 1900, i, 390; Anschütz, A., 1910, i, 158; Braun, A., 1904, i, 90; Losanitsch, A., 1892, 55; Heller and Bauer, A., 1902, i, 444).—The authors find that Losanitsch's method (*loc. cit.*) is generally applicable to the preparation of aryl thiocarbimides. As a modification of Heller and Bauer's method (*loc. cit.*), 54 g. of aniline are added with cooling and constant stirring during fifteen minutes to 54 g. of carbon disulphide and 80 g. of 28% ammonia solution. Ammonium phenyldithiocarbamate separates, and after being kept in ice for an hour is collected, washed with ethyl alcohol, and dried on a plate. On keeping, hydrogen sulphide, ammonia, carbon disulphide, aniline,

and thiocarbanilide are formed, the decomposition being hastened when the salt is boiled with water. Ammonium *p*-chloro- and *p*-bromo-phenyldithiocarbamate give 55–60% yields of the substituted thiocarbanilide. With hydrochloric acid, ammonium phenyldithiocarbamate reacts quantitatively according to the equation: $\text{NHPh}\cdot\text{CS}\cdot\text{SNH}_4 + 2\text{HCl} = \text{NH}_2\text{Ph}\cdot\text{HCl} + \text{CS}_2 + \text{NH}_4\text{Cl}$. For the production of arylthiocarbimides from ammonium aryl-dithiocarbamates, a salt must be used which will give a stable sulphide and an ammonium salt. Ferrous sulphate, zinc sulphate, copper sulphate, and lead nitrate with ammonium phenyldithiocarbamate, after keeping and distillation with steam, give, respectively, a yield of 3 c.c., 23%, 71.7%, and 77.2% of phenylthiocarbimide. Phenylthiocarbimide is prepared as follows. Ammonium phenyldithiocarbamate is obtained (see above), the mixture being stirred for thirty minutes after addition of the aniline, and then kept for thirty minutes without stirring. The precipitate is dissolved in 80 c.c. of water, 200 g. of lead nitrate in 400 c.c. of water are added with stirring, and the mixture is distilled with steam from a 5-litre flask; the receiver should contain dilute sulphuric acid to prevent formation of thiocarbanilide. Replacement of the ammonium by the sodium salt results in a yield of only 30.2% of phenylthiocarbimide. The barium salt and zinc chloride gave a 37.4% yield, and in the case of the calcium salt very little phenylthiocarbimide is formed, the main product being thiocarbanilide. The following thiocarbimides were prepared: *o*-tolyl- (yield 73.27%), *m*-tolyl-, *p*-tolyl-, *m*-4-xylyl-, *m*. *p*. 31°; ψ -cumyl-, α - and β -naphthyl-, *o*- and *p*-anisyl-, and *p*-phenetidyl-; *m*- and *p*-bromophenyl-, *p*-chlorophenyl-, and *p*-iodophenyl-derivatives were also formed, but ammonium *p*-nitrophenyldithiocarbamate could not be prepared. The success of the method is dependent on the completeness of the formation of the ammonium arylthiocarbamate, on the ease and completeness of separation from the sulphide precipitate, and on the avoidance of side reactions.

CHEMICAL ABSTRACTS.

Pinacolin Transformations. V. The Transformation of Compounds containing Six- and Seven-membered Carbon Rings. HANS MEERWEIN and JOSEPH SCHÄFER (*J. pr. Chem.*, 1922, [iii], 104, 289–310; cf. A., 1910, i, 856; 1913, i, 485; 1914, i, 850; 1919, i, 162).—The authors have shown that both 1:1-dimethylcycloheptan-2-ol and 1-methyl-1- α -hydroxyethylcyclohexane give on dehydration a mixture of 1:2-dimethyl- Δ^1 -cycloheptene and Δ^1 -isopropylcyclohexene, in a proportion which cannot exactly be estimated.

The behaviour of 1:1-dimethylcycloheptan-2-ol is therefore comparable with that of 1:1-dimethylcyclohexan-2-ol, which similarly gives 1:2-dimethyl- Δ^1 -cyclohexene (75%) and Δ^1 -isopropylcyclopentane; hence, from this comparison, no difference in the stability of six-membered and seven-membered rings can be detected. Nevertheless, whilst the dehydration of 1-methyl-1- α -hydroxyethylcyclopentane gives exclusively 1:2-dimethyl-

Δ^1 -cyclohexene, with formation of a larger ring, the analogous production from 1-methyl-1- α -hydroxyethylcyclohexane of 1:1-dimethyl- Δ^1 -cycloheptene is accompanied by the formation of Δ^1 -isopropylcyclohexene, by the wandering of a methyl group; moreover, whilst α -cyclohexyl- β -methylpropan- $\alpha\beta$ -diol on dehydration gives 1:1-dimethylcyclohexan-2-one only, α -cyclohexyl- β -methylpropan- $\alpha\beta$ -diol gives, besides 1:1-dimethylcycloheptan-2-one, some 1-acetyl-1-methylcyclohexane. Hence in both cases there is an undoubted resistance to seven-ring formation.

Nevertheless, the ready conversion of six- into seven-membered rings calls for comment, since it is improbable according to Baeyer's strain theory. The authors consider that polymethylene rings assume, as far as possible, strain-free configurations (cf. A., 1922, i, 441; this vol., i, 224; also Baker and Ingold, T., 1923, 123, 122); hence six-membered and larger rings lie in more than one plane. This view appears at first sight to conflict with the difficulty experienced in closing seven-membered and larger rings. The formation of a ring from an open chain must, however, proceed from a configuration of the latter corresponding with the strain-free configuration of the ring (cf. A., 1919, ii, 229). The more complicated the latter, the less frequently will this favourable configuration of the chain occur; hence the small tendency to production of large rings from open-chain substances is explicable without reference to strains (cf. Wojnicz-Sianozencki, A., 1922, i, 330). On the other hand, it is remarked, the strain-free configurations of cyclohexane and cycloheptane being very similar, interconversion of their derivatives requires but little intramolecular rearrangement, and the ease of the change is therefore not surprising.

When the product of the action of sulphuric acid on α -cyclohexyl- β -methylpropane- $\alpha\beta$ -diol (A., 1913, i, 485; cf. Tarboureich, A., 1913, i, 181) is oxidised by means of excess of sodium hypobromite, the 1-methyl-1-acetylcyclohexane is converted into 1-methylcyclohexane-1-carboxylic acid, which can then be separated from the 1:1-dimethylcycloheptan-2-one, b. p. 190° , d_4^{20} 0.9205, n_D^{20} 1.45694, semicarbazone, long, colourless needles, m. p. 169 — 170° (Tarboureich, 176°), oxime, tabular crystals, m. p. 83 — 85° . Reduction of this ketone by means of sodium in moist ethereal solution gives 1:1-dimethylcycloheptan-2-ol, b. p. 86.8 — $87.2^\circ/13$ mm., d_4^{20} 0.9345, n_D^{20} 1.47478, which gives a phenylurethane, long needles, m. p. 100 — 101° , and is converted in 80% yield, by heating at 180° with zinc chloride, into a mixture of hydrocarbons, b. p. 155.1 — 156.3° , d_4^{20} 0.8274, n_D^{20} 1.46073, from which the nitrosochloride of Δ^1 -isopropylcyclohexene (cf. Wallach, A., 1908, i, 402) and a second nitrosochloride, m. p. about 118° , blue crystals which become colourless (probably that of 1:2-dimethyl- Δ^1 -cycloheptene), have been isolated. Oxidation of the hydrocarbon mixture in glacial acetic acid solution by means of ozone leads to known products, (a) $\beta\zeta$ -diketononane (Blaise and Köhler, A., 1909, i, 204) derived from 1:2-dimethyl- Δ^1 -cycloheptene, which is therefore present in the mixture; (b) the acid $\text{CO}_2\text{H}\cdot[\text{CH}_2]_4\cdot\text{CO}\cdot\text{CHMe}_2$ (Wallach, loc. cit.) derived from Δ^1 -isopropylcyclohexene. By the action of mag-

nesium methyl iodide on the cold *acid chloride*, b. p. $86.5^{\circ}/23$ mm., of 1-methylcyclohexane-1-carboxylic acid (from the hypobromite oxidation, see above), 1-acetyl-1-methylcyclohexane can be prepared in relatively large quantities as a mobile oil, b. p. $186.5-187^{\circ}$, d_4^{20} 0.9178, n_D^{20} 1.45484, possessing a strong camphor-like odour, and giving a semicarbazone, thick needles, m. p. 186° (Tarboureich, 158°), and an oxime, small, lustrous needles, m. p. $38-39^{\circ}$ (Tarboureich, 45°). Reduction of the ketone by means of sodium in moist ethereal solution leads to 1-methyl-1- α -hydroxyethylcyclohexane, b. p. $87.5^{\circ}/13$ mm., d_4^{20} 0.9312, n_D^{20} 1.47203, a thick, colourless oil, possessing a musty odour characteristic of pinacolyl alcohols; the *phenylurethane* has not been obtained crystalline. The elimination of water, by heating with zinc chloride, gives an 81% yield of a mixture of *hydrocarbons*, b. p. $154-156.5^{\circ}$, d_4^{20} 0.8270, n_D^{20} 1.46083, which on oxidation by means of ozone leads to the same products as before.

The optical properties of the extracyclic pinacolins and pinacolyl alcohols described in this and preceding communications are tabulated, it being shown that all these compounds exhibit a negative exaltation. W. S. N.

Picryl Sulphide. The Binary System: Tolite-Picryl Sulphide. A. ROCHE and V. THOMAS (*Compt. rend.*, 1923, 176, 586—589).—The picryl sulphide used, after recrystallisation from acetone, melted at 213° on the Maquenne block, and almost immediately resolidified, changed colour, and remelted again at 234° . In a m. p. tube, the temperatures were 211° and 230.5° , respectively. It explodes in the neighbourhood of 300° . The addition of tolite lowers the temperature of explosion, and it is also more intense. The two constituents of the binary mixture are miscible in all proportions in the fluid state, and no definite combination is formed. The eutectic melts at 78.3° and contains 86.5% of tolite. With mixtures of approximately this composition, a phenomenon of double supercooling was observed, the thermometer falling regularly to 74.5° , then rising to 76.65° , falling again to 75.1° , and finally rising to 78.3° . The cause of this anomalous behaviour was not ascertained. G. F. M.

Effect of Relative Positions of Hydroxyl and Amino-radicles in the Migration of Acetyl from Nitrogen to Oxygen. L. CHAS. RAIFORD and HAROLD A. IDDLES (*J. Amer. Chem. Soc.*, 1923, 45, 469—475; cf. A., 1920, i, 156; 1922, i, 931).—Additional evidence is given in support of the view that the migration of the acetyl group from nitrogen to oxygen, when an *o*-acetamidophenol is benzoylated by the Schotten-Baumann method, is probably general. With *p*-acetamidophenols under the same conditions, benzoylation does not cause migration of the acetyl group. This process thus furnishes a further means of distinguishing between *o*- and *p*-aminophenols. The following new compounds are described: 2:6-dibromo-4-acetamidophenyl acetate, m. p. $172-173^{\circ}$; 2:6-dibromo-4-acetamidophenyl benzoate, m. p. 168° ; 2:6-dibromo-4-benzamidophenyl acetate, m. p. 165° ; 3-bromo-5-acetamido-*o*-tolyl

benzoate, m. p. 196°; *6-bromo-5-benzamido-o-cresol*, m. p. 189°; *3-bromo-5-benzamido-o-tolyl acetate*, m. p. 130°; *2:4-dibromo-6-acetamido-m-tolyl acetate*, m. p. 145—146°; *2:4-dibromo-6-acetamido-m-cresol*, m. p. 222°; *2:4-dibromo-6 acetamido-m-tolyl benzoate*, m. p. 182—183°; *2:4-dibromo-6-benzamido-m-tolyl acetate*, m. p. 179°; *2:6-dibromo-4-acetamido-m-cresol*, m. p. 171°, and *2:6-dibromo-4-benzamido-m-tolyl acetate*, m. p. 198—199°.

W. G.

Acetomethylamidophenyl Acetate. H. T. CLARKE (U.S. Pat. 1434429).—Acetomethylamidophenyl acetate is prepared by adding acetyl chloride beneath the surface of dimethylaminophenyl acetate contained in a bath at 190°.

CHEMICAL ABSTRACTS.

Preparation of β -Naphthol-4-Sulphonic Acid. GILBERT T. MORGAN and EVELINE JONES (*J. Soc. Chem. Ind.*, 1923, 42, 97—98r).—The preparation of β -naphthol-4-sulphonic acid from naphthalene-1-diazo-2-oxide-4-sulphonic acid, a commercially available product, is described. Sixty g. of the latter were heated with 900 c.c. of absolute alcohol in a reflux apparatus for about twenty-one hours and the resulting solution neutralised with barium carbonate. Alcohol was distilled off, the residual thick paste dissolved in water and the solution decolorised with animal charcoal, concentrated, and the residue dried over sulphuric acid. *β -Naphthalene-1-azo- β -naphthol-4-sulphonic acid*, *p-nitrobenzene-1-azo- β -naphthol-4-sulphonic acid*, and *p-toluene-1-azo- β -naphthol-4-sulphonic acid* were prepared from the resulting barium β -naphthol-4-sulphonate, which was obtained as a hard, friable mass extremely soluble in water. The three azo-colours dyed on wool and silk in varying shades of red.

J. S. G. T.

The 1:2-cycloHexanediols and o-Chlorocyclohexanol. MARCEL GODCHOT (*Compt. rend.*, 1923, 176, 448—450).—The author finds for the 2-chlorocyclohexan-1-ol, as prepared by Detœuf (Thesis, Paris, 1920), or by Osterberg and Kendall (A., 1920, i, 101), the m. p. 29°, when it has been carefully purified. It gives a *phenylurethane*, m. p. 97—98°, and with alcoholic potassium hydroxide the ether oxide described by Brunel (A., 1905, i, 695). The chlorohydrin reacts with silver acetate to give the *monoacetate* of cyclohexan-1:2-diol, b. p. 122—124°/10 mm., d_{20}^{25} 1.091, n_D^{25} 1.4685. This acetate on hydrolysis with aqueous-alcoholic potassium hydroxide gives the *cyclohexanediol*, m. p. 104°. The author considers that his results support the view of Böseken and co-workers (A., 1921, i, 663) that the diol is a *cis-trans*-compound.

W. G.

Rings through the Meta- and Para-positions of Benzene. A Study of certain Ethers of Resorcinol and *m*-Aminophenol. W. C. WILSON and ROGER ADAMS (*J. Amer. Chem. Soc.*, 1923, 45, 528—540).—An attempt has been made to produce ring structures through the meta- and para-positions of benzene by starting with various resorcinol ethers and with *m*- and *p*-aminophenol ethers, but in no instance was a meta- or para-ring obtained, such as might be expected from the reactions of compounds similar in

structure except for the presence of the oxygen atom or atoms. These results tend to confirm previous observations (cf. Mohr, A., 1919, ii, 229; and von Braun, A., 1913, i, 197; 1919, i, 40; 1920, i, 87), that a very definite kind and number of atoms are necessary for the formation of meta- and para-rings. Apparently, if there is any other reaction which has the slightest tendency to take place in preference to the formation of meta- and para-rings, such a reaction will occur. Thus when resorcinol di- γ -cyanopropyl ether was reduced according to the method used by von Braun (*loc. cit.*) for *m*-xylylene dicyanide, not a trace of a ring compound was formed, but only the corresponding diamine in excellent yield. Further, by distillation of the monohydrochloride of this diamine, no ring compound was produced. Similarly, it was not possible to obtain a ring compound by treating resorcinol di- γ -iodopropyl ether with a primary amine. The same ether and sodium under a variety of conditions gave no compound having a ring structure.

A number of resorcinol ethers have been prepared as follows. *Resorcinol di- β -bromoethyl ether*, m. p. 94.5–95°, b. p. 166–167°/9 mm., was obtained by the interaction of ethylene bromide and sodium resorcinoxide in absolute alcohol. Attempts to prepare *resorcinol di- γ -bromopropyl ether*, m. p. 67°, b. p. 204–206°/6 mm., by the same process gave principally a mixture of three other compounds, namely, *resorcinol γ -bromopropyl allyl ether*,

$\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$, m. p. 88–89°, *resorcinol diallyl ether*, $\text{C}_6\text{H}_4(\text{O}\cdot\text{CH}_2\cdot\text{CH}\text{:}\text{CH}_2)_2$, b. p. 156–158°/12 mm., d_{20}^{20} 1.1645, n_D^{20} 1.5672, and a substance which was probably *trimethylene γ -bromopropyl oxyphenyl allyloxyphenyl ether*, $\text{CH}_2\text{Br}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot[\text{CH}_2]_3\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}\text{:}\text{CH}_2$, m. p. 119–120°. *Resorcinol di- γ -bromopropyl ether* was best prepared by heating together a mixture of resorcinol, potassium carbonate, and trimethylene bromide in aqueous acetone. From this ether, by the action of sodium iodide in aqueous acetone, *resorcinol di- γ -iodopropyl ether*, m. p. 88–89°, was obtained. *Resorcinol di-*n*-propyl ether*, b. p. 127–128°/12 mm., d_{21}^{20} 1.035, n_D^{33} 1.5138, on bromination gave a *bromide*, m. p. 81°. The iodo-ether, when heated with *n*-amylamine, gave *resorcinol di- γ -*n*-amylaminopropyl ether*, b. p. 249–252°/10 mm., isolated as its *dihydrochloride*, m. p. 287°. When boiled with sodium cyanide in aqueous alcohol, the iodo-ether was converted into *resorcinol di- γ -cyanopropyl ether*, m. p. 31–32°, b. p. 236–237°/7 mm., which, when reduced with sodium in alcohol, yielded *resorcinol di- δ -aminobutyl ether*, b. p. 208–209°/7 mm., d_{20}^{20} 1.0589, n_D^{26} 1.5315, giving a *monohydrochloride*, m. p. 233–234°, and a *dihydrochloride*, m. p. 248–249°. The monohydrochloride, when heated, decomposed, giving resorcinol, pyrrolidine, and *resorcinol mono- δ -aminobutyl ether*, m. p. 119–119.5°, b. p. 198–204°/8 mm., isolated as its *hydrochloride*, m. p. 159–161°. This amine, when dissolved in sodium hydroxide solution and shaken with *p*-nitrobenzoyl chloride, yielded *resorcinol di- δ -*p*-nitrobenzamidoethyl ether*, m. p. 123–124°.

When *m*-nitrophenol was heated with trimethylene bromide in the presence of sodium ethoxide, *m*-nitrophenyl γ -bromopropyl ether,

b. p. 186—188°/7 mm., d_{20}^{20} 1.513, n_D^{25} 1.5700, was obtained, and this on reduction with stannous chloride and hydrochloric acid gave *m*-aminophenyl γ -bromopropyl ether, isolated as its *hydrochloride*, m. p. 114—115°. The free amine, when distilled, was decomposed, giving 6-aminochroman, b. p. 140—142°/7 mm., d_{20}^{20} 1.549, n_D^{25} 1.5944, which gave a *hydrochloride*, m. p. 158—160° (decomp.), a *picrate*, m. p. 182—183° (decomp.), a *chloroplatinate*, m. p. 224—225°, an *acetyl* derivative, and a *benzenesulphonyl* derivative, m. p. 148—148.5°. When the aminochroman was diazotised and the product coupled with β -naphthol, a brilliant red compound was obtained.

m-Nitrophenyl allyl ether, m. p. 31.5—32°, b. p. 136—137°/8 mm., was prepared from allyl bromide and *m*-nitrophenol, and on reduction yielded *m*-aminophenyl allyl ether, b. p. 120—122°/5 mm., d_{20}^{20} 1.0891, n_D^{25} 1.5708, giving a *hydrochloride*, m. p. 145—146°, an *acetyl* derivative, and a *benzenesulphonyl* derivative, m. p. 83—83.5°.

Under similar conditions, starting with *p*-nitrophenol, there were prepared *p*-nitrophenyl β -bromoethyl ether, m. p. 64°; *p*-aminophenyl β -bromoethyl ether, m. p. 84°, and its *hydrochloride*, m. p. 196°. This amino-ether, when heated, gave no definite product.

W. G.

Structure of Benzene. MAURICE L. HUGGINS (*J. Amer. Chem. Soc.*, 1923, 45, 264—278).—The experimental data obtained by Hull (*Physical Rev.*, 1917, 10, 692) and by Debye and Scheerer (*A.*, 1917, ii, 437) indicate a structure for graphite composed of layers of closely packed benzene complexes of the type originally proposed by Körner. When similar closely packed layers in crystals of benzene and many of its derivatives are assumed, the dimensions of the benzene hexagon can be calculated from the crystallographic data. This has been done for the following substances, for which the half length, l , and the half width, w , are recorded: quinol, $l=2.47$, $w=2.14$; benzene, $l=2.46$, $w=2.19$; resorcinol, $l=2.52$, $w=2.08$; *p*-chloroaniline, $l=2.47$, $w=2.16$; pyrocatechol, $l=2.62$, $w=2.11$; *p*-dichlorobenzene, $l=2.54$, $w=2.13$; triphenylcarbinol, $l=2.45$, $w=2.13$; triphenylbenzene, $l=2.44$; $w=2.16$; tribenzylcarbinol, $l=2.42$, $w=2.11$; tribenzylsilicol, $l=2.48$, $w=2.16$; and triphenylmethane, $l=2.47$, $w=2.16$. These values are very near to the values obtained for graphite, $l=2.47$, $w=2.14$ (Hull), $l=2.52$, $w=2.18$ (Debye and Scheerer). The arrangement of atoms, molecules, and electrons in the crystal has been partly determined.

J. F. S.

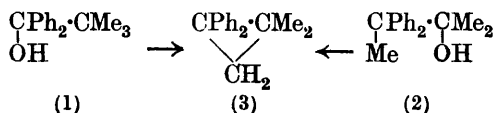
The Phenylalanine Series. II. Synthesis of 3:4-Dihydroxyphenylethylamine. E. WASER and H. SOMMER (*Helv. Chim. Acta*, 1923, 6, 54—61).—A new synthesis of 3:4-dihydroxyphenylethylamine was accomplished, starting from tyramine (*p*-hydroxyphenylethylamine). Tyramine was nitrated in aqueous suspension with nitric acid at 0—5°, and 3-nitro-4-hydroxyphenylethylamine nitrate separated. It crystallises in rosettes of yellow needles, m. p. 208° (decomp.). The free base forms microscopic prisms

or leaflets, varying from yellow to orange in colour, according to the solvent from which they are obtained, m. p. 217° (corr., decomp.). It is soluble in 200 parts of cold or 120 parts of hot water, and gives no colour reaction with Millon's reagent or with ferric chloride. The *hydrochloride* forms large, yellowish-brown leaves, decomposing, without melting, at 214.5° (corr.). The *chloroplatinate* forms golden-yellow needles decomposing at 265° , and the *picrate* deep yellow prisms, m. p. 204° . From the nitration liquor a small amount of 3:5-dinitro-4-hydroxyphenylethylamine was obtained, an orange-red, microcrystalline powder, decomposing at 290° . The *nitrate* crystallises in well-developed, yellow prisms, m. p. 163° (corr., decomp.), and the *picrate* forms a yellow, microcrystalline powder, m. p. 196° . It was identified by conversion into 3:5-dinitro-4-hydroxybenzoic acid. The reduction of 3-nitrotyramine was best accomplished with hydrogen in presence of platinum in dilute hydrochloric acid. 3-Amino 4-hydroxyphenylethylamine (aminotyramine) forms colourless, microscopic leaflets, m. p. $145-147^{\circ}$ (corr.). It is soluble in 160 parts of cold or 50 parts of boiling water, from which it crystallises as a *monohydrate*, m. p. 127° . With Millon's reagent, it gives a yellow colour in the cold, becoming turbid and brown in the hot. Ferric chloride gives a deep reddish-violet colour, becoming yellow on addition of alkali, brownish-red with sodium acetate. It reduces an ammoniacal silver solution in the cold and Fehling's solution in the hot. The diazotised base gives a brownish-red colour with α -naphthol. The base also gives the tyrosinase reaction with potato, but not so strongly as tyrosine. The *dihydrochloride* forms star- or feather-shaped groups of needles, m. p. 305° (corr., decomp.). This, when injected into the jugular vein of a dog caused a sharp rise of blood pressure. The *monopicrate* forms dark brown, pointed prisms, m. p. 204.5° (corr., decomp.); the *dipicrate* forms bright brownish-yellow leaflets, m. p. 212° (corr., decomp.). Attempts to obtain aminotyramine by decarboxylation of aminotyrosine gave a very poor yield.

3:4-Dihydroxyphenylethylamine was obtained by diazotising aminotyramine in sulphuric acid solution and running the diazo-solution into a boiling concentrated solution of copper sulphate. The *hydrochloride* forms groups of needles, m. p. 237° (corr., decomp.); the *picrate* forms brownish-yellow crystals, m. p. 189° (corr.). 3:4-Dihydroxyphenylethylamine gives a red colour with Millon's reagent, and a green colour, destroyed by excess of the reagent, with ferric chloride. It reduces an ammoniacal silver solution in the cold and Fehling's solution in the hot. E. H. R.

Molecular Transposition in the Diphenyl- ψ -butylcarbinol Series. (MME) PAULINE RAMART (*Compt. rend.*, 1923, 176, 684—686).—The action of acetyl chloride and acetic anhydride on diphenyl- ψ -butylcarbinol results in the formation of a chloro-compound and a hydrocarbon, the former having the constitution $\text{CMePh}_2\cdot\text{CMe}_2\text{Cl}$ (A., 1922, i, 34). The same hydrocarbon has now been obtained by the dehydration of diphenyl- ψ -butylcarbinol (1), and the tertiary alcohol (2) by the action of heat in presence of

infusorial earth, and from the corresponding chloro-compounds by the action of pyridine in sealed tubes at 120°.



The alcohol (2) was obtained by the action of 2 mols. of magnesium methyl iodide on ethyl $\alpha\alpha$ -diphenylpropionate, and the chloro-compounds were obtained by the action of thionyl chloride on the alcohols. The identity of the four hydrocarbons obtained and that obtained from the carbinol (1) by the action of acetyl chloride and acetic anhydride was proved by the identity of the chloro-compounds obtained from them by the action of hydrogen chloride at -10° , by the identity of the tribromides, m. p. 200° (with decomp.), obtained by the action of bromine, by their comparative indifference to acid or alkaline permanganate, and by the identity of their physical constants, $d_{25}^{20} 1.008$, $n_D^{20} 1.5746$. The hydrocarbon is therefore regarded as an intermediate product in the formation of the chloro-compound, $\text{CMePh}_2\cdot\text{CMe}_2\text{Cl}$, from diphenyl- ψ -butylcarbinol, and as having the cyclopropane structure (3).

G. F. M.

Ethers of Triphenylcarbinol. BURCKHARDT HELFERICH, PAUL ELIAS SPEIDEL, and WALTER TOELDT (*Ber.*, 1923, 56, [B], 766—770).—Triphenylmethyl chloride reacts with alcohols in the presence of anhydrous pyridine at the atmospheric temperature or when warmed to give the corresponding ethers: $\text{CPh}_3\text{Cl} + \text{R}\cdot\text{OH} = \text{R}\cdot\text{O}\cdot\text{CPh}_3 + \text{HCl}$. Since the action proceeds in the presence of an excess of pyridine, it is particularly suitable for compounds which are sensitive towards acids. The ethers generally crystallise readily and appear to be adapted to the identification and possibly the purification of alcohols. They appear to be generally stable towards boiling alcoholic alkali, but are readily hydrolysed by dilute methyl-alcoholic hydrogen chloride at the atmospheric temperature to the alcohol and triphenylcarbinyl methyl ether. The introduction of the triphenylmethyl group is therefore serviceable for the protection of hydroxyl groups.

The following individual compounds are described: *triphenylmethyl isopropyl ether*, $\text{Pr}^s\cdot\text{O}\cdot\text{CPh}_3$, colourless needles, m. p. 113°; *triphenylmethyl propyl ether*, colourless plates or prisms, m. p. 55°; *triphenylmethyl cetyl ether*, colourless plates or prisms, m. p. 40—41°; *triphenylmethyl allyl ether*, colourless plates or prisms, m. p. 76°; *triphenylmethyl cyclohexyl ether*, colourless prisms, m. p. 103°; *triphenylmethyl hydroxyethyl ether*, $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}\cdot\text{CPh}_3$, prisms or plates, m. p. 98—100°, the corresponding *bistriphenylmethyl ethylene ether*, prisms or plates, m. p. 185—186°; *triphenylmethyl α -glycerol ether*, $\text{OH}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{O}\cdot\text{CPh}_3$, m. p. 92—94°; (?) *glycerol $\alpha\alpha'$ -bistriphenylmethyl ether*, small prisms, m. p. 170—171°; *pyrocatechol bistriphenylmethyl ether*, small plates, m. p. 206—208°; *pyrocatechol triphenylmethyl ether*, needles, m. p. about 258°.

after darkening at 245° , which, however, is stable towards alcoholic hydrogen chloride, and hence, possibly, has a different constitution. H. W.

Influence of Substitution in the Components on Equilibria in Binary Solutions. XXXIX. Some Binary Systems of Triphenylmethane, Triphenylcarbinol, and Trimethylcarbinol with other Components. ROBERT KREMANN, OTTO MAUERMANN, ROBERT MÜLLER II, and WILHELM RÖSLER (*Monatsh.*, 1923, 43, 321—333).—Previous examination of the system triphenylmethane-*m*-phenylenediamine afforded no evidence for the existence of a compound (A., 1922, i, 131). Repetition of the work confirms this; there is formed simply a eutectic at 58° and 4% of triphenylmethane. The latter with *o*-phenylenediamine gives a eutectic at 76.5° and 12.5% of triphenylmethane. With *m*-phenylenediamine, the hydrocarbon gives two liquid layers in the region 25—93% of triphenylmethane, the (constant) temperature of primary crystallisation being 81° . In the case of *o*-phenylenediamine, the same holds for the region 29—50% triphenylmethane (89°). 2:4-Dinitrophenol and triphenylmethane do not form a compound, but merely a simple eutectic at 81° (86% hydrocarbon). Triphenylmethane and triphenylcarbinol give a simple eutectic at 78° and 17% of carbinol. *o*-Nitrophenol, contrary to expectation (steric effects), behaves like its meta- and para-isomerides with trimethylcarbinol, a compound of the type 1 phenol+2 carbinol being formed in all three cases (corresponding with 51.6% carbinol) (cf. A., 1895, ii, 205; 1897, ii, 476).

Triphenylcarbinol and 2:4-dinitrophenol form a simple eutectic only, at 100° and 19% carbinol. Trimethylcarbinol, on the other hand, gives, with this phenol, an equimolecular compound, m. p. 89° (28.7% carbinol). (Eutectic with phenol at 85° and 17% carbinol, that with triphenylcarbinol at 20° and 97%.)

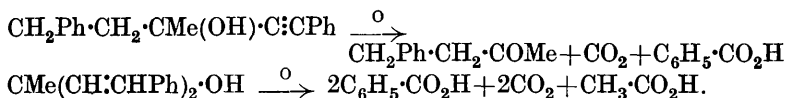
Naphthalene does not form compounds with either trimethyl- or triphenyl-carbinol, but only simple eutectics at 19° and 95% trimethylcarbinol and at 69° and 30% triphenylcarbinol, respectively. The fact that α - and β -naphthylamines form compounds with these carbinols, whilst other amines previously examined do not (A., 1919, ii, 457, 458), cannot therefore be attributed to peculiar compound-forming properties of the naphthalene nucleus. E. E. T.

Addition of Hydrogen to Acetylene Derivatives. X. Addition of Hydrogen to Diphenylphenylacetylenylcarbinol. J. S. ZALKIND and (MLLE) N. CICIANOVA (*J. Russ. Phys. Chem. Soc.*, 1918, 50, 19—23; cf. A., 1916, i, 260).—Diphenylphenylacetylenylcarbinol, $\text{CPh}_2\text{C}:\text{CPh}_2\text{OH}$, is reduced by the Sabatier method, using palladium as catalyst. No break in the rate of addition could be observed after the addition of 50% of the possible hydrogen, i.e., the process did not tend to stop with the formation of an ethylenic linking. Increase in the quantity of catalyst used accelerated the reaction, K increasing in the ratio 1:3.5:17 when the quantity of catalyst is increased as 1:2:5. The reduction

product was $\alpha\alpha\gamma$ -triphenylpropan- α -ol, m. p. 85—87°. The action of bromine on the original carbinol was also investigated, and a dibromide, m. p. 99—100°, prepared.

R. T.

Addition of Hydrogen to Acetylene Derivatives. XI. Addition of Hydrogen to Alcohols having Two Triple Linkings. J. S. ZALKIND (*J. Russ. Phys. Chem. Soc.*, 1918, 50, 23—33; cf. A., 1916, i, 260).—Diphenylacetylenylmethylcarbinol, $\text{CMe}(\text{C}:\text{CPh})_2\cdot\text{OH}$, is reduced by the Sabatier method, using a palladium catalyst. As in previous cases (*loc. cit.*), addition of hydrogen leads to complete saturation of the acetylenic linkings, with no tendency to stop at the formation of ethylenic linkings. The reduction product is an oil, γ -hydroxy- $\alpha\epsilon$ -diphenyl- γ -methylpentane, $d_4^{20}=1.0334$, $n_D^{25}=1.55153$, giving, from aqueous alcohol crystals, m. p. 51°, containing $1\text{H}_2\text{O}$. If the reduction process is stopped when half the possible hydrogen has been added, a mixture of unchanged carbinol, of saturated substance, and of γ -hydroxy- $\alpha\epsilon$ -diphenyl- γ -methyl- Δ^5 -pentadiene, $\text{CMe}(\text{CH}:\text{CHPh})_2\cdot\text{OH}$, b. p. 210—212°/13 mm., $d_4^{20}=1.0638$, $n_D^{25}=1.5880$, is obtained. In order to prove that the product of reduction is not δ -phenyl- β -phenylacetylenylbutan- β -ol, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CMe}(\text{OH})\cdot\text{C}:\text{CPh}$, the latter compound was synthesised from benzylacetone and magnesium phenylacetylenyl bromide. The oxidation of this compound leads to the production of benzylacetone and benzoic acid, whilst the oxidation of the diethylenic compound gives a mixture of benzoic and acetic acids, in the following way :

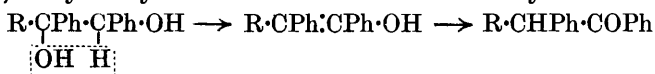


R. T.

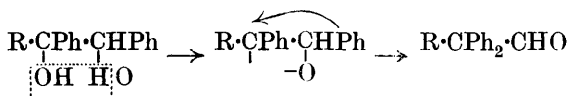
Semipinacolic and Hydrobenzoinic Transpositions in the Alkylhydrobenzoin Series. Alkylhydrobenzoins with a Branched Chain. I. isoPropyl, isoButyl, and isoAmyl Chains. M. TIFFENEAU and A. ORÉKHOFF (*Bull. Soc. chim.*, 1923, [iv], 33, 195—218).—The alkyl group in the alkylhydrobenzoins exercises a distinct and regular influence on the manner in which the dehydration of these substances occurs by the action of dilute or concentrated sulphuric acid. The results are interpreted in the light of Werner's ideas on variable affinity. When the affinity between the alkyl group and the rest of the molecule is strong, that of the tertiary hydroxyl is correspondingly weakened, and on dehydration it is eliminated with either the hydrogen contiguous to the secondary hydroxyl [vinyl dehydration (1)] or the hydrogen of the secondary hydroxyl [hydrobenzoin transformation (2)]. If, on the other hand, the affinity between the alkyl group and the rest of the molecule is feeble, as, for example, in the case of the isopropyl group, that of the tertiary hydroxyl is strengthened, and it is the secondary hydroxyl which is eliminated with the hydrogen of the tertiary hydroxyl [semipinacolic trans-

position (3)]. These reactions are expressed by the following schemes :

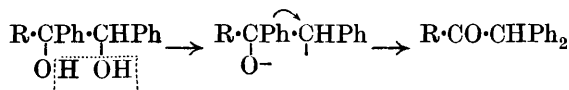
- (1) Vinyl dehydration with formation of deoxybenzoins



- (2) Hydrobenzoin transposition with formation of alkyl diphenylacetaldehydes



- (3) Semipinacolin transposition with formation of benzhydryl alkyl ketones



The dehydrating agent used also has a definite bearing on the sense of the reaction. Concentrated sulphuric acid augments the stability of the tertiary hydroxyl, or, if its affinity is weakened by the adjacent alkyl group, then it determines its elimination according to (1) above. Dilute sulphuric acid, on the other hand, has no effect on the stability of the hydroxyl but determines the aldehyde formation (2) by elimination of the hydrogen of the secondary hydroxyl. The following substances were prepared during the course of the research: $\alpha\beta$ -Diphenyl- γ -methylbutane- $\alpha\beta$ -diol (isopropylhydrobenzoin) prepared from benzoin and magnesium isopropyl bromide, forms colourless needles, m. p. 107—108°. On dehydration with cold concentrated sulphuric acid, the semipinacolin transformation occurs exclusively, with formation of $\alpha\alpha$ -diphenyl- γ -methylbutan- β -one, colourless needles, m. p. 74—75°. For purposes of identification, this ketone was also prepared from diphenylacetaldehyde and magnesium isopropyl bromide, the resulting secondary alcohol, $\alpha\alpha$ -diphenyl- γ -methylbutan- β -ol, b. p. 188—189°/16 mm., being converted into the ketone by oxidation with chromic acid. The isomeric ketone $\alpha\beta$ -diphenyl- γ -methylbutan- α -one (isopropyldeoxybenzoin), which was synthesised from deoxybenzoin and isopropyl bromide, formed needles, m. p. 70—71°, could not be found in the reaction mixture resulting from the dehydration of isopropylhydrobenzoin, and the vinyl dehydration (1) did not therefore occur at all. The dehydration of isopropylhydrobenzoin by treating with dilute sulphuric acid gave a mixture of the above $\alpha\alpha$ -diphenyl- γ -methylbutan- β -one and $\alpha\alpha$ -diphenylisobutaldehyde, a viscous liquid, b. p. 184—186°/15 mm., d_4^{20} 1.0522, produced according to the hydrobenzoin transformation (2). Its semicarbazone melts at 190—191°, and oxime at 93—94°. isoButylhydrobenzoin gives on dehydration with oxalic acid exclusively the substituted aldehyde, $\alpha\alpha$ -diphenyl- γ -methylbutaldehyde, a yellow oil, b. p. 195—196°/15 mm., d_4^{20} 1.035, forming a

semicarbazone, m. p. 147—148°, and an *oxime*, m. p. 153—154°. With concentrated sulphuric acid, vinyl dehydration occurs exclusively with formation of *isobutyldeoxybenzoin*. No trace of the isomeric ketone $\alpha\alpha$ -*diphenyl- δ -methylpentan- β -one*, m. p. 37—38°; *semicarbazone*, m. p. 168—169°, could be found in the mother-liquors. This ketone was synthesised by oxidation of $\alpha\alpha$ -*diphenyl- δ -methylpentan- β -ol*, a yellow oil, b. p. 185—195°/16 mm. $\alpha\beta$ -*Diphenyl- ϵ -methylhexan- $\alpha\beta$ -diol* (*isoamylhydrobenzoin*) prepared from magnesium *isoamyl* bromide and benzoin, forms fine needles, m. p. 127—128°, and on dehydration with weak acids gives only the aldehyde (reaction 2), $\alpha\alpha$ -*diphenyl- δ -methylhexaldehyde*, b. p. 205—210°/17 mm.; *semicarbazone*, m. p. 133—134°. With cold concentrated sulphuric acid, on the other hand, the reaction proceeds to the extent of about one-third according to the semipinacol transformation and two-thirds vinyl dehydration. The former product, $\alpha\alpha$ -*diphenyl- ϵ -methylhexan- β -one*, forms a viscid oil, b. p. 205—210°/21 mm.; *semicarbazone*, m. p. 139—140°, and was identified by synthesis from $\alpha\alpha$ -*diphenyl- ϵ -methylhexan- β -ol*, a viscous liquid, b. p. 218—220°/26 mm., which was prepared from magnesium *isoamyl* bromide and diphenylacetaldehyde. The isomeric substance $\alpha\beta$ -*diphenyl- ϵ -methylhexan- α -one* (*isoamyldeoxybenzoin*) forms small, colourless needles, m. p. 62—63°, and gives a *semicarbazone*, m. p. 127—128°. It was identified by synthesis from *deoxybenzoin* and *isoamyl* bromide. G. F. M.

Addition of Hydrogen to Acetylene Derivatives. XII. Addition of Hydrogen to Diphenylbutinenediols and to the Acetyl Ester of Diphenylbutinenediol. J. S. ZALKIND and (MLLE) Z. NEISCHTAB (*J. Russ. Phys. Chem. Soc.*, 1918, 50, 34—42; cf. *ibid.*, 1914, 46, 1532; 1917, 49, 135).— $\alpha\delta$ -Diphenylbutinene- $\alpha\delta$ -diol, $\text{OH}\cdot\text{CHPh}\cdot\text{C}\equiv\text{C}\cdot\text{CHPh}\cdot\text{OH}$ (A., 1914, ii, 258), is reduced by the Sabatier method, using a palladium catalyst. This compound exists in two stereoisomeric forms, melting at 140° and 102°, respectively, and both forms were examined. The velocity of reaction for both diminishes considerably after the triple bond has been changed to double, although it is still much greater than for ditertiary alcohols. By varying the quantity of catalyst in the order 1 : 2 : 3 : 5, *K* increased as 1 : 4 : 8 : 17. Whilst for both forms two space isomerides of the ethylenic reduction product are possible, only one form, m. p. 151°, is obtained from the less fusible isomeride, and two forms from the other, one m. p. 151—152°, but different from the one obtained previously, and the other an oil. The reduction of the diacetyl esters is next examined. This is much more rapid and complete than for the alcohols, and results in the production of $\alpha\delta$ -diphenylbutane. No sharp break occurs with the formation of the ethylenic linking, but at saturation a rapid increase in the velocity of the reaction occurs, due to the reduction of the acetyl groups. By stopping the process when 25% of the possible hydrogen has been added on, the *diacetyl* ester, m. p. 97·5°, of the ethylenic reduction product, m. p. 152°, previously prepared, is obtained. R. T.

Influence of Substitution in the Components on Equilibrium in Binary Solutions. XL. The Equilibrium in Binary Solutions of Acid Amides with Acid Anhydrides and with Acids. ROBERT KREMAN, OTTO MAUERMANN, and VIKTOR OSWALD (*Monatsh.*, 1923, 43, 335—343).—Acetamide and benzoic anhydride form an equimolecular compound, m. p. about 84°, the eutectics lying at 68° (25% mol. of anhydride) and 36° (93% mol. of anhydride). The binary systems (1) acetamide-acetic anhydride, (2) benzamide-benzoic anhydride, and (3) benzamide-acetic anhydride were examined. A complete examination of (1) and (3) could not be made (*i.e.*, beyond the limits 0—90% of acetic anhydride), owing to solubility effects, but a complete curve was obtained for (2), and shows the existence of a eutectic at 37° and 92% mol. of benzoic anhydride. Examination of the primary crystallisation curve for the system acetamide-acetic acid reveals the probable existence of an equimolecular compound (—5.5° and 50.5% acetic acid), this, with acetic acid, forming a eutectic at —16.5° and 69.5% acetic acid. Benzoic acid and benzamide form a eutectic at 78—79.5° (45.5—47.5% benzoic acid). Acetic acid and benzamide give a eutectic at —2° and 73% acid, benzoic acid and acetamide giving a eutectic at 38° and 56% acid.

E. E. T.

Production of Esters of Aromatic Acids [γ -Dialkylamino-propyl Aminobenzoates]. THE ABBOTT LABORATORIES (Brit. Pat. 191122).— γ -Dialkylaminoalkyl esters of aromatic acids in general, and particularly γ -dialkylamino-*n*-propyl benzoates and aminobenzoates in which at least one of the alkyl groups is larger than an ethyl group, are obtained by heating the corresponding γ -halogeno-alkyl esters with a dialkylamine. The γ -dialkylamino-*n*-propyl aminobenzoates and their salts possess valuable local anæsthetic properties, and a specific example of their preparation is given: γ -bromo-*n*-propyl *p*-nitrobenzoate is heated for four hours at 60° with an equal weight of dibutylamine, the excess of amine is then removed by washing with water and distillation with steam, the residue is dissolved in benzene and extracted with dilute hydrochloric acid, the hydrochloride layer is separated and rendered alkaline, and the free base extracted with benzene. The γ -di-*n*-butylamino-*n*-propyl *p*-nitrobenzoate thus obtained is converted on reduction with iron and hydrochloric acid into the corresponding aminobenzoate, which is isolated as its hydrochloride or other suitable salt. *p*-Aminobenzoyl- γ -di-*n*-butylamino-*n*-propanol hydrochloride is a crystalline solid, m. p. 151—152°. The hydrobromide melts at 143°, and the sulphate at 100°. Alternatively to the above method of preparation, the bromopropyl nitrobenzoate may first be reduced to γ -bromo-*n*-propyl *p*-aminobenzoate, m. p. 81.5°, and then afterwards condensed with dibutylamine. G. F. M.

The Addition of Bromine to the α - and β -Chloro- and Bromo-cinnamic Acids and their Esters. J. J. SUDBOROUGH and GWYLYM WILLIAMS (*J. Indian Inst. Sci.*, 1923, 5, 107—118).—The addition of bromine in chloroform solution takes place much

more readily in diffused daylight than in the dark; the esters are more reactive than the free acids, and the β -halogenated compounds than the α -halogenated compounds. α -Bromocinnamic acid and α -bromo*allocinnamic* acid and their methyl esters give the same $\alpha\alpha\beta$ -tribromo- β -phenylpropionic acid and *methyl $\alpha\alpha\beta$ -tribromo- β -phenylpropionate*, respectively, the former melting at 152—153°, and the latter at 47—48°. Similarly, the two stereoisomeric β -bromocinnamic acids and their methyl esters yield identical products, $\alpha\beta\beta$ -tribromo- β -phenylpropionic acid, m. p. 146—147° (decomp.), and *methyl $\alpha\beta\beta$ -tribromo- β -phenylpropionate*, m. p. 42—43°. The latter crystallises in tufts of slender needles. From the stereoisomeric β -chlorocinnamic acids, two different dibromides would theoretically be expected, but only one β -chloro- $\alpha\beta$ -dibromo- β -phenylpropionic acid was obtained. It formed colourless prisms from chloroform, m. p. 143—144°. Both α -chlorocinnamic acids, however, gave a mixture of isomeric dibromides, and attempts to separate them were not successful. G. F. M.

Products of the Distillation of α -Truxillic Acid. Isolation of a Fourth Truxillic Acid. HANS STOBBE and FRITZ ZSCHOCH (*Ber.*, 1923, 56, [B], 676—678).—The dry distillation of α -truxillic acid yields *transcinnamic* acid, stilbene (which is probably derived secondarily from *transcinnamic* acid and not directly from α -truxillic acid), a substance, m. p. 192—194°, which has not been definitely characterised, γ -truxillic anhydride, m. p. 189—190°, and η -truxillic anhydride, $C_{18}H_{14}O_3$, m. p. 287°, which is transformed into η -truxillic acid, m. p. 280°; the presence of benzaldehyde or truxone could not be detected.

[With FRITZ RAU.]—The dry distillation of *trans*-cinnamic acid yields mainly unchanged acid; in addition, styrene, stilbene, and indefinite products are formed. H. W.

Investigations in the Phenylalanine Series. III. The Hydrogenation of Tyrosine. E. WASER and E. BRAUCHLI (*Helv. Chim. Acta*, 1923, 6, 199—205).—Weinhagen attempted to hydrogenate tyrosine without success, and, although successful with phenylethylamine prepared from phenylalanine, failed to reduce synthetic phenylethylamine (A., 1918, i, 107). The latter failure was probably due to the presence of some impurity which interfered with the catalytic hydrogenation, since the present authors, working with most carefully purified materials, have successfully hydrogenated tyrosine, using platinum black as the catalyst. Reduction was incomplete in alkaline or neutral solution but went completely in acid solution, best when exactly 2 mols. of hydrochloric acid per mol. of tyrosine was used. *Hexahydrotyrosine* crystallises from hot water in microscopic needles, m. p. 307° (corr., decomp.). It is soluble in about 25 parts of cold water. The hexahydrotyrosine from *l*-tyrosine is dextrorotatory, $[\alpha]_D^{20} +13.18^\circ$. The *hydrochloride*, which is extremely soluble in water, crystallises in leaflets or needles, m. p. 249° (decomp.). The *chloroplatinate*, $(C_9H_{17}O_3N)_2 \cdot H_2PtCl_6 \cdot 3H_2O$, forms bright yellow needles, m. p. 204° (decomp.). The *picrate* forms yellow needles, m. p. 196° (decomp.);

the *benzoyl* derivative, $C_{16}H_{21}O_4N$, forms colourless leaflets, m. p. 186° (corr.). The *phenylhydantoin* from hexahydrotyrosine crystallises in colourless needles, m. p. 159—161° (corr.). E. H. R.

Investigations in the Phenylalanine Series. IV. The Rotation-Dispersion of Tyrosine and some of its Derivatives. E. WASER (*Helv. Chim. Acta*, 1923, 6, 206—214).—Although tyrosine itself is *lævorotatory*, most of its known derivatives are *dextro-rotatory*. The rotations of many such derivatives have now been determined for a number of wave-lengths to discover whether any relation exists between the configuration of the asymmetric carbon atom and the rotation-dispersion such as was found by Karrer and Kaase in the glutaric acid series (A., 1919, i, 570). The following table gives the specific rotations at 15° for some of the principal lines :

Substance.	C 656.3	626	D 589.3	Hg 546.3	E 527.0
<i>l</i> -Tyrosine	−10.27°	−11.30°	−12.30°	−13.76°	−14.61°
<i>l</i> -3-Nitrotyrosine	+ 1.31	+ 2.36	+ 3.21	+ 3.97	—
<i>l</i> -3-Aminotyrosine	− 3.69	− 3.69	− 3.61	− 3.54	—
<i>l</i> -Tyrosine-3-diazonium chloride	+ 7.81	+ 9.50	+11.87	—	—
<i>l</i> -3 : 4-Dihydroxyphenylalanine	−11.44	−11.80	−12.74	−15.02	—
<i>l</i> -3 : 5-Dinitrotyrosine ...	+ 7.81	+ 9.40	+11.45	+14.30	+16.48
<i>l</i> -3 : 5-Diaminotyrosine...	+ 0.00	+ 1.02	+ 2.17	+ 1.18	—
<i>l</i> -Hexahydrotyrosine.....	+10.16	+11.83	+13.18	+15.70	+17.16

No conclusions of the kind expected are to be drawn from the results. The *lævorotatory* compounds become more strongly *l*-rotatory the shorter the wave-length (tyrosine and 3 : 4-dihydroxyphenylalanine), whilst the *d*-rotatory compounds become more positive. In the cases of the two amino-derivatives there is very little change in rotation for different wave-lengths.

Natural tyrosine can be racemised readily by boiling in sodium hydroxide solution for about three days. *dl*-Tyrosine crystallises in star-shaped aggregates of extremely fine needles. The hydrochloride forms aggregates of long needles with no characteristic melting point. When given to a dog, *dl*-tyrosine is completely transformed and cannot be detected in the urine. E. H. R.

The Wandering of Acyl Groups in the Cases of Phenolcarboxylic Acids (E. Fischer). Syntheses of *p*-Di- β -resorcylic Acid and *p*-Benzoylpyrogallolcarboxylic Acid. EUGEN PACSU (*Ber.*, 1923, 56, [B], 407—424).—The cautious hydrolysis of penta-acetyl-*p*-digallic acid by cold, dilute ammonia led unexpectedly to the production of *m*-digallic acid (Fischer, Bergmann, and Lipschitz, A., 1918, i, 172), whereby a migration of the acyl group is involved (cf. A., 1908, i, 893; 1911, i, 875; 1913, i, 479). The constitution of many dipeptides, such as di- β -resorcylic acid and gentisic acid, is rendered somewhat uncertain by this observation (cf. Bergmann and Dangschat, A., 1919, i, 273). The structure of *p*-di- β -resorcylic acid is now confirmed by its synthesis, and it is established that the migration of aromatic acyl does not

take place with phenolcarboxylic acids of the type of β -resorcylic acid, or, in all probability, of gentisic acid.

It has been assumed previously that the wandering of aromatic acyl groups only takes place in phenolcarboxylic acids which contain the phenolic hydroxyl groups in the vicinal position to one another. As the result of a lengthy series of experiments the author has drawn the conclusion, however, that this view is incorrect and that the phenomenon is due to the influence of the carboxyl group which is most pronounced on the *p*-hydroxyl radicle. This influence is less marked when the carboxyl group is esterified, and is still less pronounced when a phenolic hydroxyl group is in the vicinal position; in the latter case, a migration of the acyl group is not observed.

2:4-Diacetoxybenzoic acid (cf. Bergmann and Dangschat, *loc. cit.*) is prepared by the action of acetic anhydride and pyridine on β -resorcylic acid, and is converted by phosphorus pentachloride in the presence of chloroform or by thionyl chloride into 2:4-di-acetoxybenzoyl chloride, a pale yellow liquid which solidifies when cooled to -20° , b. p. $170^\circ/12$ mm. (partial decomp.); the corresponding anilide crystallises in slender, lustrous needles, m. p. $126-127^\circ$. The action of 2:4-diacetylbenzoyl chloride and sodium hydroxide on sodium 4-hydroxy-2-acetoxybenzoate in the presence of aqueous acetone leads to the formation of triacetyl-*p*-di- β -resorcylic acid, $C_6H_3(OAc)_2 \cdot CO \cdot O \cdot C_6H_3(OAc) \cdot CO_2H$, small, ill-defined prisms, m. p. $151-153^\circ$ after softening at about 146° ; it is hydrolysed by cautious treatment with sodium hydroxide or ammonia to *p*-di- β -resorcylic acid, microscopic, prismatic needles, m. p. 206° [211° corr. (decomp.)], which differs from the corresponding ortho-compound mainly in its relative insolubility in water. It is re-converted by acetic anhydride and pyridine into triacetyl-*p*-di- β -resorcylic acid. Short treatment of *p*-di- β -resorcylic acid with diazomethane in the presence of ether yields the 4'-methyl ether of methyl *p*-di- β -resorcyate, $OMe \cdot C_6H_3(OH) \cdot CO \cdot O \cdot C_6H_3(OH) \cdot CO_2H$, slender, lustrous needles, m. p. $144-145^\circ$, whereas more protracted treatment in the presence of acetone appears to yield a fully methylated product which has not been examined completely.

4-Benzoyloxy-2-acetoxybenzoic acid (cf. Bergmann and Dangschat, *loc. cit.*) is obtained in 93% yield by the method used in the preparation of triacetyl-*p*-di- β -resorcylic acid; it is converted by diazomethane into methyl 4-benzoyloxy-2-acetoxybenzoate, hexagonal prisms, m. p. $99-100^\circ$, from which methyl 2:4-dihydroxybenzoate, colourless needles, m. p. $121-122^\circ$, is obtained by the action of 5*N*-ammonia.

The derivatives of 2:3:4-trihydroxybenzoic acid have been particularly examined, since migration of the acyl groups is to be expected if Fischer's hypothesis of the influence of vicinal hydroxyl groups is correct; such migrations are not, however, observed. 2:3:4-Triacetoxybenzoic acid, colourless prisms, m. p. 164° after previous softening, is prepared by the action of acetic anhydride and zinc chloride on 2:3:4-trihydroxybenzoic acid and is converted by cautious hydrolysis in an atmosphere of hydrogen into 4-hydroxy-

2 : 3-diacetoxybenzoic acid, long, colourless needles (+ H₂O), m. p. (anhydrous) 157° after slight previous softening; the latter acid appears to be converted by boiling water into 3 : 4-dihydroxy-2-acetoxybenzoic acid, flat prisms, decomp. 192°. The diacetoxy-acid is transformed by diazomethane into methyl 2 : 3-diacetoxy-4-methoxybenzoate, rhombic platelets, m. p. 108°, which is hydrolysed to 2 : 3-dihydroxy-4-methoxybenzoic acid, long, colourless needles, decomp. 207—208°, identical with the substance prepared by Herzig and Pollak (A., 1904, i, 808) by the partial methylation of methyl 2 : 3 : 4-trihydroxybenzoate. 4-Hydroxy-2 : 3-acetoxybenzoic acid and benzoyl chloride yield 4-benzoyloxy-2 : 3-diacetoxybenzoic acid, aggregates of colourless, slender needles, m. p. 161—162°, which is hydrolysed by 5*N*-hydrochloric acid in the presence of glacial acetic acid to 2 : 3-dihydroxy-4-benzoyloxybenzoic acid, lustrous leaflets, decomp. 210—211°; re-acetylation of the latter acid with acetic anhydride gives 4-benzoyloxy-2 : 3-diacetoxybenzoic acid. 2 : 3-Dihydroxy-4-benzoyloxybenzoic acid is converted by diazomethane into methyl 4-benzoyloxy-2 : 3-dimethoxybenzoate, coarse, colourless crystals, m. p. 79—80°, from which 4-hydroxy-2 : 3-dimethoxybenzoic acid, microscopic, colourless, rhombic platelets, m. p. 154—155° after slight previous softening, is obtained by hydrolysis.

H. W.

The Reaction of Alcohols with Bromomethylphthalimide and its Use for the Separation and Identification of Alcohols. HARRIS H. HOPKINS (*J. Amer. Chem. Soc.*, 1923, 45, 541—544; cf. Pucher and Johnson, A., 1922, i, 549).—Bromomethylphthalimide reacts with certain alcohols under anhydrous conditions to give crystalline ethers, which can be used for the identification and separation of the alcohols. This procedure may be used for detecting the presence of methyl alcohol in dry acetone. The reaction does not proceed in the presence of moisture, as the bromomethylphthalimide is converted into hydroxymethylphthalimide before it can react with the alcohol. The following ethers are described: *Phthalimidomethyl methyl ether*, C₆H₄.(CO)₂.N·CH₂·OMe, m. p. 118°; *phthalimidomethyl ethyl ether*, m. p. 86°; *phthalimidomethyl n-propyl ether*, m. p. 52—53°; *phthalimidomethyl isopropyl ether*, m. p. 92—93°; *phthalimidomethoxyacetic acid ether*, m. p. 185°; *phthalimidomethyl phenyl ether*, m. p. 171—172°; *triphtalimidomethyl glyceryl ether*, m. p. 174—175°.

W. G.

Phenolsulphonephthalein and some of its Derivatives. W. R. ORNDORFF and F. W. SHERWOOD (*J. Amer. Chem. Soc.*, 1923, 45, 486—500).—In the preparation of phenolsulphonephthalein from the chloride of *o*-sulphobenzoic acid and phenol, the ordinary method of purification, by solution in sodium hydroxide and subsequent precipitation with acid, does not remove one impurity. This substance is soluble in the alkali hydroxide, but unlike the phthalein it is not soluble in cold aqueous sodium or ammonium hydrogen carbonate. This compound only contains about half as much sulphur as phenolsulphonephthalein, and is apparently

formed from it by the action of the excess of phenol. When the aqueous filtrates from the crude phenolsulphonephthalein were concentrated and then boiled with an excess of pure barium carbonate, *p*-hydroxybenzoylbenzene-*o*-sulphonic acid was obtained as its *barium* salt. This acid may also be prepared by heating ammonium *o*-sulphobenzoate with phenol for fifteen hours at 180–210°, and is obtained in the form of pink crystals containing 1H₂O, or as a red, internal anhydride, which probably has the quinonoid structure $O:C_6H_4:C \begin{smallmatrix} \diagup C_6H_4 \diagdown \\ \diagdown O \diagup \end{smallmatrix} SO_2$. When heated at 135–140°, this acid loses water and gives phenolsulphonephthalein and the anhydride of *o*-sulphobenzoic acid. The phthalein prepared in this way is free from the impurity mentioned above.

As phenolsulphonephthalein is a coloured compound, it is represented by a quinonoid formula. Because it is the sulphonic acid derivative of benzaurin, it is highly probable that dry phenolsulphonephthalein should be represented as an inner oxonium or carbonium salt. The crystallised, air-dried product always contains about 1·26% of water, which indicates that it is a solid solution of this inner salt and the quinonoid hydrate. Phenolsulphonephthalein gives an unstable *diammonium* salt, a *monoammonium*, a *sodium*, and a *disodium* salt. It also gives a *diacetate*, m. p. 165°, and a *dibenzoate*, m. p. 185–186° (decomp.). When heated with aniline for two hours at 140–150°, the phthalein gives *diphenylamine-sulphonephthalein*, a green compound. When pure phenolsulphonephthalein, suspended in water, is boiled with zinc dust, it gives a *zinc* salt from which, by decomposition with hydrogen sulphide, *dihydroxytriphenylmethanesulphonic acid*,



is obtained. This acid gives a *sodium* salt, and is very readily oxidised in the air to the sulphonephthalein.

When boiled with methyl alcohol containing 3% of hydrochloric acid, phenolsulphonephthalein gives, not an ester, but a colourless *monomethyl ether*, m. p. 178°, which resembles the methyl ether of phenolphthalein very closely in its properties and chemical behaviour. When heated for half an hour in a current of dry air at 170°, the colourless ether is converted into a red *methyl ether*, which, unlike the colourless ether, gives a stable *monoammonium* salt. Under similar conditions, a colourless *ethyl ether*, m. p. 171°, and a coloured *ether*, giving an ammonium salt, were obtained. Phenolsulphonephthalein, its salts, the coloured ethers, and diphenylaminesulphonephthalein are coloured and have the quinonoid structure, but the diacetate, the dibenzoate, and the colourless ethers are derivatives of the lactoid modification.

When tetrabromophenolsulphonephthalein is purified by crystallisation from glacial acetic acid it is colourless and has m. p. 279° (corr.). It has the lactoid, and not the carbinolsulphonic acid structure. Like phenolsulphonephthalein, it is tautomeric and gives coloured quinonoid and colourless lactoid derivatives. Its *hydrate*, its *diammonium*, *disodium*, and *monosodium* salts, and its *methyl ether* are coloured, and have the quinonoid structure. The

diacetate, m. p. 234°, and the *dibenzoate* are colourless and are derivatives of the lactoid form. The methyl ether gives an unstable *hydrochloride* and an *ammonium salt*. W. G.

The Nitration of Benzaldehyde and the Monotropy of o-Nitrobenzaldehyde. OSCAR LISLE BRADY and SAMUEL HARRIS (T., 1923, 123, 484—494).

Syntheses of Coumarin- and Conifer-aldehydes. H. PAULY and K. WÄSCHER (*Ber.*, 1923, 56, [B], 603—610).—Hydroxyphenylacraldehydes have hitherto been difficultly accessible substances, since their unusual tendency towards resinification under the influence of alkali hydroxide inhibits their preparation by alkaline condensation of hydroxyphenylaldehydes and acetaldehyde. A certain amount of success has been achieved by Tiemann by masking the hydroxyl group by using substances such as glucovanillin; it is not possible to use alkali for the removal of the glucose residue, but this can be effected with the aid of emulsin. A more convenient method is now described, which consists in masking the hydroxyl group by transforming it into the methoxymethoxy-residue, $\text{OMe}\cdot\text{CH}_2\cdot\text{O}-$; the latter is ultimately removed by cautious and rapid treatment with very dilute acid.

o-Methoxymethoxybenzaldehyde (cf. Höring and Baum, A., 1909, i, 572) condenses with acetaldehyde in aqueous-alcoholic, alkaline solution at 60° to form *o*-methoxymethoxycinnamaldehyde, $\text{OMe}\cdot\text{CH}_2\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{CHO}$, pale yellow crystals, m. p. 55°, b. p. 158—159°/3 mm., the yield being 37% of that theoretically possible. It is converted by short ebullition with acetic acid (50%) containing 0.3% of sulphuric acid into *o*-hydroxycinnamaldehyde, m. p. 133°. Similarly, *p*-methoxymethoxybenzaldehyde, b. p. 132—134°/9 mm. (cf. Höring and Baum, *loc. cit.*) is transformed into *p*-methoxymethoxycinnamaldehyde, a very viscous liquid which could not be caused to solidify, b. p. 158—160°/3 mm., and is converted into *p*-hydroxycinnamaldehyde, pale yellow needles, m. p. 134° (*semicarbazone*, m. p. 224°). 3-Methoxy-2-methoxymethoxybenzaldehyde, $\text{OMe}\cdot\text{CH}_2\cdot\text{O}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{CHO}$, colourless plates, m. p. 56°, b. p. 128—130°/2 mm., is obtained in 11% yield by the action of chloromethyl ether on a suspension of the sodium derivative of *o*-vanillin in toluene. It is converted by acetaldehyde into 3-methoxy-2-methoxymethoxycinnamaldehyde, pale yellow, lustrous platelets, m. p. 91°, which is hydrolysed in the usual manner to 2-hydroxy-3-methoxycinnamaldehyde, pale yellow leaflets, m. p. 131° (*semicarbazone*, almost colourless crystals, m. p. 198° after softening at 195°). 3-Methoxy-4-methoxymethoxybenzaldehyde, colourless needles, m. p. 40°, b. p. 145—149°/4 mm., is transformed in the usual manner into 3-methoxy-4-methoxymethoxycinnamaldehyde, pale yellow needles, m. p. 77—78°, b. p. 165—167°/4 mm., which is further transformed into 4-hydroxy-3-methoxycinnamaldehyde, pale yellow needles, m. p. 82.5° (*semicarbazone*, pale yellow crystals, m. p. 218°); the sodium hydrogen sulphite compound is described. The aldehyde is slowly oxidised to vanillin on exposure to air.

H. W.

Ring Closures from γ -Aryl-*n*-butyric Acids to Derivatives of 1-Ketotetrahydronaphthalene. F. KROLLPFEIFFER and W. SCHÄFFER (*Ber.*, 1923, 56, [B], 620—632).—The conversion of γ -phenyl-*n*-butyryl chloride into 1-ketotetrahydronaphthalene has been described by Kipping and Hill (*T.*, 1899, 75, 146). Since, however, Schroeter (*Chem. Ztg.*, 1920, 759) has succeeded in effecting similar ring closures with the tetrahydronaphthyl-*n*-butyric acids without the employment of a condensing agent, the authors have endeavoured with partial success to avoid the indirect method through the chloride in the case of the simpler phenyl compounds.

The preparation of the requisite γ -aryl-*n*-butyric acids is effected by the condensation of the necessary benzenoid hydrocarbon with succinic anhydride in the presence of aluminium chloride and subsequent reduction of the ketonic acid thus produced by amalgamated zinc and hydrochloric acid; the latter action only gives satisfactory yields if carried out at the atmospheric temperature.

γ -Phenyl-*n*-butyric acid is converted by treatment with concentrated sulphuric acid at the temperature of boiling water into 1-keto-1 : 2 : 3 : 4-tetrahydronaphthalene, b. p. 127°/13 mm. (semicarbazone, m. p. 217—220°), the yield being about 50% of that theoretically possible. Similarly, γ -*p*-tolyl-*n*-butyric acid is transformed into 1-keto-7-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene, colourless, crystalline aggregates, m. p. 32·5—33·5°, d_4^{25} 1·0569, d_4^{20} 1·072, n_a^{35} 1·55168, n_b^{35} 1·55674, n_β^{35} 1·57160, n_γ^{35} 1·58479, n_δ^{35} 1·563. The corresponding semicarbazone crystallises in colourless, slender needles, m. p. 224—225°. The ketone is reduced by amalgamated zinc and concentrated hydrochloric acid to 2-methyl-5 : 6 : 7 : 8-tetrahydronaphthalene, a colourless, mobile liquid, b. p. 224—226°, d_4^{25} 0·9541, d_4^{20} 0·950, $n_a^{15·1}$ 1·53316, $n_b^{15·1}$ 1·53719, $n_\beta^{15·1}$ 1·54907, $n_\gamma^{15·1}$ 1·55897, n_δ^{20} 1·535 (cf. Schroeter, A., 1921, i, 861). It is converted by bromine in the presence of carbon disulphide into 2-bromo-1-keto-7-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene, slender, colourless needles, m. p. 80·5°, which is transformed by boiling diethylaniline into a mixture of 1-keto-7-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene and 7-methyl- α -naphthol, small, colourless needles, m. p. 109°, b. p. 158—159°/12 mm.

p-Ethylbenzoylpropionic acid, m. p. 98—99°, is converted successively into γ -*p*-ethylphenyl-*n*-butyric acid, colourless, lustrous leaflets, m. p. 69—70°, and 1-keto-7-ethyl-1 : 2 : 3 : 4-tetrahydronaphthalene, a colourless liquid, b. p. 152—153°/12 mm., $d_4^{17·2}$ 1·0556, d_4^{20} 1·053, $n_a^{17·2}$ 1·55478, $n_b^{17·2}$ 1·55988, $n_\beta^{17·2}$ 1·57454, $n_\gamma^{17·2}$ 1·58752, n_δ^{20} 1·559 (semicarbazone, colourless needles, m. p. 223—225°). 2-Ethyl-5 : 6 : 7 : 8-tetrahydronaphthalene has b. p. 245—246°, $d_4^{17·6}$ 0·9499, d_4^{20} 0·948, $n_a^{17·6}$ 1·53072, $n_b^{17·6}$ 1·53474, $n_\beta^{17·6}$ 1·54627, $n_\gamma^{17·6}$ 1·55594, n_δ^{20} 1·534.

β -2 : 4-Dimethylbenzoylpropionic acid, m. p. 111—112°, yields γ -*m*-xylyl-*n*-butyric acid, m. p. 71°, which is converted by concentrated sulphuric acid in poor yield into 1-keto-5 : 7-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene, coarse prisms, m. p. 49—50°.

$d_4^{15.5}$ 1.0654, d_4^{20} 1.061, $n_a^{15.5}$ 1.55986, $n_D^{15.5}$ 1.56496, $n_B^{15.5}$ 1.57971, $n_\gamma^{15.5}$ 1.59284, n_D^{20} 1.563 (*semicarbazone*, slender, colourless needles, m. p. 234—235°). (The poor yield is due to the sulphonation of the acid; the sodium salt of sulpho-*m*-xylyl-*n*-butyric acid is described.) The ketone is more conveniently prepared from γ -*m*-xylyl-*n*-butyryl chloride either by the action of heat or, more rapidly, by means of aluminium chloride in the presence of light petroleum. It is reduced by amalgamated zinc and hydrochloric acid to 5 : 7-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene, a colourless liquid, b. p. 250—252°/atmospheric pressure, d_4^{20} 0.960, d_4^{21} 0.9589, n_a^{21} 1.53683, n_D^{21} 1.54094, n_B^{21} 1.55287, n_γ^{21} 1.56297, n_D^{20} 1.541.

1 : 2 : 3 : 4-Tetrahydronaphthalene and succinic anhydride yield β -2-tetrahydronaphthoylpropionic acid, m. p. 121—122°, which is converted into γ -tetrahydronaphthyl-*n*-butyric acid, colourless crystals, m. p. 49—50°. The latter substance is transformed by concentrated sulphuric acid into 1-keto-octahydroanthracene, m. p. 46—47°, b. p. 202°/13 mm. (*semicarbazone*, m. p. 252—253°). 2-Bromo-1-keto-octahydroanthracene crystallises in colourless needles, m. p. 110°; it is converted by boiling diethylaniline into 1-keto-octahydroanthracene and 1-hydroxy-5 : 6 : 7 : 8-tetrahydroanthracene, a colourless powder, m. p. 124°, which becomes brown on exposure to air.

The condensation of naphthalene with succinic anhydride leads to the formation of a difficultly separable mixture of β -1- and -2-naphthoylpropionic acids. β -1-Naphthoylpropionic acid, m. p. 131—132°, is prepared by the action of heat on α -naphthoyliso-succinic acid, decomp. 158°, which is obtained by condensing ethyl sodiomalonate with α -naphthyl bromomethyl ketone in the presence of benzene and subsequent hydrolysis of the product. Attempts to effect ring closure with mixtures of γ -1- and -2-naphthyl-*n*-butyric acids did not lead to any decisive result (cf. Schäfer, *Diss.*, Marburg, 1922).

β -*p*-Methoxybenzoylpropionic acid, m. p. 147—148°, is reduced to γ -*p*-methoxyphenyl-*n*-butyric acid, colourless leaflets, m. p. 59—60°. The latter acid is readily sulphonated by sulphuric acid, so that this reagent cannot be used for converting it into 7-methoxy-1-keto-1 : 2 : 3 : 4-tetrahydronaphthalene, which, however, is prepared by the action of heat or of aluminium chloride in the presence of light petroleum on γ -*p*-methoxyphenyl-*n*-butyryl chloride; it crystallises in colourless platelets, m. p. 60—61° (*semicarbazone*, m. p. 222—224° when rapidly heated).

β -Benzoyl- α -methylpropionic acid, $\text{CH}_3\text{Bz}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$, colourless needles, m. p. 139—140°, is converted into γ -phenyl- α -methyl-*n*-butyric acid, b. p. 174°/15 mm. (*anilide*, slender, colourless prisms, m. p. 140°). Concentrated sulphuric acid transforms the latter acid into 1-keto-2-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene, a colourless liquid, b. p. 132°/15 mm., $d_4^{20.9}$ 1.0600, d_4^{21} 1.061, $n_a^{20.9}$ 1.54669, $n_D^{20.9}$ 1.55154, $n_B^{20.9}$ 1.56542, $n_\gamma^{20.9}$ 1.57764, n_D^{20} 1.552; the *semicarbazone* crystallises in colourless leaflets, m. p. 199—201°, when rapidly heated.

H. W.

Halogenation. XXII. The Action of Bromine and Nitric Acid on Organic Compounds. Preparation of Nitrosyl Tribromide and the Formation of Tetrabromobenzoquinone.

RASIK LAL DATTA and NIHAR RANJAN CHATTERJEE (*J. Amer. Chem. Soc.*, 1923, 45, 480—482).—It has previously been shown (A., 1916, i, 705) that chloropicrin and tetrachloro-*p*-benzoquinone are formed by the exhaustive action of aqua regia on organic compounds. It has now been found that bromine and nitric acid behave similarly on organic compounds, giving rise to tetrabromobenzoquinone and a mixture of bromonitro-derivatives of methane. A mixture of hydrobromic and nitric acids gives the same results, but in this case nitrosyl tribromide is formed in the first instance. W. G.

β -Halogen-substituted Anthraquinone Compounds. F. W. ATACK (U.S. Pat. 1434980).— α -Halogenanthraquinone derivatives are converted into the corresponding β -derivatives when heated at 200° (or lower for a longer period) with concentrated sulphuric acid; chlorination may be effected simultaneously in presence of a chlorine carrier, such as iodine, if necessary. Generally, β -bromo-derivatives can be produced from α -bromo-derivatives, even in the presence of other substituents, such as sulpho-groups, and of amino-groups if in a different nucleus from the bromine.

CHEMICAL ABSTRACTS.

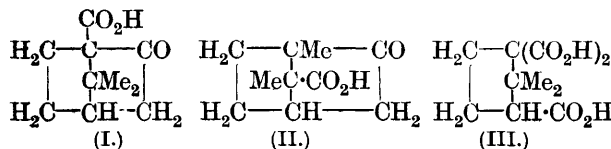
The Stereoisomeric Forms of Menthone. REGINALD SLATER HUGHESDON, HENRY GEORGE SMITH, and JOHN READ (*Proc. Roy. Soc. New South Wales*, 1922, 56, 170—175).—Four optically active menthones are theoretically capable of existence, and they may be respectively represented by the symbols *Dd*, *Ll*; *Ld* and *Dl*, where *d* and *l* indicate the optical effects of the 1-carbon atom and *D* and *L* are similarly used for the 4-carbon atom. Reasons are given for regarding the *l*-menthone obtained by the oxidation of natural *l*-menthol as having the *Ld* configuration, and the *d*- and *l*-isomenthones as being the *Dd* and *Ll* compounds, respectively. The optical effects of the two asymmetric carbon atoms would thus be opposed in the menthones and conjoined in the isomenthones. The catalytic hydrogenation of *dl*-, *d*-, and *l*-piperitones gave an inactive isomenthone, forming a sparingly soluble semicarbazone, m. p. 219—220°, and two highly active isomenthones having $[\alpha]_D^{20} +58.33^\circ$ and -57.40° , respectively. It is suggested that these substances belong to a type of partly racemic compounds, of which four are theoretically possible, namely, *Dd*, *Dl*; and *Ld*, *Ll*, representing 1-racemic isomenthones, and *Dd*, *Ld*; and *Dl*, *Ll*, representing 4-racemic isomenthones. Finally, two wholly racemic compounds are to be expected, *Dd*, *Ll*; and *Ld*, *Dl*, being *i*-menthone, and *i*-isomenthone, respectively. G. F. M.

Two Definite Compounds of Nitrogen Peroxide and Camphor. PAUL PASCAL and GARNIER (*Compt. rend.*, 1923, 176, 450—452).—A thermal analysis of the binary mixture, nitrogen

peroxide and camphor, shows the existence of two definite compounds, namely, $5\text{N}_2\text{O}_4 \cdot 4\text{C}_{10}\text{H}_{16}\text{O}$, m. p. -52° , and $2\text{N}_2\text{O}_4 \cdot 3\text{C}_{10}\text{H}_{16}\text{O}$, m. p. -45.5° . The former gives with nitrogen peroxide a series of solid solutions containing a maximum of 27% of camphor at -60° . The binary system gives three eutectic mixtures, namely, a mixture, m. p. -60° , containing 60.5% of nitrogen peroxide, a mixture, m. p. -55.5° , containing 34.5% of nitrogen peroxide, and a mixture, m. p. -46.5° , containing 26% of nitrogen peroxide.

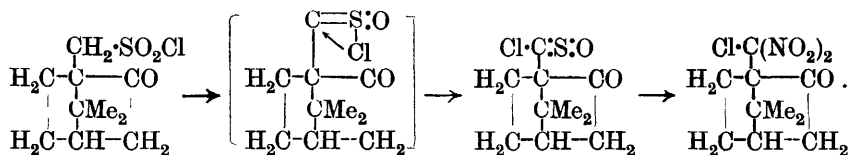
W. G.

Transformation of *d*- and *l*-Camphorsulphonyl Chlorides into 10-*d*- and -*l*-Chlorosulphoxidocamphor. The Constitution of Ketopinic Acid and of Reyckler's Camphorsulphonic Acid. E. WEDEKIND, D. SCHENK, and R. STÜSSER (*Ber.*, 1923, 56, [B], 633—649).—It has been shown previously (Wedekind and Schenk, A., 1911, i, 190) that the action of strong tertiary bases on simple aromatic sulphonyl chlorides does not lead to the isolation of the expected "sulphens," $\text{CHAr} \cdot \text{SO}_2$, which, however, are possibly formed as unstable intermediate products which break down into stilbenes and sulphur dioxide. In the hope of isolating such sulphens or derived substances containing sulphur, an examination has been made of more complex sulphonyl chlorides, for which purpose Reyckler's *d*-camphorsulphonyl chloride has been selected. The substance reacts readily with triethylamine (or pyridine), giving a mixture of equimolecular amounts of *d*-chlorosulphoxidocamphor, $\text{C}_{10}\text{H}_{13}\text{O}_2\text{SCl}$, and triethylammonium *d*-camphorsulphonate. The constitution of the former compound is mainly deduced from a study of its action on boiling dilute nitric acid, with which it yields sulphuric acid, a chlorodinitrocamphor (thus showing that the camphor skeleton is preserved practically unchanged in chlorosulphoxidocamphor and that the chlorine is united to a carbon atom), and *d*-ketopinic acid. *r*-Ketopinic acid has been obtained by Gilles and Renwick (T., 1897, 69, 1397, 1402) by oxidising pinene hydrochloride with fuming nitric acid, but its constitution has not previously been elucidated. Its



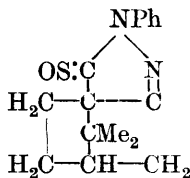
mode of formation renders one of the annexed formulae (I or II) possible, and the choice in

favour of I is rendered possible by the observation that it is oxidised to a tricarboxylic acid [carboxyapocamphoric acid (formula III)], which loses carbon dioxide when heated and yields apocamphoric acid. Since ketopinic acid is derived from camphor solely by alteration of the groups attached to the carbon atom 10, it follows that the substituents in chlorosulphoxidocamphor must also be present in this position, and the reaction may therefore be shown by the scheme :



Reychler's camphorsulphonic acid was regarded by the discoverer as an α -compound, whereas subsequently Armstrong and Lowry (T., 1902, 81, 1469) brought forward evidence to show that the sulphonic acid group is attached to carbon atom 6 or 10, preference being finally accorded to the first possibility. The relationship of camphorsulphonyl chloride to ketopinic acid places beyond doubt the attachment of the acid residue to carbon atom 10, and this conception is in excellent agreement with the observed ability of camphorsulphonamide to yield an internal anhydride, since it indicates the production of a heterocyclic five-membered ring.

d-Camphorsulphonyl chloride reacts very energetically with triethylamine or pyridine, giving *d*-chlorosulphoxidocamphor, pale yellow, prismatic needles, m. p. 85° , $[\alpha]_D^{25} + 58.28^\circ$ in benzene, $[\alpha]_D^{25} + 136.2^\circ$ in chloroform. *l*-Chlorosulphoxidocamphor, prepared in a similar manner, has $[\alpha]_D^{25} - 58.40^\circ$ in benzene and $[\alpha]_D^{25} - 136.2^\circ$ in chloroform. *r*-Chlorosulphoxidocamphor is prepared by mixing equal quantities of its optically active components; it has m. p. 103.5° , and is shown to be a true racemate. The chlorine atom in these compounds is relatively firmly attached, and is not removed by silver oxide or by boiling aqueous silver nitrate solution. The protracted action of steam leads to the production of hydrogen chloride, sulphur dioxide, and sulphur, the latter being also prepared by the action of methyl-alcoholic ammonia. Reduction with stannous chloride gives an uncrystallisable substance containing sulphur. It is remarkable that the chlorine atom is very readily removed by the action of phenylhydrazine, with the production of phenylhydrazine hydrochloride, a substance which the author terms *norcamphorylsulphoxide-N-phenylpyrazolone* (annexed formula), decomp. 155° after forming a clear, reddish-brown resin at about 80° . Chlorosulphoxidocamphor reacts with semicarbazide to give a chlorine-free product, m. p. $165-167^\circ$ (decomp.), which could not be caused to crystallise.



The oxidation of the 10-chlorosulphoxidocamphors with nitric acid leads to the optically active 10-chloro-10:10-dinitrocamphors, m. p. 150.5° (decomp.), $[\alpha]_D^{25}$ for which is respectively $+52.06^\circ$ and -52.13° in benzene and $+55.47^\circ$ and -55.40° in chloroform. The optically active *ketopinic acids* are simultaneously produced; they can also be obtained by the oxidation of the chlorosulphoxidocamphors with potassium permanganate or by the hydrolysis of the active 10-chloro-10:10-dinitrocamphors with water or, preferably, with water and calcium carbonate or slaked lime. *d*-Ketopinic acid has m. p. 234° , $[\alpha]_D^{25} + 28.02^\circ$ in benzene, whereas the

constants of the *l*-isomeride are m. p. 234°, $[\alpha]_D^{18} -27.67^\circ$ in benzene; *r*-ketopinic acid has m. p. 234°. The active ketopinic acids are converted into the corresponding *phenylhydrazones*, m. p. 150.5°, by the union of equal quantities of the antipodes, of which *r*-ketopinic acid phenylhydrazone, m. p. 126.5°, is prepared; this is identical with the product obtained from *r*-ketopinic acid derived from pinene hydrochloride [the m. p. 146° recorded for the inactive phenylhydrazone by Gilles and Renwick (*loc. cit.*) appears to be erroneous].

The chlorodinitrocampaophors are reduced by stannous chloride and hydrogen chloride in the presence of glacial acetic acid to the corresponding *ketopinonitriles*, m. p. 197—198°, $[\alpha]_D^{18} +26.45^\circ$ and $[\alpha]_D^{18} -26.10^\circ$, respectively, when dissolved in chloroform. Reduction appears to proceed along the lines indicated by the schemes $R \cdot CCl(NO_2)_2 \rightarrow R \cdot C(NH_2) \cdot NOH + HCl, NH_2 \cdot OH \rightarrow R \cdot CN$ and $R \cdot CCl(NO_2)_2 \rightarrow R \cdot CCl(NH_2)_2 + HCl, NH_3 \rightarrow R \cdot CN$, since both ammonia and hydroxylamine are also formed. The nitriles are hydrolysed by boiling sulphuric acid (50%) to the ketopinic acids, m. p. 234°. H. W.

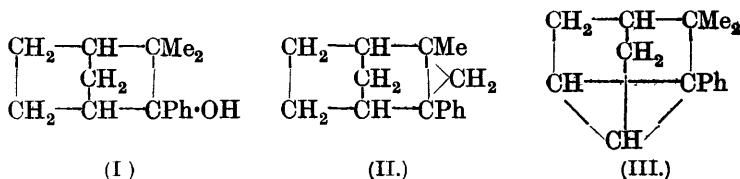
Optically Active Heavy Metal Complexes. I. LIFSCHITZ (*Rec. trav. chim.*, 1922, 41, 627—636).—Complex heavy metal salts and co-ordination compounds of hydroxymethylenecamphor are described. Earlier measurements of the rotatory dispersion of, for instance, aqueous solutions of tartaric acid in the presence of alkali and the salt of a heavy metal are open to the objection that such solutions may contain several optically active complexes, and that the observed experimental figures may be due to the superposition of the effects of their various components. The ferric, acid copper, normal copper, nickel, uranyl, aluminium, chromic, cobaltic, carbonatotetrammine and diethylenediamine-carbonato salts of hydroxymethylenecamphor are described. These compounds are soluble in organic media, so that the above objection presumably does not apply. The salts are all well-defined compounds with high rotatory powers, and, with the exception of the aluminium salt, all are brightly coloured. The rotatory dispersion of these compounds has been measured in the neighbourhood of their absorption bands, and has been found to be normal in some cases and anomalous in others. With the exception of the normal copper salt, however, none of these compounds exhibits the Cotton effect in the visible region of the spectrum, in spite of the fact that they all show characteristic selective absorption. The chromic salt is noteworthy in that its solutions in organic liquids exhibit strong dichroism and its rotatory dispersion curve shows both a maximum and a minimum in the visible region of the spectrum.

Similar ferric, chromic, and cobaltous derivatives of nitrocamphor are described. H. H.

***tert*-Phenylcamphenilol, its Conversion into Phenyl- α -pericycloapocamphane and Transformation into Phenylapocamphor.** MARIA BREDT-SAVELSBERG (*Ber.*, 1923, 56, [B], 554—561).—*tert*-Phenylcamphenilol has been prepared and its dehydration investigated since the process appeared to be of con-

siderable interest owing to the accompanying, enforced change of the carbon skeleton.

[With FRANZ TOUSSAINT.]-*tert.*-*Phenylcamphenilol* (formula I), a colourless, viscous liquid, b. p. $122^{\circ}/4$ mm., $160-166^{\circ}/13$ mm.,



about 276° /atmospheric pressure (slight decomp.), d_4^{14} 1.0717, n_D^{14} 1.55518, is obtained by the action of magnesium phenyl bromide on camphenilone in the presence of ether (the corresponding optically active compound has $[\alpha]_D +11.2^{\circ}$). It is a remarkably stable substance which is only slowly attacked by metallic sodium. It does not appear to yield a crystalline phenylurethane. The action of thionyl chloride or phosphorus pentachloride on it yields a mixture of the chloride and the hydrocarbon formed from the latter by loss of hydrogen chloride; treatment of the crude product with sodium phenoxide (or prolonged heating of *tert.*-phenylcamphenilol with acetic anhydride at $170-180^{\circ}$) yields *phenyl- α -pericycloapocamphane*, a colourless, mobile liquid, b. p. $96-97^{\circ}/5$ mm., d_4^{25} 1.00609, n_D^{25} 1.54710, which is stable towards permanganate. Its mode of formation renders possible the alternative formulæ II and III, of which the latter is preferred mainly on account of the observation that the inactive hydrocarbon is obtained from the optically active tertiary alcohol, whereas a substance of the constitution II is asymmetric, and would probably therefore be optically active.

Phenyl- α -pericycloapocamphane is converted by glacial acetic acid in the presence of a little concentrated sulphuric acid at $60-65^{\circ}$ into *phenylapoisobornyl acetate*, b. p. $142-143^{\circ}/4$ mm., d_4^{20} 1.06888, n_D^{20} 1.53003, and by anhydrous formic acid at 70° into *phenylapoisobornyl formate*, b. p. $127-128^{\circ}/2$ mm. The esters are hydrolysed with some difficulty to *phenylapoisoborneol* (annexed formula), a liquid, b. p. 145° , d_4^{12} 1.0666, n_D^{21} 1.55518. The latter substance is oxidised by chromic acid in glacial acetic acid solution to *phenylapocamphor*, b. p. $143^{\circ}/55$ mm. (*semicarbazone*, decomp. 199°) and by potassium permanganate in alkaline solution to *phenylapocamphoric acid* (annexed formula), decomp. 206° , which is transformed when distilled into the corresponding *anhydride*, m. p. $208-209^{\circ}$.

H. W.

Chemistry of the Phellandrenes. ERIC HURST, HENRY GEORGE SMITH, and JOHN READ (*Proc. Roy. Soc. New South Wales*, 1922, 56, 176-179).—*l*- α -Phellandrene gives as already recorded by Wallach and by Schreiner a mixture of two nitrosites, of which

the less soluble, or α -nitrosite, was found to melt at 120—121°, agreeing with the figure given by Schreiner, but somewhat higher than that given by Wallach. Solutions of *l*- α -phellandrene α -nitrosite in chloroform and in other organic solvents exhibited pronounced mutarotation, leading in every case to optical inversion in course of time. This observation has an important bearing on the discrepancy between the values for $[\alpha]_D$ given by the above-mentioned authors, and on the application of the nitrosite reaction for the diagnosis of phellandrenes in essential oils. The initial value found for $[\alpha]_D^{20}$ in freshly prepared chloroform solution was +137.7°. The β -nitrosite of *l*- α -phellandrene also appears to exhibit somewhat similar changes. G. F. M.

Australian *Melaleucas* and their Essential Oils. VI

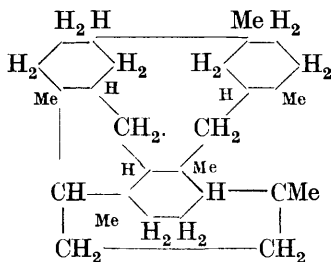
R. T. BAKER and H. G. SMITH (*Proc. Roy. Soc. New South Wales*, 1922, 56, 115—124).—The oil of *Melaleuca ericifolia* has the following constants: d^{15}_4 0.8938, α_D +13.3, n^{20}_D 1.4705. Between 168° and 190°, 52% distilled, consisting principally of *d*-pinene, *d*-limonene and dipentene, together with some cineol and terpineol; 26% distilled between 190° and 215°, consisting largely of terpineol. The remainder, about 15%, was mainly a sesquiterpene. The cineol was less than 10% of the total oil, and the oil cannot therefore replace the cajuput oil of commerce, which should contain at least 50% of cineol, and much less terpenes. The chief oxygenated constituent is terpineol, which imparts a more aromatic odour to the oil than that of cajuput oil. The oil of *M. Deanei* was only obtained in 0.7% yield from the leaves of the plant, and it was found to consist largely of *d*-pinene, together with about 15% of cineol and 4% of a high boiling alcohol, probably terpineol. The oil had the following characters: d^{15}_4 0.8888, α_D +22.7°, and n^{22}_D 1.4646. It has no economic value. G. F. M.

The Occurrence of *l*-Phellandrene in the Oil of *Melaleuca acuminata*. HENRY G. SMITH (*Proc. Roy. Soc. New South Wales*, 1922, 56, 159—161).—The oil of *Melaleuca acuminata* has the following characters: d^{15}_4 0.8935, α_D -12.8°, n^{20}_D 1.4690, acid value 1.1, saponification value 4.5, saponification value after esterification 21.2, cineol content 43.7%. Thirty per cent. distilled between 165° and 170°, and 62% between 170° and 190°. After separation of the cineol as phosphate, the residual terpenes distilled to the extent of 80% between 166° and 172°. The chief constituent was apparently *l*-phellandrene, which was identified by its nitrosite. It is probable that this *l*-phellandrene will be found not to be identical with the *l*-phellandrene occurring in the oils of species of the "peppermint group" of eucalypts. G. F. M.

The Constituents of Indian Turpentine from *Pinus longifolia*, Roxb. II. JOHN LIONEL SIMONSEN and MADYAR GOPAL RAU (*T.*, 1923, 123, 549—560).

Constitution of Caoutchouc. MAITLAND C. BOSWELL [with A. HAINBLETON, R. R. PARKER, and R. R. McLAUGHLIN] (*Trans. Roy. Soc. Canada*, 1922, 16, III, 27—47).—The reactions used in

the investigation of the constitution of caoutchouc have been too drastic, and have given misleading indications of a fairly simple molecule. The earlier work is reviewed and certain new derivatives



are described. On the result of these researches a new formula (appended) is suggested which, it is claimed, adequately expresses the whole of the facts. Oxidation of caoutchouc dissolved in carbon tetrachloride by aqueous hydrogen peroxide yields a white, gummy mass, $C_{30}H_{48}O$, which readily undergoes atmospheric oxidation to a compound, $C_{25}H_{40}O_2$; this compound can also be obtained by

the atmospheric oxidation of the pasty compound, $C_{25}H_{40}O$ which is produced by the action of cold aqueous potassium permanganate on a solution of deresinised caoutchouc in carbon tetrachloride. Another compound isolated from the hydrogen peroxide reaction product had the composition $C_{15}H_{24}O$. By the action of iodine and aqueous hydrogen peroxide on caoutchouc dissolved in carbon tetrachloride a compound, $C_{25}H_{40}O_8I$, was obtained. Atmospheric oxidation of thinly sheeted deresinised caoutchouc in sunlight gave a tough, rubbery substance, $C_{10}H_{16}O$, and a brittle, transparent mass, $C_{25}H_{40}O_9$, which were separable by making use of the solubility of the former in carbon disulphide. Structural formulæ are given showing the relationship of these products with the parent caoutchouc (see also *J.S.C.I.*, 1923, 42, 63A).

D. F. T.

Amber. A. TSCHIRCH, E. AWENG, C. DE JONG, and E. S. HERMANN (*Helv. Chim. Acta*, 1923, 6, 214—225; cf. Tschirch and Aweng, A., 1895, i, 384).—A chemical comparison has been made of the two forms of amber, succinite and gedanite. The material was extracted with alcohol, the soluble portion again extracted with light petroleum, and the insoluble portion dissolved in ether. By extracting the ethereal solution with ammonium carbonate solution, two *succinoxyabietic acids* were obtained, that from succinite having the composition $C_{30}H_{30}O_4$, m. p. 122°, and that from gedanite, $C_{19}H_{28}O_4$, m. p. 120°. It is suggested that these may be homologues; they are present to the extent of about 0.5% in the amber. They are monobasic acids. By extracting the above ethereal solution next with sodium carbonate solution there was obtained a solution of *succinoabietinolic acid*, $C_{40}H_{60}O_5$, the composition being the same from both forms of amber. This also is a monobasic acid, and is present to the extent of 12%. These acids may be formed by autoxidation of resinic acids of the type of abietic acid, $C_{20}H_{30}O_2$. When the extract soluble in light petroleum is treated with 5% sodium hydroxide solution, a residue is left which after purification has the composition $C_{40}H_{60}O_2$ and is termed *succinoabietinol*; it is present to the extent of 6%. Distillation of the alkaline solution with steam yielded about 0.2% of *d-borneol*, and from the alkaline solution addition of acid precipitates a new

monobasic acid, *succinosilvinic acid*, $C_{24}H_{36}O_2$, m. p. 104° , present to the extent of about 4%. The portion of amber insoluble in alcohol when hydrolysed with alkali gives succinic acid, about 2%, and a *succinoresinol*, $C_{12}H_{20}O$, about 3% on the original amber. The latter is undoubtedly the alcohol with which the succinic acid is combined. The trace of sulphur which is present in succinite but not in gedanite is associated with the succinoresinol. The remainder of the portion of the amber insoluble in alcohol, the *succinoresen*, which forms 65% of the whole in both succinite and gedanite, has m. p. 324° , and is quite indifferent to alkalis. It has the composition $C_{22}H_{36}O_2$ and by distillation in a vacuum gives a mixture of phenols and terpenes. The possibility of the formation of the above constituents of amber from the resinic acids such as abietic acid found in recent conifer resins is discussed.

E. H. R.

Studies of the Glucosides. II. Arbutin. ALEXANDER KILLEN MACBETH and JOHN MACKAY (T., 1923, 123, 717—724).

Tannins. II. Chinese Tannin. P. KARRER, HARRY R. SALOMON, and J. PEYER (*Helv. Chim. Acta*, 1923, 6, 3—36).—E. Fischer considered Chinese tannin to be practically identical with penta-*m*-digalloyl-glucose (A., 1919, i, 87, 278). It is now shown, however, that the tannin is not a uniform substance, but can be separated by a suitable process into fractions differing considerably in rotatory power. The fractionation was accomplished by precipitating an aqueous solution of the tannin with aluminium hydroxide. The latter first dissolves in the tannin solution, but after a short time a precipitate appears, a compound of tannin and alumina, the nature of which is not yet understood. The compound was decomposed with acid in the cold, and the tannin extracted with ethyl acetate. The tannin first precipitated had the lowest rotatory power, the last had the highest. After a series of about eighty fractionations, the extreme fractions had rotations of $+30^\circ$ and $+157^\circ$, respectively, in water, and $+40.6^\circ$ and $+51.5^\circ$ in pyridine. Similar results were obtained with different commercial samples of tannin and with samples extracted from the galls with acetone.

When the fractions having $[\alpha]_D +80^\circ$ and above were treated with glacial acetic acid and hydrogen bromide at the ordinary temperature, they gave a 1-bromotetra g alloylglucose, a substance difficult to purify, which was readily converted by acetyl bromide into 1-bromotetra(triacetyl g alloyl)-glucose, $C_{58}H_{51}O_{34}Br$, an amorphous substance, $[\alpha]_D +59.5^\circ$ in acetone. This was identical with a substance obtained in an exactly similar manner from synthetic penta(triacetyl g alloyl)-glucose, this product having $[\alpha]_D +58.83^\circ$. When warmed with sodium acetate and acetic anhydride, the above compound gave tetra(triacetyl g alloyl)-1-acetylglucose, $C_{34}H_{22}O_{15}(OAc)_{13}$. This is a white, amorphous substance; the specimen from the high rotating tannin fraction had $[\alpha]_D +44.3^\circ$ in acetone, sinters from 110° , m. p. 130 — 135° ; the sample from synthetic penta(triacetyl g alloyl)-glucose had $[\alpha]_D +44.6^\circ$ and a

similar m. p. When treated with methyl alcohol and silver carbonate, bromo-1-tetra(triacetylgalloyl)-glucose gave *tetra(triacetylgalloyl)- β -methylglucoside*, $C_{58}H_{51}O_{33} \cdot OMe$, $[\alpha]_D +31.8^\circ$ in acetone (from tannin) and $+31.5^\circ$ (synthetic). Further, this methylglucoside was proved identical with that prepared from β -methylglucoside and triacetylgalloyl chloride, which had $[\alpha]_D +32.9^\circ$. On the other hand, *tetra(triacetylgalloyl)- α -methylglucoside* from α -methylglucoside and triacetylgalloyl chloride had $[\alpha]_D +42.3^\circ$ in acetone.

The above observations establish conclusively that the higher rotating fractions of Chinese tannin are derived from a penta-galloylglucose. The variations among the higher rotating fractions must be due to variations in the number and disposition of the depsidic galloyl groups present as digalloyl residues. The yield of tetra(triacetylgalloyl)-1-acetylglucose from any particular tannin fraction may be regarded as practically quantitative; hence the weight of this compound obtained gives a quantitative estimate of the number of gallic acid residues originally present. The mean number found for the different fractions was between 8 and 9 gallic acid residues per mol. of dextrose. Probably the different fractions contain from octa- to deca-galloylglucoses.

The lower rotating tannin fractions gave 1-bromotetra(triacetylgalloyl)-glucose and other derivatives differing markedly in rotatory power from those derivatives obtained from penta(triacetylgalloyl)-glucose. These fractions probably contain impurities besides the higher galloylated glucoses. It is concluded that Chinese tannin is a mixture of closely related galloylated glucoses, and that this complexity is the cause of its colloidal character. The pure substances must be very sparingly soluble in water, but the mixture forms colloidal supersaturated solutions. The living organism here makes use, as in the case of albumin, of the property possessed by insoluble substances of forming colloidal solutions in admixture with other substances of closely related structure.

E. H. R.

Structure and Formation of Humic Acids and Coal. J. MARCUSSEN (*Z. angew. Chem.*, 1923, **36**, 42—43; cf. A., 1921, ii, 590; 1922, i, 437).—The absence of furan derivatives from, and the presence of benzene derivatives among, the products of the oxidation under pressure of humic acids furnishes no evidence whatever for the absence of furan nuclei in these substances, or for a benzene structure, since in the first place furan derivatives would not remain undecomposed under the conditions of the oxidation, and, secondly, benzene derivatives are obtained under similar conditions from cellulose and similar substances which certainly do not themselves possess a benzene structure. Eller's synthesis of humic acids by the oxidation of phenols with permanganate likewise furnishes no proof of a hydroxyquinonoid structure, since the boiling nitric acid used to obtain the nitro-compound, which was similar to the nitro-derivatives of the humic acids, would have oxidised the quinone nuclei, just as benzo-

quinone is converted by oxidising agencies into maleic acid, of which the anhydride is actually a furan derivative. The formation of chloranil by the oxidation of humic acids with potassium chlorate and hydrochloric acid can equally well have originated from a difuran derivative. With regard to the formation of coal, the humic acids originating from wood are converted by loss of carbon dioxide and water into pyrohumic acid and pyrohumic ketone, which, together with bitumen, cellulose, lignin, and mineral matter form brown coal. This is then converted by heat and pressure into ordinary coal and anthracite, and the synthetic production can be carried out by heating brown coal in a light mineral oil at 300° for twelve hours in a closed tube. The product is black, and shows all the properties of coal, being, unlike the original material, insoluble in molten alkali hydroxide, and giving no lignin reaction with dilute nitric acid. The synthetic coal differed from the natural product only in the absence of the asphaltic substances, the carboides, which are formed in nature from the waxy constituents of brown coal, and to which the lustre of the coal is due.

G. F. M.

Benzopyronesulphonic Acids and Coumarinmercaptans.

MARGARETE KRÜGER (*Ber.*, 1923, 56, [B], 480—488).—4 : 7-*Dimethylcoumarin-6-sulphonic acid*, colourless, slender needles, m. p. above 285° after previous darkening, is obtained by the addition of 4 : 7-dimethylcoumarin to sulphuric acid containing 20% of sulphur trioxide at 0° and heating the mixture at 80° after solution has become complete at the atmospheric temperature; the *sodium*, *potassium*, and *ammonium* salts are described. The dry sodium salt is transformed by phosphorus pentachloride at 160—170° into 4 : 7-dimethylcoumarin-6-sulphonyl chloride, large, colourless prisms, m. p. 175°, which is converted by ethyl alcohol into *ethyl 4 : 7-dimethylcoumarin-6-sulphonate*, lustrous needles, m. p. 172°. The sulphonyl chloride is reduced by zinc dust in the presence of alcohol to 4 : 7-dimethylcoumarin-6-thiol, small needles, m. p. 255°, the *mercury* and *lead* derivatives of which are described.

In a similar manner, 4-methylcoumarin-6-sulphonic acid (cf. Harnisch, *Diss.*, Berlin, 1911) is transformed into 4-methylcoumarin-6-sulphonyl chloride, pale yellow rhombs, m. p. 137°, *ethyl 4-methylcoumarin-6-sulphonate*, colourless, lustrous needles, m. p. 151—152°, and 4-methylcoumarin-6-thiol, pale yellow, rhombic prisms, m. p. 180—181°.

4 : 6-Dimethylcoumarin-8-sulphonyl chloride crystallises in long, colourless needles, m. p. 179°, and is reduced with some difficulty to 4 : 6-dimethylcoumarin-8-thiol, colourless needles, incipient decomp. 246° (the *mercury* and *lead* derivatives are described). *Ethyl 4 : 6-dimethylcoumarin-8-sulphonate* forms lustrous needles, m. p. 182°.

3 : 4 : 7-Trimethylcoumarin is only slowly converted by sulphuric acid containing 50% of sulphur trioxide at 100° into 3 : 4 : 7-trimethylcoumarin-6-sulphonic acid, m. p. above 300°, the *sodium*, *lead*, and *potassium* salts of which are described. 3 : 4 : 7-Tri-

methylcoumarin-6-sulphonyl chloride crystallises in short, thick needles, m. p. 214°.

7-Methoxy-4-methylcoumarin is transformed into the corresponding *sulphonic acid*, a colourless, crystalline mass, under the same conditions as is 4:7-dimethylcoumarin. *Sodium 7-methoxy-4-methylcoumarin-6-sulphonate*, needles, and the corresponding *potassium* and *barium* salts are described. The sodium salt is converted by phosphorus pentachloride at 180° into *7-methoxy-4-methylcoumarin-6-sulphonyl chloride*, lustrous rhombs, m. p. 201°, which is further transformed into *ethyl 7-methoxy-4-methylcoumarinsulphonate*, needles or leaflets, m. p. 199°, and *7-methoxy-4-methylcoumarin-6-thiol*, small leaflets, m. p. 178° (the *mercury*, *lead*, and *sodium* compounds are described).

The coumarinthiols resemble the coumarins in their behaviour towards bromine; thus 4:7-dimethylcoumarin-6-thiol gives the corresponding *dibromide*, $C_{11}H_{10}O_2SBr_2$, long needles, m. p. 271°, which is readily decomposed by water into the thiol and bromide.

Chromone is not sulphonated at 70–80° by sulphuric acid containing 50% of sulphur trioxide. Under closely similar conditions, 2:3-dimethylchromone is transformed into 2:3-dimethylchromone-6-sulphonic acid, $SO_3H \cdot C_6H_3 \begin{smallmatrix} \diagup CO \cdot CMe \\ | \\ O - CMe \end{smallmatrix}$, a colourless mass which

does not melt at a definite temperature. The corresponding *sodium* salt (+4H₂O) and *lead* salt (+2H₂O) are described. Attempts to convert the sodium salt into the sulphonyl chloride were unsuccessful.

H. W.

Syntheses of Arylsulphone Derivatives of Naphthapyrones, Hydroxynaphthapyrones, and Trihydroxybenzopyrones.

JULIUS TRÖGER and RICHARD DUNKEL (*J. pr. Chem.*, 1922, [ii], 104, 311–334).—By a method previously described (Tröger and Bolte, A., 1922, i, 267), arylsulphone derivatives of naphthapyrones, hydroxynaphthapyrones, and trihydroxybenzopyrones have been prepared, and their fission by alkaline hydrolysis has been studied.

The arylsulphonylnaphthapyrones resemble, in their behaviour towards alkali hydroxides, the arylsulphonylcoumarins (Tröger and Bolte, *loc. cit.*). The action of moderately strong aqueous potassium hydroxide leads first, with disruption of the lactone ring, to the potassium salt of the coumarinic acid, from which, on acidification, the original pyrone is regenerated; if, however, the hydrolysis is continued, potassium carbonate and a styrene derivative are produced. Concentrated alkali hydroxide (30–40%) causes fission of the pyrone into the hydroxyaldehyde and the salt of the arylsulphonylacetic acid, the latter then passing into potassium carbonate and an arylmethylsulphone.

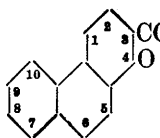
The hydroxyarylsulphonylcoumarins undergo fission more readily (*loc. cit.*) than the arylsulphonylcoumarins, but alkali carbonate and a styrene derivative are the sole products, the hydroxyaldehyde and the arylsulphonylacetic acid, or the arylmethylsulphone, not being formed. In contrast to this, the arylsulphonylhydroxynaphthapyrones are broken down by concentrated or

dilute alkali hydroxide into the relevant dihydroxynaphthaldehyde and an arylmethylsulphone.

Since trihydroxybenzaldehydes, which would be produced by the hydrolytic fission of arylsulphonyldihydroxycoumarins, are readily decomposed by alkali, the behaviour of the arylsulphonyldiethoxycoumarins has been studied, it being shown that whilst aqueous potassium hydroxide leads first to the salt of the coumarinic acid, acidification giving the original pyrone, by continued action neither an arylsulphone nor a styrol derivative is produced. The actual products have not yet been fully investigated.

It should be noted that the use of sodium ethoxide (Biilmann, A., 1912, i, 461), for the fission of the pyrones described, is impracticable owing to their insolubility in alcohol. With the exception of the 3-arylsulphonyl-5:7-dihydroxycoumarins and the arylsulphonyldihydroxynaphthapyrones, all the compounds described show a pronounced fluorescence.

The reaction between β -naphthaldehyde, benzenesulphonylacetic acid (one-third of this as sodium salt), and acetic anhydride commences in the cold, is completed on warming, and leads to 2-benzenesulphonyl-4:3- β -naphthapyrone, pale yellow prisms, m. p. 258°. Similarly, acetic anhydride, β -naphthaldehyde, and *p*-toluenesulphonylacetic acid give 2-*p*-toluenesulphone- β -naphthapyrone, pale yellow prisms, m. p. 275°, whilst the use of *p*-chlorobenzenesulphonylacetic acid leads to 2-*p*-chlorobenzenesulphonyl- β -naphthapyrone, small, yellow prisms, m. p. 285°. The action of aqueous potassium hydroxide solution (10–30%) leads to known products (see above). 2:6-Dihydroxynaphthaldehyde condensed with benzenesulphonylacetic acid gives 8-acetoxy-2-benzenesulphonyl- β -naphthapyrone, yellow leaflets, m. p. 246°, which on hydrolysis with 50% aqueous sulphuric acid gives 8-hydroxy-2-benzenesulphonyl- β -naphthapyrone, flat, yellow prisms, m. p. above 270°. 8-Acetoxy-2-*p*-toluenesulphonyl- β -naphthapyrone, flat, yellow prisms, m. p. above 265°, derived from *p*-toluenesulphonylacetic acid, gives 8-hydroxy-2-*p*-toluenesulphonyl- β -naphthapyrone, m. p. above 270°, on hydrolysis; if *p*-chlorobenzenesulphonyl acetic acid is used, 8-acetoxy-2-*p*-chlorobenzenesulphonyl- β -naphthapyrone, a reddish-yellow, microcrystalline powder, m. p. about 274°, is produced, giving on hydrolysis 8-hydroxy-2-*p*-chlorobenzenesulphonyl- β -naphthapyrone, thin needles of high m. p. 2:7-Dihydroxynaphthaldehyde, when condensed with the same three sulphonylacetic acids, gives 9-acetoxy-2-benzenesulphonyl- β -naphthapyrone, yellow leaflets, 9-acetoxy-2-*p*-toluenesulphonyl- β -naphthapyrone, yellow prisms, and 9-acetoxy-2-*p*-chlorobenzenesulphonyl- β -naphthapyrone, yellowish-red prisms; hydrolysis gives, respectively, 9-hydroxy-2-benzenesulphonyl- β -naphthapyrone, slender, yellow prisms, 9-hydroxy-2-*p*-toluenesulphonyl- β -naphthapyrone, flat, yellow leaflets; and 9-hydroxy-2-*p*-chlorobenzenesulphonyl- β -naphthapyrone, small, slender, yellowish-red prisms; all these compounds have high melting points. The action of aqueous alkali hydroxides on these hydroxy- or acetoxy-derivatives leads to known products (see above). The



condensation of pyrogallaldehyde with the same three acids gives 3-benzenesulphonyl-7:8-diacetoxycoumarin, small, white needles, m. p. 183°; 3-p-toluenesulphonyl-7:8-diacetoxycoumarin, white needles, m. p. 234°, and 3-p-chlorobenzenesulphonyl-7:8-diacetoxycoumarin, white needles, m. p. 223°, from which by hydrolysis 3-benzenesulphonyl-7:8-dihydroxycoumarin (+H₂O), yellow prisms, m. p. 255°, 3-p-toluenesulphonyl-7:8-dihydroxycoumarin (+H₂O), yellow needles, m. p. 258°, and 3-p-chlorobenzenesulphonyl-7:8-dihydroxycoumarin, yellow needles, m. p. 268° (decomp.), respectively, are obtained. From 2:4:5-trihydroxybenzaldehyde, 3-benzenesulphonyl-6:7-diacetoxycoumarin, white needles, m. p. 252°, 3-p-toluenesulphonyl-6:7-diacetoxycoumarin, white needles, m. p. 228°, and 3-p-chlorobenzenesulphonyl-6:7-diacetoxycoumarin, nodular aggregates of needles, m. p. 221°, are produced; hydrolysis gives, respectively, 3-benzenesulphonyl-6:7-dihydroxycoumarin, white needles of high m. p., 3-p-toluenesulphonyl-6:7-dihydroxycoumarin, yellow needles, m. p. 278° (decomp.), and 3-p-chlorobenzenesulphonyl-6:7-dihydroxycoumarin, small, yellowish-white needles of high melting point. From 2:3:5-trihydroxybenzaldehyde, 3-benzenesulphonyl-5:7-diacetoxycoumarin, white needles, m. p. 191°, 3-p-toluenesulphonyl-5:7-diacetoxycoumarin, white needles, m. p. 213°, and 3-p-chlorobenzenesulphonyl-5:7-diacetoxycoumarin, white needles, m. p. 211°, are obtained, giving on hydrolysis 3-benzenesulphonyl-5:7-dihydroxycoumarin, yellowish-brown, difficultly fusible needles, 3-p-toluenesulphonyl-5:7-dihydroxycoumarin, yellowish-white needles, m. p. 258—260° (decomp.), and 3-p-chlorobenzenesulphonyl-5:7-dihydroxycoumarin, very small, yellowish-white, difficultly fusible needles, respectively. The three last-mentioned dihydroxycoumarin derivatives, when alkylated by means of ethyl-alcoholic sodium ethoxide and ethyl iodide, give, respectively, 3-benzenesulphonyl-5:7-diethoxycoumarin, yellowish-white needles, m. p. 187°, 3-p-toluenesulphonyl-5:7-diethoxycoumarin, yellowish-white prisms, m. p. 227°, and 3-p-chlorobenzenesulphonyl-5:7-diethoxycoumarin, yellowish-white needles, m. p. 226°; the hydrolytic fission of these ethoxy-compounds requires the use of 20% aqueous alkali hydroxide, and has so far given, apart from recovered material, no recognisable product.

W. S. N.

The Composition of "Chelalbines." P. KARRER (*Helv. Chim. Acta*, 1923, 6, 232).—Fresh analyses of methylchelalbine (A., 1917, i, 349) give the empirical formula C₂₁H₁₇O₄NMe, instead of C₁₆H₁₂O₃NMe. The chelalbines are therefore to be regarded as alkyl dihydrochelerythrines, their formation corresponding with that of the alkyl dihydroberberines by the action of Grignard's reagent on berberine.

E. H. R.

Gel Formation in Quinine and Eucupine Solutions. PETER RONA and MAKI TAKATA (*Biochem. Z.*, 1922, 134, 97—107).—The conditions for gel formation in quinine and eucupine solutions have been rigidly defined. The range of variation of conditions for quinine is very small, 1.5 c.c. of a 1% quinine hydrochloride

solution with 3 c.c. of a $M/3$ phosphate mixture of P_H 6.85 giving a stiff gel which crystallised after five to ten minutes. In the case of eucupine, gels of considerable stability are obtainable. Gel formation depends on the P_H , values above 4.5 being inimical, on the particular buffering solution used, and on the concentration of the eucupine solution. The process of gelation can be followed by viscosity measurements, change of surface tension, and conductivity measurements. The gelation is reversible and the gel is suitable for Liesegang ring formation. H. K.

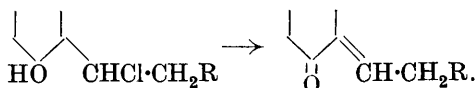
Indian Opium. III. The Meconic Acid Content of Indian Opium. HAROLD E. ANNETT and MATHURA NATH BOSE (*Mem. Dept. Agric. India*, 1922, 6, 215—221).—The meconic acid was estimated in various samples of opium by the addition of calcium chloride solution to an aqueous extract of the opium and decomposition of the calcium salt by hydrochloric acid (A., 1922, ii, 791). The quantity of meconic acid is in all cases found to be roughly equivalent to that of the total alkaloids present, whereas the soluble sulphate content of the latex increases as the alkaloidal content diminishes, and it is concluded that the alkaloids are present as meconates only, the sulphate being present in a mineral form. The acid reaction of the latex is due to dissociation of the weakly basic alkaloids such as narcotine and papaverine. P. M.

Preparation of Papaverine Nitrite. C. H. BOEHRINGER SOHN and HANS STENZL (Brit. Pat. 192298).—An aqueous solution of a papaverine salt is slowly treated with a 20% sodium nitrite solution either in the presence or absence of an organic solvent such as benzene. In the latter case, the oily reaction product consisting of a mixture of papaverine and papaverine nitrite is allowed to solidify, and after washing and drying is extracted with benzene until all the free alkaloid has been dissolved out. The residue consists of a 40% yield of the nitrite. When the reaction is carried out in presence of benzene the oil which separates quickly solidifies, and consists of almost pure papaverine nitrite. The substance forms an almost colourless, sandy powder which decomposes at about 140°, and, therapeutically, exhibits the tissue dilating properties of its components in an enhanced degree.

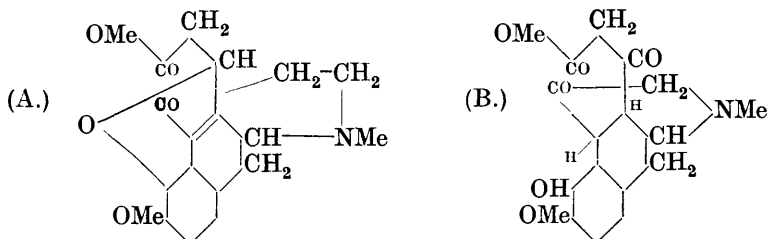
G. F. M.

Constitution of isoChondodendrine and Thebaine. FRANZ FALTIS and THEODOR HECKZO (*Monatsh.*, 1923, 43, 377—385).—Ethyl chloroformate, in presence of potassium hydroxide, converts isoChondodendrine into a mixture of dicarbethoxyhydrochloroisochondodendrine, dicarbethoxyisochondodendrine, and N-carbethoxyhydrochloroisochondodendrine. Only a partial interaction occurs with respect to the phenolic group in the alkaloid, as in the case of bulbocapnine (A., 1921, i, 579). The product is optically active, giving $[\alpha]_D -20^\circ$ in 96% alcohol. The chlorine atom present, from its reactivity, is apparently in the α -position with respect to the benzene ring. On evaporating an alcoholic solution of the

above mixture, a carmine-red *substance* is formed, presumably as shown below :



By applying the Angeli-Rimini "nitroxyl reaction" to thebaizone, it is shown that the latter does not contain a free aldehyde-group, and therefore probably has the annexed formula (A), a certain amount of tautomeric change occurring, giving, also, (B). This result points to the correctness of the formula suggested by Faltis (A., 1917, i, 411) for thebaine.



E. E. T.

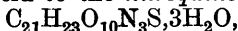
Strychnos Alkaloids. XXXVIII. Transformations of the Four Isomeric Brucinesulphonic Acids. HERMANN LEUCHS and HEINZ ZANDER (*Ber.*, 1923, 56, [B], 502—509).—An extension of the work of Leuchs and Geiger (A., 1909, i, 828) and Leuchs and Fricker (A., 1922, i, 677).

Brucinesulphonic acid II is converted by hot 5*N*-nitric acid into the *nitroquinone hydrate* II, $\text{C}_{21}\text{H}_{21}\text{O}_{10}\text{N}_3\text{S}$, orange-red, hexagonal, domatic prisms or rectangular plates which gives a *monosemicarbazone*, $\text{C}_{22}\text{H}_{24}\text{O}_{10}\text{N}_6\text{S}$, thin, lemon-yellow needles or prisms. It is reduced by tin and concentrated hydrochloric acid to the *aminoquinol hydrochloride*, $\text{C}_{21}\text{H}_{23}\text{O}_7\text{N}_3\text{S}\cdot\text{HCl}$, colourless prisms, the water added previously to give the $\cdot\text{CO}_2\text{H}|\text{HN}\cdot$ groups being again eliminated to $\cdot\text{CO}\cdot\text{N}\cdot$. It is converted by sulphurous acid into the *nitroquinol hydrate* II, $\text{C}_{21}\text{H}_{23}\text{O}_{10}\text{N}_3\text{S}\cdot 3\text{H}_2\text{O}$, aggregates of blackish-violet prisms or needles, which, like the corresponding compound from brucinesulphonic acid I, is converted by alcoholic hydrogen chloride into a violet *diethyl* derivative containing the carbethoxyl and the quinonoid, $\cdot\text{NO}\cdot\text{OEt}$, groups. It is transformed by acetic anhydride and sodium acetate into a *triacetyl* compound, $\text{C}_{27}\text{H}_{29}\text{O}_{13}\text{N}_3\text{S}$, short needles or five-sided plates.

Brucinesulphonic acid III is transformed by 5*N*-nitric acid into the *nitroquinone hydrate* III, $\text{C}_{21}\text{H}_{21}\text{O}_{10}\text{N}_3\text{S}$, orange-coloured, hexagonal platelets which is reduced by sulphurous acid to the *nitroquinol hydrate* III, $\text{C}_{21}\text{H}_{23}\text{O}_{10}\text{N}_3\text{S}\cdot 3\text{H}_2\text{O}$, lustrous, blackish-violet prisms or leaflets.

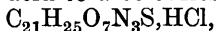
Brucinesulphonic acid, IV, and 5*N*-nitric acid at 0—10° yield the *quinone nitrite*, $\text{C}_{21}\text{H}_{20}\text{O}_7\text{N}_2\text{S}\cdot\text{HNO}_2\cdot 5\text{H}_2\text{O}$, red plates, whereas when the substances are heated together on the water-bath after

being diluted, the *nitroquinone hydrate*, $C_{21}H_{21}O_{10}N_3S \cdot H_2O$, orange-coloured, domatic prisms, separates. The latter substance is reduced by sulphurous acid to the *nitroquinol hydrate* IV,

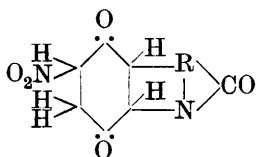


lustrous, pale reddish-violet needles or dark violet-red prisms.

The nitroquinone hydrate I is converted by saturated bromine water at 15–20° into the *product*, $C_{21}H_{23}O_{11}N_3Br_2S \cdot 2H_2O$, pale yellow, oblique platelets or short prisms in which the water may be present as solvent of crystallisation; this cannot be regarded as definitely established, since the compound is so unstable that it can only be desiccated at 20°. A profound change appears, however, to have taken place, since sulphurous acid removes the bromine without regenerating the violet nitroquinol, in place of which a *product*, $C_{21}H_{23}O_9N_3S$, pale yellow, oblique, four-sided plates, is obtained in which the nitro-group is retained, since it is reduced by tin and hydrochloric acid to a colourless *amine* salt,



which evolves ammonia when boiled with potassium hydroxide solution. The absence of an oxygen atom in the new nitro-compound as compared with the nitroquinol hydrate is explained by the loss of water involved in the conversion of the groups $\cdot CO_2H|:NH$ to $:N \cdot CO \cdot$; in this case, four atoms of hydrogen must



have been added, which occurs probably as indicated in the annexed formula, or a tautomeric form of it. One of the bromine atoms of the dibromide is certainly attached to the carbon atom united to the nitro-group, since it evolves bromonitromethane when boiled with water and gives a bromine-

free *acid*, $C_{19}H_{22}O_9N_2S$; the latter contains the sulphonic acid group, thus indicating that this radicle cannot have been present in the aromatic nucleus of brucine, which suffers fission under these conditions.

The nitro-compound, $C_{21}H_{23}O_9N_3S$, gives with bromine a *product*, $C_{21}H_{23}O_9N_3SBr_2$, which differs completely from the previous bromo-derivative. It is not de-halogenated by sulphurous acid; it gives bromopicroin when boiled with water.

H. W.

Halogen Derivatives of Quinine. SIGMUND FRÄNKEL, OTTO HERSCHMANN, and CHARLOTTE TRITT (*Ber.*, 1923, 56, [B], 433–438).—With the ultimate object of preparing derivatives of quinine in which the secondary alcoholic hydroxyl is replaced by an amino-group or the latter is present in the vinyl residue, the preparation of halogenated quinine compounds has been investigated. Quinine chloride is readily prepared by a modified method, but does not react in the desired sense with ammonia. On the other hand, quinine does not react simply with the bromides of phosphorus. Quinine chloride does not yield the bromide when heated above its melting point with potassium bromide, whereas with potassium iodide it gives a brown, amorphous substance.

Quinine is converted by phosphorus pentabromide (molecular

ratio, 3 : 7) in the presence of boiling chloroform into a resin which is partly dissolved when subsequently treated with ice-water. Addition of ammonia to the aqueous solution causes the precipitation of a colourless base, which rapidly becomes red. The precipitate does not appear to be uniform; after repeated purification, it gives analytical results approximating to those required by a dibromide. The portion which is undissolved by water contains two crystalline *tribromides*, $C_{20}H_{23}ON_2Br_3$, which have, respectively, m. p. 109° and $[\alpha]_D^{20} + 198^\circ$ in methyl-alcoholic solution and $235-245^\circ$ (corr. decomp.), $[\alpha]_D^{20} + 119^\circ$ in chloroform. When quinine and phosphorus pentabromide in the molecular ratio 3 : 5 are allowed to react under similar conditions, the product is a *tribromide*, decomp. 217° , whereas when the substances are employed in molecular proportions a *dibromide*, m. p. 130° , is obtained. When quinine is treated with a molecular proportion of phosphorus tribromide, a monobromide appears to be produced, which, however, is mixed with a considerable proportion of unchanged quinine, from which it cannot be separated.

The preparation of quinine chloride, $C_{20}H_{23}ON_2Cl$, from quinine hydrochloride and phosphorus pentachloride is described in detail; the substance crystallises with half a molecular proportion of benzene.

H. W.

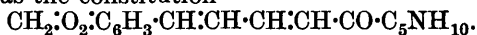
Japanese Yew Leaves. I. [Taxine]. HEISABURO KONDO and UMETARO AMANO (*J. Pharm. Soc. Japan*, 1922, 1074—1084; cf. Thorpe and Stubbs, T., 1902, **81**, 874).—Taxine isolated from the leaves of yew (*Taxus baccata*) produced in the Province of Hida is a white, amorphous powder of bitter taste, m. p. $105-111^\circ$ after sintering at 82° . Analysis confirmed the formula $C_{37}H_{51}O_{10}N$ previously assigned to the alkaloid; in 5 and 10% alcoholic solutions it has $[\alpha]_D^{18} + 32^\circ 20'$ and $+35^\circ$, respectively. Two chloroaurates were obtained (cf. *loc. cit.*), one, m. p. $90-105^\circ$ (decomp.), soluble into hot dilute hydrochloric acid, and the other, $C_{37}H_{51}O_{10}N \cdot HAuCl_4$, m. p. 110° (decomp.), insoluble in hot dilute hydrochloric acid. When heated with 5% sulphuric acid, the alkaloid is partly decomposed, a compound reducing Fehling's solution being produced, which, however, has not the characteristics of sugar. Emulsin is without action on the alkaloid. When heated with alcoholic potash taxine is decomposed into formic and acetic acids, an amorphous acid, m. p. $94-95^\circ$, and molecular weight 215, a crystalline acid (perhaps cinnamic acid), m. p. 133° , and a compound, $C_{23}H_{33}O_4N$, m. p. $105-110^\circ$, insoluble in dilute sulphuric acid. By bromination in glacial acetic acid, the alkaloid gave a *tetrabromide*, $C_{37}H_{51}O_{10}NBr_4$, a yellow, amorphous powder, whilst in dilute sulphuric acid solution, a *tribromide*, $C_{37}H_{51}O_{10}NBr_3$ or $C_{37}H_{51}O_{10}NBr_2 \cdot HBr$, a light yellow, amorphous powder, is formed.

K. K.

The Relationship between Constitution and Taste of Pepper. I. H. STAUDINGER and HERMANN SCHNEIDER (*Ber.*, 1923, 56, [B], 699—711).—The investigation was undertaken with the object of finding a suitable substitute for pepper. The taste

of the latter is due to the presence of piperine, the physiological action of which is largely influenced by the dispersivity; the required taste is only developed when it is very finely divided.

Piperine has the constitution



For the development of the pepper taste, it is essential that the piperidine should be in amide-like union with an aliphatic-aromatic acid. It is most noticeable with derivatives of δ -phenyl-*n*-valeric acid. The possibilities of variation of the acidic component have been fully examined whilst those connected with the basic portion will be described in a subsequent communication. It is found that the presence of the methylenedioxy-group and of double bonds is not essential to the development of pepper taste, whilst also the stereochemical configuration of the chain does not appear to exert a marked influence. On the other hand, it is necessary that the phenyl group and the four carbon atoms in the side chain should be present. Piperine may be completely replaced by a mixture of the piperidides of δ -phenyl- Δ^β - and - Δ^α -pentoic acids dissolved in phellandrene.

Cinnamylidenemalonic acid is conveniently prepared in 88.6% yield by the action of glacial acetic acid on a mixture of calcium malonate and cinnamaldehyde at 60–70° and subsequent protracted heating of the product at 80°, and finally at 100°. It is converted by phosphorus pentachloride in the presence of benzene into *cinnamylidenemalonyl chloride*, golden-yellow crystals, m. p. 83°, which is stable towards water, and is transformed into a piperide which has not a pronounced taste of pepper.

Cinnamaldehyde reacts with malonic acid in the presence of pyridine to give cinnamenylacrylic acid, m. p. 165°, whereas in the presence of quinoline, *allocinnamenylacrylic acid*, m. p. 138°, is produced. (*Pyridine hydrogen cinnamylidenemalonate* crystallises in colourless needles, m. p. 114–115°, decomp., and gives when heated cinnamenylacrylic acid, m. p. 165°, in about 60% yield, and an acid of lower melting point which has not been investigated. *Quinoline hydrogen cinnamylidenemalonate* has m. p. 114–115° and decomposes at about 130° yielding mainly *allocinnamenylacrylic acid*, m. p. 138°, other non-crystalline acids and very little acid, m. p. 165°.) Cinnamenylacrylic acid, m. p. 165°, is converted into the corresponding *chloride*, m. p. 47°, by the action of a solution of thionyl chloride in boiling light petroleum and thence into the *piperidide*, m. p. 91–92°, which after being ground with flour during ten days has a very pronounced taste of pepper. *allo*-Cinnamenylacrylic acid is converted by similar methods into a non-crystalline *chloride* and *piperidide*; the taste of the latter appears to be indistinguishable from that of its isomeride.

Cinnamylidenemalonic acid is reduced by sodium amalgam in faintly alkaline solution to dihydrocinnamylidenemalonic acid, which is decomposed in boiling aqueous solution into δ -phenyl- Δ^β -pentoic acid; the corresponding *chloride*, a colourless liquid, b. p. 139–140°/12 mm., 98–100°/0.2 mm., prepared by the action of thionyl chloride in the presence of benzene or light petroleum;

the *anilide*, m. p. 80—82°; the *ethyl* ester, b. p. 154—156°/11 mm., and the *piperidide*, a viscous liquid, b. p. 163—165°/0·2 mm., are described. If, on the other hand, dihydrocinnamylidenemalononic acid is decomposed in the presence of boiling pyridine, it gives mainly δ -phenyl- Δ^{α} -pentenoic acid; the corresponding *chloride*, a colourless liquid, b. p. 149—150°/15 mm., *anilide*, m. p. 115°; *ethyl* ester, a colourless liquid, b. p. 156—159°/13 mm., and *piperidide*, a viscous liquid, b. p. 164—169°/0·2 mm., are described.

[With E. PRISTER.]— δ -Phenyl- Δ^{γ} -pentenoic acid is converted by thionyl chloride in the presence of boiling light petroleum into the corresponding *chloride*, b. p. 100—105°/0·15 mm., and thence into the *piperidide*, a pale yellow, viscous liquid, b. p. 165—167°/0·2 mm., which has a very marked taste of pepper.

[With H. BRÜTSCH.]— α -Phenylcinnamylacrylyl chloride, m. p. 87—89°, is prepared by the protracted action of a solution of thionyl chloride in boiling benzene on the corresponding acid and is converted into the *piperidide*, m. p. 135°, which has not a sharp taste.

[With A. GIUGLIEMMETTI.]—Sorbyl chloride, b. p. 69—71°/12 mm., prepared from the acid and thionyl chloride in the presence of boiling benzene, gives the corresponding *piperidide*, m. p. 83—84°. H. W.

The Relationship between Constitution and Taste of Pepper. II. The Piperidides of Fatty-aromatic Acids. H. STAUDINGER and FRITZ MÜLLER (*Ber.*, 1923, 56, [B], 711—715; cf. preceding abstract).—The taste of the piperidides of fatty-aromatic acids is influenced in an oscillating manner by the number of methylene groups in the chain, compounds with 2, 4, or 6 such groups having a sharper taste than those with 1, 3, or 5 groups. The taste of pepper is particularly pronounced in the case of the piperidide of δ -phenyl-*n*-valeric acid. With unsaturated acids, the connexion between taste and constitution is not so marked, but the amount of material available scarcely permits exact conclusions to be drawn.

Phenylacetopiperidide, prepared from phenylacetyl chloride and piperidine, is an almost colourless liquid, b. p. 138—139°/0·4 mm. β -Phenylpropionylpiperidide, prepared similarly, has b. p. 147—150°/0·14 mm. γ -Phenylbutyric acid, m. p. 46—47°, is conveniently prepared in 94% yield of heating β -benzoylpropionic acid with hydrazine hydrate and sodium ethoxide at 180°; the corresponding *piperidide* has b. p. about 155°/0·25 mm. δ -Phenylvaleric acid is readily prepared in large quantity by reducing cinnamylidenemalononic acid with sodium amalgam to dihydrocinnamylidenemalononic acid, and converting the latter by loss of carbon dioxide into δ -phenyl- Δ^{β} -pentenoic acid, which is hydrogenated in alcoholic solution in the presence of platinum or in neutral aqueous solution in the presence of palladium; the acid has m. p. 57°. The corresponding *piperidide* is a liquid, b. p. about 164°/0·24 mm. ϵ -Phenylhexoic acid is converted by thionyl chloride and benzene into the corresponding *chloride*, b. p. 151—

152°/11 mm., and thence into the *piperidide*, a pale yellow liquid, b. p. about 177°/0·05 mm. ζ -Phenylheptoic acid, a colourless liquid which solidifies when strongly cooled, is conveniently prepared from ϵ -phenylamyl bromide by the malonic ester synthesis; it yields successively the *chloride*, b. p. 166—168°/11 mm., and the *piperidide*, a pale yellow liquid, b. p. 184—188°/0·01 mm.

[With H. HALTEN.]—The *piperidide* of γ -phenyl- Δ^8 -isocrotonic acid crystallises in colourless needles, m. p. 64—65°. H. W.

The Formation of Quaternary Ammonium Salts. I.

EDWARD DE BARRY BARNETT, JAMES WILFRED COOK, and ERNEST PERCY DRISCOLL (T., 1923, 123, 503—518).

The Dissociation of *N*-Pentamethylene-*S*-triarylmethyldithiourethanes [Triarylmethyl Piperidine-1-carbodithionate] with the Formation of Triarylmethyls. F. F. BLICKE (*J. Amer. Chem. Soc.*, 1923, 45, 544—549).—Triphenylmethyl piperidine-1-carbodithionate and some of its homologues were prepared by the interaction of piperidine piperidine-1-carbodithionate and the corresponding triarylchloromethane. These esters in solution, at the ordinary temperature, dissociate with the formation of free triarylmethyl radicles, which on exposure to air are converted into their insoluble peroxides. Thus triphenylmethyl piperidinocarbodithionate, $C_5H_{10}N \cdot CS \cdot S \cdot CPh_3$, m. p. 155—160° (decomp.), gives triphenylmethyl peroxide; the diphenyl- α -naphthylmethyl ester gives diphenyl- α -naphthylmethyl peroxide, and the diphenyldiphenylmethyl ester gives diphenyldiphenylmethyl peroxide. W. G.

Pyrroles. IV. Pyrrolealdehydes (II) and Pyrrolenitriles.

HANS FISCHER and WERNER ZERWECK (*Ber.*, 1923, 56, [B], 519—527).—2 : 3 : 5-Trimethylpyrrole-4-aldehyde, $NH < \begin{matrix} CMe:CMe \\ CMe:CCHO \end{matrix}$, colourless crystals, m. p. 143·5°, is prepared in 66·6% yield by the action of hydrogen chloride on a solution of 2 : 3 : 5-trimethylpyrrole and anhydrous hydrogen cyanide in chloroform and decomposition of the product of the reaction with water; it is remarkable that the chloroform cannot be replaced by ether as solvent. The following derivatives are described: *phenylhydrazone*, coarse, brown crystals, m. p. 138°; *oxime*, colourless needles, m. p. 164°; *semicarbazone*, m. p. 198°; *aldazine*, m. p. 273° after previous darkening. Attempts to convert the aldehyde into 2 : 3 : 5-trimethylpyrrole-4-propionic acid were unsuccessful. The aldehyde is converted by hippuric acid and sodium acetate into the *azlactone*, $C_{17}H_{16}O_2N_2$, orange or reddish-brown needles, m. p. 198°, which is transformed by sodium hydroxide into 2 : 3 : 5-trimethylpyrrole-4-benzoylaminoacrylic acid, $C_{17}H_{18}O_3N_2$, m. p. 178° (decomp.), which could not, however, be reduced. Similarly, the propionic acid derivative could not be obtained through the *product* (m. p. 286°) of the condensation of the aldehyde with rhodamine.

2 : 4-Dimethylpyrrole-5-aldehyde is prepared in 92% yield by

the action of hydrogen chloride and hydrogen cyanide on 2:4-dimethylpyrrole in the presence of chloroform, whereas the yield is only moderate if ether is used as solvent (cf. Fischer and Zerweck, A., 1922, i, 758).

4-Cyanoacetyl-2:3:5-trimethylpyrrole is converted by alcoholic sodium hydroxide solution at 160° into 4-acetyl-2:3:5-trimethylpyrrole, m. p. 207°.

A series of pyrrolenitriles, in which the cyano-group is attached to a ring carbon atom, has been prepared from the aldehydes through the oximes; reaction proceeds so smoothly that the method is of preparative value. Thus, ethyl 4-aldehydo-2:5-dimethylpyrrole-3-carboxylate is converted into the *oxime*, colourless crystals, m. p. 223° (decomp.), which is transformed by acetic anhydride and anhydrous sodium acetate into *ethyl 4-cyano-2:5-*

dimethylpyrrole-3-carboxylate,
$$\text{NH} \begin{array}{c} \text{CMe}=\text{C}\cdot\text{CN} \\ \text{CMe}=\text{C}\cdot\text{CO}_2\text{Et} \end{array}$$
 colourless,

lustrous needles, m. p. 152°. *Ethyl 5-cyano-2:4-dimethylpyrrole-3-carboxylate* forms colourless crystals, m. p. 159°; *4-cyano-2:3:5-trimethylpyrrole* has m. p. 140°.

Attempts to prepare 2:3:4:5-tetramethylpyrrole by the action of hydrogen iodide and glacial acetic acid on 2:3:5-trimethylpyrrole-4-aldehyde were unsuccessful, owing to loss of the formyl groups. (*Ethyl 5-aldehydo-2:4-dimethylpyrrole-3-carboxylate* is converted under similar conditions into 2:4-dimethylpyrrole.) The tetramethyl compound is, however, obtained by the action of alcoholic sodium ethoxide solution at 150–160° on the semicarbazone of 2:3:5-trimethylpyrrole-4-aldehyde; it is isolated as the *picrate*, coarse, yellow crystals, m. p. 130°. Similarly, *ethyl 4-aldehydo-2:5-dimethylpyrrole-3-carboxylate semicarbazone*, colourless crystals, decomp. 257° after softening at about 244°, yields 2:3:5-trimethylpyrrole.

The stability of the formyl group in substituted pyrroles towards alkali hydroxide is remarkable. Thus, 2:3:5-trimethylpyrrole-4-aldehyde is unchanged by boiling, aqueous sodium hydroxide solution (20%); *ethyl 5-aldehydo-2:4-dimethylpyrrole-3-carboxylate* is converted into *5-aldehydo-2:4-dimethylpyrrole-3-carboxylic acid*, m. p. 283–284° (decomp.), and *ethyl 4-aldehydo-2:5-dimethylpyrrole-3-carboxylate* gives *4-aldehydo-2:5-dimethylpyrrole-3-carboxylic acid*, m. p. 248° (decomp.).

2:4-Dimethylpyrrole-5-aldehyde is transformed by concentrated hydrochloric acid into *di-2:4-dimethylpyrrylmethene*, m. p. 118°. *Di-3-carbethoxy-2:4-dimethylpyrrylmethene hydrochloride* is most conveniently prepared by heating *ethyl 2:4-dimethylpyrrole-3-carboxylate* dissolved in concentrated hydrochloric acid with an excess of formic acid; the corresponding *base* crystallises in long, dark red needles, m. p. 190°.

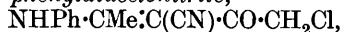
4-Chloroacetyl-2:3:5-trimethylpyrrole is converted by an alcoholic solution of dimethylamine into *4-dimethylaminoacetyl-2:3:5-trimethylpyrrole hydrochloride*, colourless crystals, m. p. 248°; the corresponding *base* has m. p. 130°. *4-Phthalimidoacetyl-2:3:5-trimethylpyrrole* has m. p. 227°.

H. W.

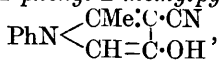
Hydroxypyrrole Derivatives. III. ERICH BENARY and WILHELM LAU (*Ber.*, 1923, 56, [B], 591—597; cf. Benary and Silbermann, A., 1913, i, 651).—An account of partly completed work induced by the recent publications of Küster (A., 1922, i, 857), Küster and Maag (this vol., i, 242), and Fischer and Hermann (A., 1922, i, 1054).

C-Chloroacetyldiacetonitrile, $\text{NH}_2\cdot\text{CMe}\cdot\text{C}(\text{CN})\cdot\text{CO}\cdot\text{CH}_2\text{Cl}$, colourless needles, m. p. 155° , is prepared by the action of chloroacetyl chloride on diacetonitrile in the presence of pyridine. The constitution of the compound follows from the observation that it is converted by potassium hydrogen sulphide into the corresponding *sulphide*, $[\text{NH}_2\cdot\text{CMe}\cdot\text{C}(\text{CN})\cdot\text{CO}\cdot\text{CH}_2]_2\text{S}$, colourless, matted needles, m. p. $178\text{--}179^\circ$, in which the amino-group is readily replaced by hydroxyl by means of *N*-sodium hydroxide solution with production of the *dienol*, $[\text{OH}\cdot\text{CMe}\cdot\text{C}(\text{CN})\cdot\text{CO}\cdot\text{CH}_2]_2\text{S}$, colourless needles, m. p. 130° . The conversion of the chloroacetyl compound into the corresponding hydroxypyrrole has not yet been accomplished definitely. In general, the preparation of the latter compounds can frequently be satisfactorily effected only under very definite experimental conditions, which must be established for each particular case.

C-Chloroacetyl-*N*-phenyldiacetonitrile,



colourless leaflets, m. p. $103\text{--}104^\circ$, is prepared from *N*-phenyldiacetonitrile and chloroacetyl chloride in the presence of pyridine and ether, and is transformed by potassium hydrogen sulphide into the *sulphide*, $\text{C}_{24}\text{H}_{22}\text{O}_2\text{N}_4\text{S}$, colourless needles, m. p. $170\text{--}172^\circ$. It is transformed by potassium hydroxide in the presence of methyl alcohol into 4-hydroxy-1-phenyl-2-methylpyrrole-3-nitrile,



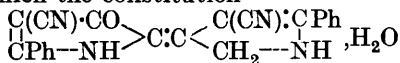
colourless needles, m. p. 167° , which is converted by nitrous acid into 5-oximino-4-keto-1-phenyl-2-methylpyrroline-3-nitrile, orange-yellow needles, decomp. 178° after darkening at about 160° , and by sodium nitrite and glacial acetic acid into 5-nitroimino-4-keto-

1-phenyl-2-methylpyrroline-3-nitrile, $\text{PhN} \begin{array}{l} \text{CMe}=\text{C}\cdot\text{CN} \\ \diagdown \quad \diagup \\ \text{C}(\text{N}\cdot\text{NO}_2)\cdot\text{CO} \end{array}$, an orange-coloured precipitate, decomp. 225° . The latter substance is transformed by sodium hydroxide solution (5%) into the *substance*, $\text{NPh}\cdot\text{CMe}\cdot\text{C}(\text{CO}\cdot\text{NH}_2)\cdot\text{C}(\text{OH})\cdot\text{CO}\cdot\text{NH}\cdot\text{NO}_2$, pale-yellow, four-sided plates, decomp. $240\text{--}241^\circ$ after becoming altered at 237° , which, with phenylhydrazine in the presence of acetic acid (50%), yields the *compound*, $\text{C}_6\text{H}_4\cdot\text{C}(\text{CO}\cdot\text{NH}_2)\cdot\text{CMe}\cdot\text{NPh}$, brownish-yellow

needles or four-sided prisms, decomp. 225° after gradual darkening and softening above 205° .

C-Chloroacetylbenzoacetodinitrile, $\text{NH}_2\cdot\text{CPh}\cdot\text{C}(\text{CN})\cdot\text{CO}\cdot\text{CH}_2\text{Cl}$, long, colourless needles, m. p. 116° , is converted in the usual manner into the corresponding *sulphide*, $\text{C}_{22}\text{H}_{18}\text{O}_2\text{N}_4\text{S}$, colourless needles, m. p. $195\text{--}198^\circ$. Attempts to transform it into the corresponding

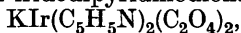
pyrrole resulted in the production of a reddish-violet *dye*, decomp. about 250°, for which the constitution



is suggested.

H. W.

Potassium Iridodipyridinodioxalates. MARCEL DELÉPINE (*Compt. rend.*, 1923, 176, 445—447).—When *r-cis*-potassium irido-dichlorodioxalate is heated with pyridine at 130° for four hours, a crystalline potassium iridodipyridinodioxalate,



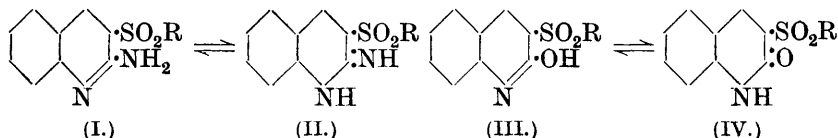
is obtained together with an amorphous product, which has the same composition as the crystalline product. The crystalline salt when treated with aqua regia is converted into a dipyridino-iridium tetrachloride, which with ammonia gives the same special complexes as the chloride from the red salts. Similarly, if the dioxalate is treated with hydrochloric acid, it gives a series of compounds among which is an iridodipyridino-tetrachloride of iridodichlorodiaquodipyridine. This salt reacts with alkalis to give a red iridodipyridino-tetrachloride, and a hydroxy-compound which is an anhydride of the theoretical hydroxide of the salt, $\text{Ir}(\text{C}_5\text{H}_5\text{N})_2(\text{H}_2\text{O})(\text{OH})\text{Cl}_2$. The other products formed in the decomposition by hydrochloric acid are the aquodipyridinoiridium chloro-oxalate, $\text{Ir}(\text{C}_5\text{H}_5\text{N})_2(\text{H}_2\text{O})\text{Cl}(\text{C}_2\text{O}_4)$, a neutral substance insoluble in water but soluble in alkalis, and iridodichlorodiaquodipyridine chloride, $\text{Cl}[\text{Ir}(\text{C}_5\text{H}_5\text{N})_2(\text{H}_2\text{O})_2\text{Cl}_2]$, and traces of potassium pyridinoiridium pentachloride. The iridodipyridinodioxalate is therefore, apparently a *trans*-dipyridino-compound formed by intramolecular transpositions. The amorphous compounds obtained along with it are the *cis*-compounds and give orange-coloured salts under the influence of hydrochloric acid. W. G.

Amino-alcohols, Ketones, and other Derivatives of the Quinoline Series. K. MIESCHER (U.S. Pat. 1434306).—*Ethyl 2-phenylquinoline-4-acetate*, yellow prisms, m. p. 52—54°, is obtained from the reaction products of ethyl 2-phenylquinoline-4-carboxylate, sodium ethoxide, and ethyl acetate heated in toluene for twenty-four hours. It forms a sparingly soluble, bright green *copper* salt, and intensely yellow *salts* with hydrochloric and sulphuric acids. *2-Phenyl-4-quinolyl methyl ketone*, yellow crystals, m. p. 75°, is formed by heating ethyl 2-phenylquinoline-4-acetate with eight times its weight of 25% sulphuric acid and treating the reaction mass with sodium carbonate and ether, or from a solution of 4-cyano-2-phenylquinoline in benzene treated drop by drop, with cooling, with a solution of magnesium methyl iodide in ethyl ether (*hydrobromide*, yellow, m. p. 240°). Bromination of the ketone in concentrated hydrobromic acid or an organic solvent yields the *hydrobromide*, m. p. about 225° (decomp.), of *2-phenyl-4-quinolyl bromomethyl ketone*, bright yellow crystals, m. p. 91°. The latter hydrobromide reacts in benzene cooled with ice with dimethylamine, subsequent treatment with alcoholic hydrogen

chloride giving 2-phenyl-4-quinolyl dimethylaminoethyl ketone monohydrochloride, yellow crystals, m. p. 208° (decomp.) (hydrobromide, m. p. about 206°). 2-Phenyl-4-quinolyl diethylaminoethyl ketone monohydrochloride forms bright yellow needles, m. p. about 164° (decomp.); 2-phenylquinolyl 4-piperidylethyl ketone monohydrochloride has m. p. 235° [monohydrobromide, m. p. about 241° (decomp.)]. Amino-alcohols containing a primary amino-group can be prepared by reducing the corresponding oximinoketones, *N*-substituted amino-alcohols being similarly obtained from amino-ketones. 2-Phenyl-4-quinolylaminoethanol dihydrochloride forms yellow crystals, m. p. 145°. 2-Phenyl-4-quinolyl dimethylaminoethanol dihydrochloride has m. p. about 175° (decomp.), and the corresponding diethylamino-compound, m. p. about 185°. 2-Phenyl-4-quinolyl piperidylethanol has m. p. about 54° (monohydrochloride, m. p. about 162°; dihydrochloride, m. p. about 199°).

CHEMICAL ABSTRACTS.

Syntheses of 2- and 3-Substituted Quinolines. JULIUS TRÖGER and PAUL KÖPPEN-KASTROP (*J. pr. Chem.*, 1922, [ii], 104, 335—367).—The condensation of *o*-aminobenzaldehyde with an arylsulphonylacetonitrile, using pyridine as catalyst, gives, instead of the expected product $\text{RSO}_2\cdot\text{C}(\text{CN})\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$, a quinoline derivative (I), in the formation of which both hydrogen atoms of the amino-group must have migrated to the nitrogen of the cyano-group (cf. Pshorr, A., 1898, i, 491); the same compound is produced by the re-



duction in alcoholic hydrogen chloride solution with stannous chloride of the condensation product, $\text{RSO}_2\cdot\text{C}(\text{CN})\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$, of *o*-nitrobenzaldehyde and an arylsulphonylacetonitrile. Nitrous acid converts these aminoquinolines into carbostyryl derivatives (III), the structure of which is firmly established by their synthesis from *o*-aminobenzaldehyde and (a) the arylsulphonylacetic acid, (b) its ester, or (c) its amide, with elimination of (a) water, (b) alcohol, or (c) ammonia, respectively. Although these carbostyryl derivatives are insoluble in aqueous alkali, they form sodio-derivatives in the absence of water, which lead to 3-arylsulphonyl-2-alkoxyquinolines when treated with alkyl halides under pressure; moreover, the hydroxyl may be replaced by chlorine by means of phosphorus pentachloride. Hence these carbostyryls are best represented as tautomeric in the sense $(\text{III}) \rightleftharpoons (\text{IV})$. The properties of the amino-compounds are less easy to explain. They are insoluble in concentrated hydrochloric acid, and cannot be diazotised even at a high temperature and pressure, neither do they react with methyl iodide, although with this reagent the β -arylsulphonylmethylquinolines (Tröger and Menzel, A., 1922, i, 269) form crystalline derivatives. It is equally surprising that the salts and double

salts are much more readily dissociated than those of the corresponding 2-methyl derivatives. This is even difficult to understand if a tautomeric form (II) is assumed, since this should give at least a mono-alkyl derivative. Nitrous acid would then convert (II) into (IV). The formation of the α -chloro-compound is certainly more easily explained on formula (III); nevertheless, the action of a large excess of phosphorus halide leads to a dichloro-derivative, possibly derived from the keto-form (IV).

The 2-chlorine atom is readily replaceable by ethoxyl (using sodium ethoxide); also by the $\cdot\text{SH}$ group (by means of alcoholic potassium hydrosulphide) giving a thiocarbostyryl, which is soluble in aqueous alkali and more readily alkylated than the carbostyryl itself. Replacement by the group $\text{R}\cdot\text{SO}_2\cdot$, by the action of a salt of an arylsulphinic acid, proceeds only slowly, whilst the replacement by the group $\text{Na}\cdot\text{SO}_3\cdot$ (by means of sodium sulphite, cf. Besthorn and Geisselbrecht, A., 1920, i, 563) has not been accomplished.

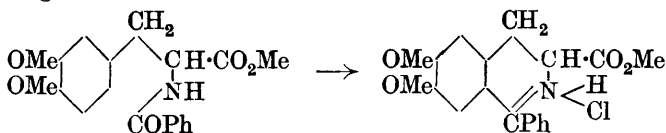
The above reactions have been investigated when R is $\text{C}_6\text{H}_5\cdot$, $\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot(p)$, and $\text{Cl}\cdot\text{C}_6\text{H}_4\cdot(p)$.

Equimolecular quantities of *o*-nitrobenzaldehyde and benzenesulphonylacetonitrile give, when treated in concentrated alcoholic solution with a little pyridine, β -*o*-nitro- α -benzenesulphonylcinnamonnitrile, long, slender, white needles, m. p. 149° , which on reduction by means of stannous chloride and hydrochloric acid in alcoholic solution is converted into 2-amino-3-benzenesulphonylquinoline, long, white needles, m. p. 206° , which is also produced by heating *o*-aminobenzaldehyde and benzenesulphonylacetonitrile in alcoholic solution with a little aqueous sodium hydroxide. The *hydrochloride*, needles, decomp. 100° , the *nitrate*, needles, decomp. 70° , the *hydrogen sulphate*, yellow needles, decomp. 105° , the *hydrogen oxalate*, the *perchlorate*, the *chloroplatinate*, $(\text{C}_{15}\text{H}_{12}\text{O}_2\text{N}_2\text{S})_2\cdot\text{H}_2\text{PtCl}_6\cdot\text{H}_2\text{O}$, reddish-yellow needles, and the *chloroaurate*, $\text{C}_{15}\text{H}_{12}\text{O}_2\text{N}_2\text{S}\cdot\text{HAuCl}_4$, golden needles, m. p. 200° , are described. The amino-compound, which cannot be alkylated, reacts in somewhat dilute acetic acid solution with sodium nitrite to give 3-benzenesulphonylcarbostyryl, long, rod-like prisms, m. p. 312° , which is also produced when *o*-aminobenzaldehyde is heated under pressure with either ethyl benzenesulphonylacetate or benzenesulphonylacetamide. 3-Benzenesulphonyl-2-ethoxyquinoline, small, pale yellow prisms, m. p. 190° , is produced by heating the sodium salt of the carbostyryl in alcoholic suspension with methyl iodide under pressure, more readily by the action of sodium ethoxide at 100° on 2-chloro-3-benzenesulphonylquinoline, broad, rod-like crystals, m. p. 150° , which is produced by heating the α -hydroxy-compound at 160° with phosphorus pentachloride and a few drops of phosphoryl chloride. When this chloro-derivative is heated at 100° with sodium benzenesulphinate, 2 : 3-dibenzenesulphonylquinoline, small, yellowish-white needles, m. p. 204° , is formed, the 2-substituent of which is replaced by hydroxyl by fusion with alkali hydroxide; with alcoholic potassium hydrosulphide at 100° , the product is 3-benzenesulphonylthiocarbostyryl, long slender, yellow needles, m. p. 241° , which, when shaken with

methyl sulphate and dilute aqueous sodium hydroxide, gives a *s-methyl* derivative, long, yellow needles, m. p. 175°. The condensation of *o*-nitrobenzaldehyde with *p*-toluenesulphonylacetonitrile by means of pyridine in alcoholic solution leads to *o*-nitro- α -*p*-toluenesulphonylcinnamionitrile, long, yellowish-white needles, m. p. 152°, which on reduction gives 2-amino-3-*p*-toluenesulphonylquinoline, sulphur-yellow, rod-like crystals, m. p. 214°, which is also produced by the condensation of *o*-aminobenzaldehyde with *p*-toluenesulphonylacetonitrile; the *hydrochloride*, slender needles, decomp. 100°, the *nitrate*, slender needles, decomp. 70°, the *hydrogen sulphate*, decomp. 100°, the *hydrogen oxalate*, the *chloroplatinate* (+H₂O), reddish-yellow prisms, and the *chloroaurate*, slender, golden-yellow needles, m. p. 207°, are described. 3-*p*-Toluenesulphonylcarbostyryl, small, yellow prisms, m. p. 300°, is formed from the amino-compound by the action of nitrous acid, and also by heating α -aminobenzaldehyde at 160–170° with ethyl *p*-toluenesulphonylacetate, *p*-toluenesulphonylacetic acid, or *p*-toluenesulphonylacetamide; it forms a yellowish-white *sodium* salt when treated with alcoholic sodium ethoxide. The *O-ethyl ether*, m. p. 207–207·5°, can only be prepared by the action of alcoholic sodium ethoxide at 100° on 2-chloro-3-*p*-toluenesulphonylquinoline, m. p. 178–179°, which is best prepared by the action of a slight excess of phosphorus pentachloride and a little phosphoryl chloride on the carbostyryl. By the use of a large excess of these reagents, a material, m. p. 132°, probably 2 : 2-dichloro-3-*p*-toluenesulphonylquinoline, has been isolated (see above), and also a *product*, m. p. 122–124°, containing 2% more chlorine than the dichloro-compound. α -*p*-Chlorobenzenesulphonyl-*o*-nitrocinnamionitrile, long, white needles, m. p. 156°, is formed from *o*-nitrobenzaldehyde and *p*-chlorobenzenesulphonylacetonitrile, and gives on reduction 2-amino-3-*p*-chlorobenzene-sulphonylquinoline, yellow prisms, m. p. 205°, which is also produced by the condensation of *o*-aminobenzaldehyde with *p*-chlorobenzenesulphonylacetonitrile; the *hydrochloride*, fine needles, the *nitrate*, slender, white needles, the *hydrogen sulphate*, fine, white needles, and the *hydrogen oxalate*, white needles, have been prepared. This amino-compound gives, with nitrous acid, 3-*p*-chlorobenzenesulphonylcarbostyryl, yellow prisms (+16% water or acetic acid), m. p. 287°, which is also formed by the condensation at 170° of *o*-aminobenzaldehyde with ethyl *p*-chlorobenzenesulphonylacetate, and gives with sodium ethoxide a yellow, amorphous *sodium* salt. The *O-ethyl ether*, slender, white needles, m. p. 173°, is formed by the action of alcoholic sodium ethoxide under pressure on 2-chloro-3-*p*-chlorobenzenesulphonylquinoline, slender, ivory-coloured needles, m. p. 170°, which is produced by the action of phosphorus pentachloride and a little phosphoryl chloride on the carbostyryl. This 2-chloro-derivative, when heated at 100° in alcoholic solution with potassium hydrogen sulphide, gives impure 3-*p*-chlorobenzene-Sulphonylthiocarbostyryl, a yellow, amorphous substance, which with dilute aqueous sodium hydroxide and methyl sulphate gives the *S-methyl ether*, long, slender, yellow needles, m. p. 194°.

W. S. N.

Preparation of Derivatives of Dihydroisoquinoline. SOCIETY OF CHEMICAL INDUSTRY IN BASLE (Brit. Pat. 191233).—Therapeutically active derivatives of dihydroisoquinoline are obtained by hydrogenising α -acylaminocinnamic esters or their nuclear substitution derivatives, and converting the dihydrocinnamic acid derivatives thus produced into derivatives of dihydroisoquinoline-3-carboxylic acid by suitable condensing agents such as phosphoryl chloride. The parent materials are obtained by heating equimolecular proportions of an aromatic aldehyde, an acylated glycine, and sodium acetate with 3 mols. of acetic anhydride, and esterifying the product, and details are given of the conversion of the following substances into isoquinoline derivatives. Methyl veratralhippurate (methyl α -benzamido-3:4-dimethoxycinnamate) is hydrogenised by means of a nickel catalyst at 55° to methyl α -benzamido- β -3:4-dimethoxyphenylpropionate, fleecy needles, m. p. 104 – 105° , which when heated with an equal weight of phosphoryl chloride is converted into methyl 6:7-dimethoxy-1-phenyl-3:4-dihydroisoquinoline-3-carboxylate, m. p. 122.5° , according to the following scheme :



The hydrochloride and hydrobromide form yellow crystals easily soluble in water, and in common with other 6:7-dihydroxy-derivatives they have the same therapeutic action as hydrastinine, but are less poisonous. With the free ester methyl iodide gives a N-methiodide which is sparingly soluble in water. Piperonylidenehippuric acid is in a similar way converted through α -benzamido- β -piperonylpropionic acid into methyl 6:7-methylenedioxy-1-phenyl-3:4-dihydroisoquinoline-3-carboxylate, small, colourless needles, m. p. 140.5° , which gives a hydrochloride, and a methiodide similar to those above described. Methyl α -piperonylamino-3:4-methylenedioxy-cinnamate, m. p. 156 – 157° , yields on hydrogenation methyl α -piperonylamino-3:4-methylenedioxyphenylpropionate, lustrous needles, m. p. 139 – 140° , which on condensation with phosphoryl chloride gives methyl 1-piperonyl-6:7-methylenedioxy-3:4-dihydroisoquinoline-3-carboxylate, m. p. 140 – 141° . The hydrochloride dissociates partly when dissolved in water. Methyl α -cinnamoylamido-3:4-methylenedioxy-cinnamate, m. p. 192° , is in like manner converted into methyl α -[β -phenylpropionylamido]-3:4-methylenedioxyphenylpropionate, m. p. 127° , and then into methyl 6:7-methylenedioxy-1-phenylethyl-3:4-dihydroisoquinoline-3-carboxylate, thick prisms, m. p. 111° . The hydrochloride gives a bluish-green fluorescence in aqueous solution, and the methochloride is readily soluble in water, but less strongly fluorescent. G. F. M.

Synthesis of Asymmetric Homotetrahydroisoquinoline. JULIUS VON BRAUN and FRIEDRICH ZOBEL (Ber., 1923, 56, [B], 690–696).—Previous attempts to synthesise homotetrahydroiso-

quinoline, $\text{C}_6\text{H}_4\langle\text{CH}_2\rangle_3\text{NH}$, starting from *o*- γ -phenoxypropylbenzonitrile, have been unsuccessful, since the initial step, namely the reduction of the cyano- to the amino-methylene group could not be effected by nascent hydrogen. Since, however, the author's experience has shown that catalytic hydrogenation is frequently more effective than treatment with nascent hydrogen, the study has been resumed. A preliminary series of experiments shows that the change can be effected under sufficiently great pressure in the presence of nickel compounds in the cases of simpler and less costly compounds. The desired synthesis is finally effected on the lines of the scheme: $\text{CN}\cdot\text{C}_6\text{H}_4\cdot[\text{CH}_2]_3\cdot\text{OPh} \rightarrow \text{NH}_2\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot[\text{CH}_2]_3\cdot\text{OPh} \rightarrow \text{NH}_2\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot[\text{CH}_2]_3\cdot\text{Cl} \rightarrow \text{C}_6\text{H}_4\langle\text{CH}_2\rangle_3\text{NH}$. The product appears to contain a seven-membered ring, but the authors promise an exact proof of its constitution later.

[With (Frl.) A. NELKEN.]—*o*-Methoxy-*o*-toluonitrile, a colourless liquid, b. p. 114°/14 mm., is converted by hydrogenation at 100° in the presence of tetra- or deca-hydronaphthalene into a mixture of *o*-methoxymethylbenzylamine, $\text{OMe}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{NH}_2$, a mobile liquid, b. p. 127—128°/13 mm. (*hydrochloride*, m. p. 113°; *picrate*, m. p. 164°; *benzoyl* derivative, m. p. 71°), and *di*-*o*-methoxymethylbenzylamine, $[\text{OMe}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2]_2\text{NH}$, an almost colourless, viscous liquid, b. p. 200—205°/13 mm. (the *hydrochloride* and *nitroso*-derivative are non-crystalline; the *picrate* has m. p. 156°).

[With G. BLESSING.]—*o*-Phenoxy-*o*-toluonitrile, m. p. 65°, is transformed into a mixture of *di*-*o*-phoxymethylbenzylamine, m. p. 53°, which yields a very sparingly soluble *hydrochloride*, lustrous leaflets, m. p. 158°, and *o*-phoxymethylbenzylamine b. p. 195—200°/13 mm., m. p. 26—27° (*hydrochloride*, m. p. 200°; *picrate*, m. p. 190°).

o-Methoxy-*o*-toluonitrile, b. p. 125—127°/12 mm., yields *p*-methoxymethylbenzylamine, a colourless, mobile liquid, b. p. 125—130°/12 mm. (*hydrochloride*, needles, m. p. 205°; *picrate*, m. p. 179°; *acetyl* derivative, colourless crystals, m. p. 86—87°; *phenylthiocarbamide* compound, m. p. 102—103°), *di*-*p*-methoxymethylbenzylamine, a colourless, rather viscous liquid, b. p. 195—200°/1 mm. (*hydrochloride*, m. p. 215°; a non-crystalline *picrate*; *nitroso*-derivative, m. p. 120°), and apparently a small quantity of tri-*p*-methoxymethylbenzylamine.

o- γ -Phenoxypropylbenzonitrile is readily hydrogenated in the presence of decahydronaphthalene at 115°, although the action does not proceed quite to completion. The products of the change are *o*- γ -phenoxypropylbenzylamine (about 30%) and *di*-*o*- γ -phenoxypropylbenzylamine, which could not be distilled without undergoing decomposition, and for the present has not been investigated further. The primary base crystallises in colourless needles, m. p. 55°, b. p. 230°/18 mm.; it yields a *hydrochloride*, m. p. 154°, and a *picrate*, pale yellow, lustrous needles, m. p. 171°. It is converted by concentrated hydrochloric acid at 130° (the experimental conditions must be exactly observed) into *o*- γ -chloropropylbenzylamine,

a colourless, somewhat unstable liquid, which is characterised as the *hydrochloride*, m. p. 172° , and the *picrate*, coarse needles, m. p. 175° , after slight previous softening. An aqueous solution of the hydrochloride is converted by an excess of warm dilute alkali hydroxide solution into *as.-homotetrahydroisoquinoline*, which is volatile with steam. It is a colourless liquid with an odour of tetrahydroisoquinoline, b. p. $120^{\circ}/17$ mm. It could not be caused to solidify. On exposure to air it becomes transformed into the carbonate. It yields a solid, very hygroscopic *hydrochloride*, a *chloroplatinate*, a crystalline powder, m. p. 192° , and a *nitro-derivative*, m. p. $73-74^{\circ}$. When treated with methyl iodide and alkali hydroxide, it gives the quaternary *iodide*, $C_{12}H_{18}NI$, m. p. 182° .

H. W.

Derivatives of Tetrahydrocarbazole. II. WILLIAM HENRY PERKIN, jun., and SYDNEY GLENN PRESTON PLANT (T., 1923, 123, 676—695).

The Action of Nitrobenzene on the Sodium and Potassium Derivatives of Carbazole. GUILLAUME DE MONTMOLIN and MARCEL DE MONTMOLIN (*Helv. Chim. Acta*, 1923, 6, 94—101).—The sodium and potassium derivatives of carbazole dissolve in nitrobenzene with a dark red colour, but no compound is formed at first. On heating for some hours at $45-50^{\circ}$, however, reaction takes place with formation of *9-p-nitrophenylcarbazole*, crystallising in yellow spangles with a green reflex, m. p. 212° ; *picrate*, garnet-red needles. The oxygen required for the reaction is provided by excess of nitrobenzene. That the nitrobenzene has, contrary to its usual behaviour, reacted in the para-position, is shown as follows. The nitro-compound was reduced and the product diazotised and converted by Gattermann's method into chlorophenylcarbazole, which was proved to be identical with that obtained by heating potassium carbazole with *p*-chlorobromobenzene. Further, the aminophenylcarbazole gave with phthalic anhydride a phthalimide isomeric but not identical with that obtained by heating potassium carbazole with *m*-bromophthalanil.

p-Aminophenylcarbazole, from the nitro-compound, forms a resin; its *picrate* forms yellowish-brown needles, m. p. 200° (decomp.). *p*-Acetamidophenylcarbazole crystallises in colourless plates, m. p. 257° . *p*-Phthalimidophenylcarbazole forms colourless needles, m. p. 210° ; *m*-phthalimidophenylcarbazole, obtained in only small yield by heating potassium carbazole with *m*-bromophthalanil, forms brilliant, pale red spangles, m. p. 216° .

The diazo-compounds of *p*-aminophenylcarbazole are characterised by their stability in acids and their intense colour, orange in solution or in hydrated crystals, yellow when anhydrous. *9-Phenylcarbazole-p-diazonium chloride*, $C_{12}H_8N^+C_6H_4 \cdot N_2Cl$, and *sulphate* are soluble in a dilute acid solution at 70° , crystallising on cooling in long, silky needles; the *nitrate*, which has a remarkably slight solubility in water, forms a yellow, microcrystalline precipitate. The salts are rapidly decomposed by acetates and alkalis.

β -Naphtholazophenylcarbazole, $C_{12}H_8N \cdot C_6H_4 \cdot N:N \cdot C_{10}H_6 \cdot OH$, forms garnet-red needles, m. p. 230° . 9-p-Chlorophenylcarbazole forms small, pale yellow crystals, m. p. 146° ; 9-p-cyanophenylcarbazole, obtained by acting on the diazonium salt with cuprous cyanide, forms pale yellow crystals, m. p. 165° . Azophenylcarbazole, $C_{12}H_8N \cdot C_6H_4 \cdot N:N \cdot C_6H_4 \cdot C_{12}H_8N$, obtained by partial reduction of p-nitrophenylcarbazole with zinc in acid solution, forms orange spangles, m. p. 277° .

p-Nitrophenylcarbazole is destroyed by concentrated sulphuric acid, but when treated with a mixture of sulphuric and chlorosulphonic acids in nitrobenzene suspension it gives a crystalline sulphonic acid, green needles. When reduced, this gives an amino-sulphonic acid which, when diazotised and coupled with naphthols, yields red dyes inclined to violet. The colour obtained with β -naphthol gives a particularly brilliant barium lake.

By nitrating p-nitrophenylcarbazole in nitrobenzene suspension a dinitrophenylcarbazole, small, yellow crystals, m. p. 274° , is obtained. The second nitro-group is probably in the 3-position in the carbazole nucleus. The alcoholic solution of the diaminophenylcarbazole prepared from this shows a vivid blue fluorescence; its diacetyl derivative forms a white, crystalline powder, m. p. 274° . Nitration of p-acetamidophenylcarbazole gave a p-acetamidophenyl-dinitrocarbazole, yellow crystals, m. p. 234° ; it is probably the 3:6-derivative. When hydrolysed it gives p-aminophenyl-dinitrocarbazole, m. p. 320° . 9-m-Nitrotolylcarbazole, obtained by the action of m-nitrotoluene on potassium carbazole, is a yellow substance, m. p. 138° . E. H. R.

Condensation Products of Phenylhydroxylamine with Hydroxymethylene Compounds and Carbinols. IV. Hydroxymethylenephénylacetic Ester and Hydroxymethylenebenzylcyanide with Phenylhydroxylamine. H. RUPE and J. GRÜNHOLZ (*Helv. Chim. Acta*, 1923, 6, 102—110; cf. A., 1921, i, 425; 1922, i, 448, 449).—Ethyl α -hydroxymethylenephénylacétate condenses in the normal way with phenylhydroxylamine, but the direct product cannot be isolated as it at once loses alcohol, forming

the diphenylisooxazolone, $\begin{matrix} \text{CPh} \cdot \text{CH} \\ | \\ \text{CO} \text{---} \text{O} \end{matrix} > \text{NPh}$, white needles, m. p. 175° .

The substance quickly turns yellow in the light; it dissolves in sulphuric acid with an intense blue colour, turned dark green by ferric chloride. The same compound is obtained from methyl α -hydroxymethylenephénylacétate. In chloroform solution, the isooxazolone combines with bromine to form a dibromide, white, glistening leaflets, m. p. about 180° ; the compound cannot be recrystallised, as it immediately loses hydrogen bromide, forming

diphenylbromoisooxazolone, $\begin{matrix} \text{CPh} \cdot \text{CBr} \\ | \\ \text{CO} \text{---} \text{O} \end{matrix} > \text{NPh}$, which has no definite

m. p., but decomposes at 164 — 166° . When the diphenylisooxazolone is warmed with alcoholic potassium hydroxide, the ring is opened, with formation of trans- β -phenylhydroxylaminomethylene-

phenylacetic acid, small, glistening, pyramidal crystals, m. p. 135°. This forms a grey, crystalline *silver* salt, and an *ethyl* ester, m. p. 75°. The fact that this ester is quite stable and cannot be converted into the *isooxazolone* is taken as evidence that it is the *trans*-form; it follows that the product obtained by the action of phenylhydroxylamine on ethyl hydroxymethylenepherylacetate, which immediately gives the *isooxazolone*, is the *cis*-form. When the above *trans*- β -phenylhydroxylaminomethylenepherylacetic acid is heated above its m. p., it loses carbon dioxide, forming β -phenyl- β -styrylhydroxylamine (Rupe and Wittwer, A., 1922, i, 448), which forms a somewhat unstable *dibromide*, small, white needles, m. p. 125°.

Hydroxymethylenepherylacetoneitrile condenses with phenylhydroxylamine to give *phenyl- β -cyanostyrylhydroxylamine*, $\text{CN}\cdot\text{CPh}\cdot\text{CH}\cdot\text{NPh}\cdot\text{OH}$, golden-yellow needles, m. p. 155°. Attempts to hydrolyse the nitrile to an acid were unsuccessful. Hydroxymethylenepherylacetoneitrile condenses with aniline to form an *anilino*-derivative, $\text{NHPh}\cdot\text{CH}\cdot\text{CPh}\cdot\text{CN}$, white needles, m. p. 156°; with phenylhydrazine to a *phenylhydrazino*-derivative, white needles, m. p. 155—156°; and with *p*-aminophenol to form a *p*-hydroxyanilino-derivative, greyish-green needles, m. p. 150°. The last forms a *copper* salt, $(\text{C}_{15}\text{H}_{11}\text{ON}_2)_2\text{Cu}$, a nearly black powder.

E. H. R.

The Interaction of Aliphatic Alcohols and $\beta\gamma$ -Dibromopropylthiocarbimide. RAYMOND M. HANN (*J. Amer. Chem. Soc.*, 1923, 45, 482—486).—Dixon (T., 1892, 61, 545; 1895, 67, 564; 1896, 69, 22) records the formation of 5-bromo-2-alkyloxy-4:6-dihydro-1:3-thiazines by the action of aliphatic alcohols on dibromopropylthiocarbimide. Gabriel (A., 1906, i, 889) considered these compounds to be 2-alkyloxy-5-bromomethyl- Δ^2 -thiazolines. From a consideration of the reaction of *n*-butyl and *isoamyl* alcohols with the thiocarbimide and from a crystallographic study of the products, the author is of the opinion that the product formed in every case, regardless of the aliphatic alcohol used, is 2-hydroxy-5-bromomethyl- Δ^2 -thiazoline, m. p. 95—96°. Secondary alcohols appear to react similarly. W. G.

Halogenated Derivatives of Ketodihydro-1:4-benzthiazines and the Products of their Transformations. Conversion of Thiazine into Thiazole Compounds. K. ZAHN (*Ber.*, 1923, 56, [B], 578—587).—Ketodihydro-1:4-benzthiazines react readily with halogens to yield mono- and di-substituted derivatives, in which the halogen atoms are highly reactive. In the case of the dichloro-compounds, there is a remarkable tendency for the thiazine to contract to the thiazole ring.

The monohalogenated derivatives are obtained by the action of the requisite quantity of bromine, sulphuryl chloride, or gaseous chlorine on a solution of the thiazine in the necessary amount of boiling benzene. 2-Bromo-3-keto-2:3-dihydro-1:4-benzthiazine,

$\text{C}_6\text{H}_4 \begin{array}{l} \text{NH}\cdot\text{CO} \\ \diagup \quad \diagdown \\ \text{S} \quad \text{CHBr} \end{array}$, colourless crystals, decomp. about 220° after

previous darkening; 2-chloro-3-keto-2:3-dihydro-1:4-benzthiazine, decomp. . 215°; 2:7-dichloro-3-keto-5-methyl-2:3-dihydro-1:4-benzthiazine, decomp. about 245° after darkening at 200°, and 2-chloro-3-keto-2:3-dihydro- α -naphthathiazine, gradual decomp. above 200°, are described. When boiled with the requisite alcohol, the halogenated compounds exchange the halogen atom for the alkoxy-group. The following compounds are obtained in this manner: 2-methoxy-3-keto-2:3-dihydro-1:4-benzthiazine, almost colourless leaflets, m. p. 188—189°; 2-ethoxy-3-keto-2:3-dihydro-1:4-benzthiazine, colourless crystals, m. p. 168—169°; 7-chloro-2-methoxy-3-keto-5-methyl-2:3-dihydro-1:4-benzthiazine, pale brown prisms, m. p. 189—190°, and the corresponding ethoxy-derivative, colourless needles, m. p. 197°; 2-methoxy- and 2-ethoxy-3-keto-2:3-dihydro- α -naphthathiazine, prisms, m. p. 223—224°, and lustrous leaflets, m. p. 208—209°, respectively. These compounds are soluble in alkali hydroxide solutions with the formation of salts of the enolic forms which, however, could not be isolated. 2-Methoxy-3-keto-2-methyl-2:3-dihydro-1:4-benzthiazine, long, colourless needles, m. p. 80—81°, is prepared by the action of sodium hydroxide and methyl sulphate on the 2-methoxy-compound. 2-Acetoxy-3-keto-2:3-dihydro-1:4-benzthiazine, colourless, prismatic crystals, m. p. 172—173°, is obtained by the action of sodium acetate dissolved in glacial acetic acid on the 2-chloro-derivative; it is converted by sulphuric acid in the presence of ethyl alcohol into 2-ethoxy-3-keto-2:3-dihydro-1:4-benzthiazine and by concentrated sulphuric acid at about 50° into the ether, $(C_6H_4 \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{S} - \text{CH} \end{smallmatrix})_2 O$, a colourless powder, decomp. above 300°.

The following dichloro-derivatives are prepared by the gradual addition of sulphuryl chloride to a solution of the requisite thiazine in nitrobenzene and subsequently heating the mixture at about 60° until hydrogen chloride ceases to be evolved: 2:2-dichloro-3-keto-2:3-dihydro-1:4-benzthiazine, colourless needles, m. p. 195—196°; 2:2:7-trichloro-5-methyl-3-keto-2:3-dihydro-1:4-benzthiazine, m. p. 205—206°; 2:2-dichloro-3-keto-2:3-dihydro- α -naphthathiazine, a pale yellow, crystalline powder, decomp. about 240° after previous darkening. Cautious treatment of the dichloro-compounds with methyl alcohol leads to the isolation of 2:2-dimethoxy-3-keto-2:3-dihydro-1:4-benzthiazine, colourless crystals, m. p. 129—130°; 7-chloro-2:2-dimethoxy-3-keto-2:3-dihydro-1:4-benzthiazine, prisms, m. p. 203—204°, and 2:2-dimethoxy-3-keto-2:3-dihydro- α -naphthathiazine, pale yellow prisms, m. p. 171—172°, whereas under more drastic treatment methyl benzthiazole-2-carboxylate, $C_6H_4 \begin{smallmatrix} \text{N} \\ \text{S} \end{smallmatrix} > C \cdot CO_2Me$, and methyl α -naphthathiazole-2-carboxylate, needles, m. p. 119°, are produced. Boiling ethyl alcohol transforms the dichloroketothiazine into ethylbenzthiazole-2-carboxylate, m. p. 70—71°. Ethyl 6-chloro-4-methylbenzthiazole-2-carboxylate crystallises in colourless needles, m. p. 97—98°; the corresponding amide, colourless leaflets, m. p. 250—251°, and acid, m. p. 140°, are described. Ethyl α -naphthathiazole-

2-carboxylate forms pale yellow needles, m. p. 129—130° (*amide*, m. p. 253—254°; corresponding *acid*, m. p. 140°).

2 : 2-Dichloro-3-keto-2 : 3-dihydro-1 : 4-benzthiazine is converted by cold concentrated sulphuric acid or, preferably, by boiling glacial acetic acid into 2 : 3-diketodihydro-1 : 4-benzthiazine, $C_6H_4 \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{S} \text{---} \text{CO} \end{smallmatrix}$, pale yellow prisms, m. p. 250° (decomp.). The

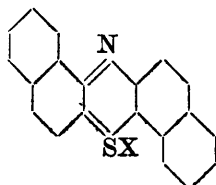
diketone is converted by dilute alkali hydroxide solutions into *o*-thiolphenyloxamic acid, $SH \cdot C_6H_4 \cdot NH \cdot CO \cdot CO_2H$, and finally into *o*-aminophenylmercaptan and oxalic acid. It is transformed by aniline into benzthiazole-2-carboxyanilide, m. p. 157—158°, and by phenylhydrazine into benzthiazole-2-carboxyphenylhydrazide, pale yellow needles or coarse crystals, m. p. 220—222° after previous softening. 7-Chloro-2 : 3-diketo-5-methyldihydro-1 : 4-benzthiazine, m. p. 255° (decomp.), and 2 : 3-diketodihydro- α -naphthathiazine, yellow needles, decomp. 315°, are described.

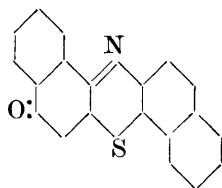
The dichloroketothiazines react with great readiness with amines, hydrazines, and phenylhydrazine. Thus, 2 : 2-dichloro-3-keto-2 : 3-dihydro-1 : 4-benzthiazine and aniline yield 2 : 3-diketodihydro-1 : 4-benzthiazine-2-anil, pale yellow, lustrous leaflets, m. p. 254—256°, which is converted by boiling alcohol into benzthiazole-2-carboxyanilide, m. p. 157—158°. In a similar manner, 7-chloro-5-methyldiketodihydro-1 : 4-benzthiazine-2-anil, golden-yellow leaflets, m. p. 247—248°, gives 6-chloro-4-methylbenzthiazole-2-carboxyanilide, colourless needles, m. p. 140—141°, and diketodihydro- α -naphthathiazine-2-anil, m. p. 290—292°, yields α -naphthathiazole-2-carboxyanilide, colourless needles, m. p. 202—203°. 2 : 3-Diketodihydro-1 : 4-benzthiazine-2-phenylhydrazone crystallises in lustrous leaflets, m. p. 270—272° (decomp.); the corresponding azine is an orange-red powder.

2 : 2-Dichloro-3-keto-2 : 3-dihydro-1 : 4-benzthiazine is transformed by oxythionaphthen into the dye, $C_6H_4 \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{S} \text{---} \text{C} : \text{C} < \text{CO} \\ \text{S} \text{---} \end{smallmatrix} C_6H_4$, identical with the substance prepared by Herzog (A., 1920, i, 182) in a different manner. H. W.

Azthionium Salts of the Naphthalene Series. II. F. KEHRMANN, ALFRED GRESSLY, WLADIMIR CHIFFÈRE, and MARIE RAMM (*Ber.*, 1923, 56, [B], 649—654).—A continuation and amplification of previous work (cf. A., 1902, i, 566; 1921, i, 449).

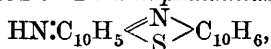
Thio- $\alpha\beta$ -dinaphthylamine (cf. Gressly, *Diss.*, Geneva, 1902) pale, orange-yellow prisms, m. p. 185—186°, is prepared by the action of sulphur on $\alpha\beta$ -dinaphthylamine at a temperature not exceeding 240°. It is readily converted by the action of the requisite acid in the presence of a suitable oxidising agent into di- $\alpha\beta$ -naphthazthionium salts (annexed formula), of which the *nitrate* (+H₂O), bronze crystals, the *perchlorate*, dark-violet crystals, and the *picrate*, dark-violet needles, are described in detail. Oxidation of thio- $\alpha\beta$ -dinaphthylamine by ferric chloride





leads to the formation of *di-αβ-naphthathiazine* (annexed formula), lustrous, dark brownish-red needles, m. p. 256—257°.

Thiodi-α-naphthylamine (cf. Kehrman and Dardel, A., 1922, i, 1064), m. p. 164—166°, in a capillary filled with carbon dioxide, is oxidised with great readiness in substance or in solution to α-dinaphthathiazone (cf. A., 1902, i, 566). It is converted by acetic anhydride and anhydrous zinc chloride into the *acetyl* derivative, $C_{20}H_{12}SNAC$, colourless crystals, m. p. 214—215°. *Di-αα-naphthazthionium nitrate*, brown needles, *perchlorate*, and *ferrichloride*, $C_{20}H_{12}NSCl_4Fe$, are described. The salt last mentioned is transformed by aniline hydrochloride and aniline in the presence of alcohol (80%) into di-α-naphthathiazone and *N-phenyl*di-2-naphthathiazime, $PhN:C_{10}H_5 \begin{smallmatrix} \text{N} \\ \text{S} \end{smallmatrix} > C_{10}H_6$, small lustrous black crystals, m. p. 250—254°. *Di-α-naphthathiazime*,



yellowish-red crystals, gives a dark, violet-brown *chloroplatinate*, a blackish-violet *hydrochloride*, and a *perchlorate*. H. W.

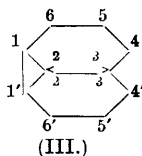
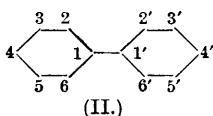
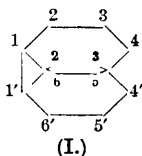
Influence of Substitution in the Components on Equilibrium in Binary Solutions. XXXVIII. The Binary Systems of Trinitrobenzene and Trinitrotoluene with the Three Isomeric Phenylenediamines. ROBERT KREMANN and OTTO MAUERMANN (*Monatsh.*, 1923, 43, 315—320).—Both trinitrobenzene and trinitrotoluene form equimolecular compounds with each of the phenylenediamines. For 1 : 3 : 5-trinitrobenzene and *o*-phenylenediamine, the equimolecular compound melts at 163° (33·7% by weight of diamine), the eutectic between the compound and diamine occurs at 92° and 93% of the diamine, that between the compound and trinitrobenzene occurring at 108° and 3% of diamine. The six corresponding figures for the other binary systems examined are as follows: 2 : 4 : 6-Trinitrotoluene and *o*-phenylenediamine, 97·5° (32·3%), 83° (57%), and 65° (9%). 1 : 3 : 5-Trinitrobenzene and *m*-phenylenediamine, 168° (33·7%), 45° (82%), and 105° (7%). 2 : 4 : 6-Trinitrotoluene and *m*-phenylenediamine, 105° (32·3%), 57·5° (90·5%), and 70° (6%). 1 : 3 : 5-Trinitrobenzene and *p*-phenylenediamine, 145·5° (33·7%), 106° (64%), and 101·5° (9%). 2 : 4 : 6-Trinitrotoluene and *p*-phenylenediamine, 93° (32·3%), 88° (38%), and 64° (8%). The results fall in line with those previously obtained with dinitrobenzenes, taking into account the effect of a third nitro-group (cf. A., 1919, ii, 54). E. E. T.

The Structure of Benzidine. ROGER ADAMS, J. E. BULLOCK, and W. C. WILSON (*J. Amer. Chem. Soc.*, 1923, 45, 521—527).—It has been found that benzidine and certain of its derivatives condense readily with meta- and para-disubstituted benzene compounds, namely with terephthalaldehyde and isophthalaldehyde, to form substances which presumably have the structures



These compounds are characterised by their extreme insolubility and high melting or decomposition points. Their analysis is difficult, because the moment the combustion starts all the material is burned at once. Benzidine gives with *isophthalaldehyde* an amorphous compound, $\begin{matrix} \text{C}_6\text{H}_4\cdot\text{N}=\text{CH} \\ \text{C}_6\text{H}_4\cdot\text{N}=\text{CH} \end{matrix} > \text{C}_6\text{H}_4$, with *terephthalaldehyde* a yellow compound, and with *terephthalaldehyde monazine*, m. p. 232° , an orange-coloured compound. Dianisidine gives with *terephthalaldehyde* a yellowish-green compound. *Terephthalaldehyde dihydrazone*, m. p. 165° , was obtained by treating *terephthalaldehyde* with an excess of hydrazine hydrate.

From the above results it seems probable that the benzene rings in diphenyl derivatives are in motion within the limiting positions of the two possible Kaufler formulæ, I and III (cf. A., 1907, i, 307, 794), and the intermediate position, II, which is usually assigned to diphenyl.



W. G.

Interaction of Formaldehyde and the Nitronaphthylamines. GILBERT T. MORGAN and FRANK RAYMOND JONES (*J. Soc. Chem. Ind.*, 1923, 42, 92—97T).—The condensation of formaldehyde with each of the known nitronaphthylamines has been investigated in order to determine the effect of orientation of the substituent groups on the reactivity of the amines towards formaldehyde. The simplest form of condensation occurs with 1-nitro- β -naphthylamine, a methylene group becoming associated with two imino-groups from the primary nitroamine, producing *methylene-bis-1-nitro- β -naphthylamine*, which exists as two chromo-isomerides having the same melting point, 222 — 223° . The yellow isomeride, obtained as needles when the condensation is effected in glacial acetic acid, is transformed by solution in hot pyridine into the red form, which crystallises in hard, bright red prisms. With 4-nitro- α -naphthylamine, in cold glacial acetic acid, formaldehyde condenses to form 4:4'-dinitro-1:1'-diamino-2:2'-dinaphthylmethane, m. p. 268 — 270° (decomp.), in which the methylene group has probably entered the ring in the remaining reactive position 2. The product is soluble in hot nitrobenzene, from which it crystallises on cooling as yellow needles. An analogous condensation occurs, but less readily, with 2-nitro- α -naphthylamine,

leading to the production of 3:3'-dinitro-4:4'-diamino-1:1'-dinaphthylmethane, m. p. 299—301° (decomp.). The product dissolves readily in nitrobenzene, from which it crystallises in fine, silky, voluminous, rectangular, golden-yellow prisms. With the heteronuclear nitronaphthylamines, the condensations are more complicated and comparable with the reactions arising in the case of the unsubstituted naphthylamines (Morgan, T., 1898, 73, 536; Senier and Goodwin, 1902, 81, 288; Möhlau and Haase, A., 1903, i, 118, 126). The condensation of 5-nitro- β -naphthylamine with formaldehyde in cold alcohol probably results in the production of methylenebis-5-nitro- β -naphthylamine and 5:5'-dinitro-2:2'-diamino-1:1'-dinaphthylmethane, m. p. 233—235°. The methylene base, the primary condensation product, was not isolated in a state of purity, but the succeeding products were obtained separately by effecting the condensation in alcohol in the presence of mineral acid. On prolonged heating, 5:5'-dinitro-2:2'-diamino-1:1'-dinaphthylmethane was further condensed to the corresponding dihydronaphthacridine, which by aerial oxidation was converted into 4:10-dinitrodinaphthacridine. Experiments with 8-nitro- β -naphthylamine indicate that, in position 8, the nitro-group appears to exert steric hindrance on the entry of the methylene radicle into the ring, so that the primary condensation product, methylenebis-8-nitro- β -naphthylamine, m. p. 178°, appears in alcoholic solution, but in alcohol acidified with hydrochloric acid the reaction proceeds to the production of a small yield of 8:8'-dinitro-2:2'-diamino-1:1'-dinaphthylmethane. The behaviour of 8-nitro- α -naphthylamine is similar to that of the corresponding β -naphthylamine. In glacial acetic acid, 5:5'-dinitro-4:4'-diamino-1:1'-dinaphthylmethane is produced and separates out with three molecular proportions of formaldehyde, as a pale yellow, crystalline powder. The yield is almost quantitative, and the m. p. of the additive compound is 172—173°. 5-Nitro- α -naphthylamine resembles α -naphthylamine in condensing with formaldehyde to give ill-defined and inseparable products. Evidence was obtained of the presence in the condensed products of a hydrolysable methylene base and a base of the dinaphthacridine series. J. S. G. T.

Action of the Oxides and the Oxy-acids of Nitrogen on the Phenylcarbamides. HUGH RYAN and PETER K. O'TOOLE (*Proc. Roy. Dublin Soc.*, 1923, 17, 139—155; cf. this vol., i, 321, 322, 323).—The nitration of phenylcarbamide, *s*-diphenylcarbamide, *as*-diphenylcarbamide, and triphenylcarbamide has been systematically investigated. In regard to ease of nitration, the phenylcarbamides resemble the corresponding phenylurethanes; they are much less easily nitrated than the analogous phenylnitrosoamines.

When treated with cold dilute nitric acid, phenylcarbamide forms its nitrate; *s*- and *as*-diphenylcarbamides are unchanged; and triphenylcarbamide yields a dinitrotriphenylcarbamide, yellow prisms, m. p. 190—191°, and a trinitrotriphenylcarbamide, slightly yellow leaves, m. p. 205—206°. Under similar conditions, but in

carbon tetrachloride suspension, phenylcarbamide forms the nitrate, *p*-nitro-, and 2:4-dinitro-derivatives; *s*-diphenylcarbamide is nitrated to the 4-nitro-, 4:4'-dinitro-, and 2:4:2':4'-tetranitro-derivatives; from *as*-diphenylcarbamide no pure compound is obtained; triphenylcarbamide gives the above dinitro- and trinitro-compounds, and a *pentanitrotriphenylcarbamide*, yellow prisms, decomp. 180°, m. p. 235—236° (decomp.). Cold fuming nitric acid converts phenylcarbamide into 2:4-dinitrophenylnitrocarbamide; *s*-diphenylcarbamide forms the 4:4'-dinitro- and 2:4:2':4'-tetranitro-derivatives; whilst both *as*-diphenylcarbamide and triphenylcarbamide give 2:4:2':4'-tetranitrodiphenylamine.

In cold glacial acetic acid solution, nitrous acid converts phenylcarbamide into nitrosophenylcarbamide, whilst *as*-diphenylcarbamide and triphenylcarbamide are apparently not acted on. *s*-Diphenylcarbamide forms *dinitroso-s-diphenylcarbamide*, prismatic needles, decomp. 103°, which is converted on being boiled with alcohol into *s*-diphenylcarbamide, gives 2:4:2':4'-tetranitro-*s*-diphenylcarbamide on direct nitration, and with nitric acid in acetic acid solution gives 4:4'-dinitro-*s*-diphenylcarbamide. A synthesis of the latter by the condensation of 1 mol. of carbamide with 2 mols. of *p*-nitroaniline is described. The same dinitroso-compound is produced by the action of nitrous fumes in acetic acid solution on *s*-diphenylcarbamide, but by the prolonged action of nitrogen peroxide, 4:4'-dinitrodiphenylcarbamide is produced. Phenylcarbamide is converted by nitrous fumes in carbon tetrachloride suspension into *o*-nitrophenol and *p*-nitrophenol. *as*-Diphenylcarbamide is decomposed by nitrogen peroxide at the ordinary temperature, forming 4:4'-dinitrodiphenylnitrosoamine; triphenylcarbamide under similar conditions gives the trinitrotriphenylcarbamide (above).

W. S. N.

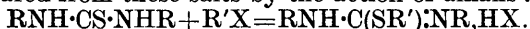
Action of the Oxides and the Oxy-acids of Nitrogen on Phenylmethylcarbamide. HUGH RYAN and MICHAEL J. SWEENEY (*Proc. Roy. Dublin Soc.*, 1923, 17, 157—162; cf. preceding abstract).—No nitro-derivatives of phenylmethylcarbamide have been obtained, because nitrous acid converts phenylmethylcarbamide into methylaniline; nitro-derivatives of the latter are in all cases isolated.

Gaseous nitrogen peroxide converts phenylmethylcarbamide into 2:4:6-trinitrophenylmethylnitrosoamine (tetryl), but in solution 4-nitrophenylmethylnitrosoamine, 2:4-dinitro-, and 2:4:6-trinitromethylaniline are successively produced. In the presence of carbamide nitrate, nitric acid has little, if any, action on phenylmethylcarbamide, but in the presence of nitrous acid, phenylmethylnitrosoamine, 4-nitrophenylmethylnitrosoamine, 2:4-dinitromethylaniline, 2:4:6-trinitromethylaniline, and tetryl are formed.

Tetryl may readily be obtained pure by the nitration of phenylmethylcarbamide or of phenylmethylnitrosoamine.

W. S. N.

Thiocarbamide Ethers. F. B. DAINS and W. C. THOMPSON (*Univ. Kansas Sci. Bull.*, 1922, **13**, 118—120; cf. Will, A., 1881, 905; Will and Bielschowski, A., 1882, 1090; Evers, A., 1888, 600; Foerster, A., 1888, 944).—Substituted thiocarbamides form additive products with alkyl halides, the free thiocarbamide ethers being prepared from these salts by the action of alkalis :



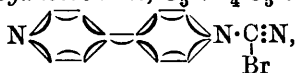
When 15 g. of thiocarbamilide and 10 g. of propyl iodide are heated for one hour on the steam-bath, a light brown, viscous liquid separates and solidifies on cooling. When crystallised from alcohol, colourless *N-diphenyl-S-propylthiocarbamide hydriodide*, m. p. 103°, is obtained; the free *base* forms needles, m. p. 61·5°. Butyl iodide and thiocarbamilide yield *N-diphenyl-S-butylthiocarbamide hydriodide*, m. p. 122°, which could not be crystallised, but was well washed with ethyl ether; the corresponding *base* is a colourless oil. Propyl iodide and di-*p*-tolylthiocarbamide give *N-di-p-tolyl-S-propylthiocarbamide hydriodide*, m. p. 165° (*base*, fine, white needles, m. p. 99°). The corresponding *butyl* derivative is a thick, colourless liquid (*hydriodide*, m. p. 145°). Di-*m*-xylylcarbamide and propyl iodide yield directly *N-di-m-xylyl-S-propylphenylthiocarbamide*, m. p. 113·5°. The unsymmetrical nature of the molecule did not prevent addition of the alkyl iodide, since methyl iodide and phenylbromophenylthiocarbamide yield *N-phenyl-p-bromophenyl-S-methylthiocarbamide hydriodide*, m. p. 152° (*base*, white needles, m. p. 79°); *N-phenyl-p-bromophenyl-S-propylthiocarbamide hydriodide*, a red oil (*base*, m. p. 84°), and *N-phenyl-p-bromophenyl-S-butylthiocarbamide hydriodide*, a thick oil (*base*, a viscid oil) were also prepared. When phenylthiocarbamide and butyl iodide are warmed together on a water-bath, a gummy mass is produced which on treatment with sodium carbonate yields *N-phenyl-S-butylthiocarbamide*, a heavy oil.

CHEMICAL ABSTRACTS.

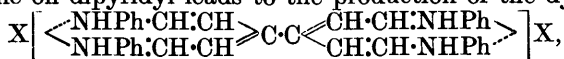
The Presumed Reaction of 4 : 4'-Dipyridyl with Potassium Ferrocyanide. J. P. WIBAUT and ELISABETH DINGEMANSE (*Rec. trav. chim.*, 1923, **42**, 184—185).—It has been stated that 4 : 4'-dipyridyl gives a characteristic blue precipitate with potassium ferrocyanide (Anderson, *Annalen*, 1870, **78**, 274; Weidel and Russo, A., 1883, 483), and Heuser and Stoehr obtained reddish-brown crystals which they assert, apparently without experimental evidence, to be 4 : 4'-dipyridyl ferrocyanide (A., 1892, 75). The authors have prepared the blue precipitate and found it to be Berlin-blue, whilst the reddish-brown crystals obtained in hydrochloric acid solution are now proved to be the dipyridyl ferrocyanide. The reaction, however, is not specific for 4 : 4'-dipyridyl.
H. J. E.

Fission of 4 : 4'-Dipyridyls by Cyanogen Halides. W. KÖNIG [with G. EBERT and K. CENTNER] (*Ber.*, 1923, **56**, [B], 751—758).—The action of cyanogen bromide and amines on 4 : 4'-dipyridyls has been investigated with the object of preparing pentamethine dyes.

4 : 4'-Dipyridyl 1-cyanobromide, $C_5NH_4 \cdot C_5NH_4Br \cdot CN$, or



is prepared by the addition of an ethereal solution of cyanogen bromide to 4 : 4'-dipyridyl dissolved in alcohol; the use of anhydrous materials and the exclusion of moisture are essential to the success of the preparation, the special apparatus for which is fully described in the original. The substance forms a pale brown precipitate which decomposes into dipyridyl and cyanogen bromide when heated. It gives *salts* with picric acid and sodium perchlorate. It is converted by aniline and subsequent treatment with sodium perchlorate, picric acid, or potassium iodide into the corresponding dipyridyl, salts of which the *iodide*, $C_{20}H_9N_2I \cdot H_2O$, brownish-yellow leaflets which commence to sublime at 65° , is described in detail. The simultaneous action of cyanogen bromide and aniline on dipyridyl leads to the production of the dye



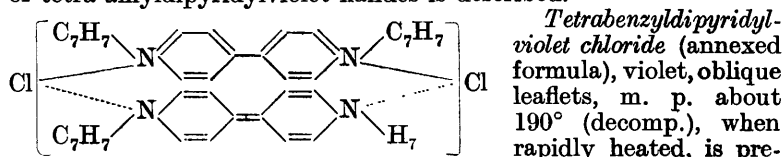
which is converted into 1 : 1'-diphenyl-4 : 4'-dipyridylium bromide; the corresponding *perchlorate*, $C_{22}H_{18}O_8N_2Cl_2$, pale, greenish-yellow needles, m. p. 299° (decomp.), the *picrate*, $C_{34}H_{22}O_{14}N_8$, slender, yellow needles, m. p. 170° , and the *chloroferrate*, $C_{22}H_{18}N_2Cl_6Fe_2$, small, yellow needles, m. p. 210 — 215° , are described. 1 : 1'-Diphenyl-4 : 4'-dipyridylium di-iodide is precipitated as a yellow, unstable polyhydrate which passes into the stable salt ($+0.5H_2O$), small, dark red prisms.

The 1 : 1'-diphenyldipyridylium salts exhibit the "triphenylmethyl phenomenon" particularly distinctly when they are warmed with zinc dust and glacial acetic acid; the deep bluish-green coloration disappears immediately when the solutions are shaken with air, and the process may be repeated as long as unused zinc dust is present. The same change is observed in aqueous-alcoholic solution in the presence of hyposulphite, zinc dust, or ferrous sulphate, or in aqueous solution in the presence of free hydroxylamine; a meriquinonoid compound appears to be thereby produced (cf. Emmert, A., 1922, i, 1064). A pure green coloration is caused by the addition of alkali hydroxide to aqueous solutions of 1 : 1'-diphenyldipyridylium salts; its formation is explained on the assumption that the ammonium base is partly converted into the *pseudo*-base, which passes into a mixture of 1 : 1'-diphenyl-2 : 2'-dipyridone and 1 : 1'-diphenyl-2 : 2'-tetrahydro-4 : 4'-dipyridyl; the latter substance becomes tautomerised to the 4 : 4'-tetrahydro-compound which reacts with unchanged ammonium base to give a green, quinhydrone-like compound.

H. W.

Quinhydrone-like Compounds of 1 : 1'-Dialkyldihydro-4 : 4'-dipyridyls. BRUNO EMMERT and OTTO VARENKAMP (*Ber.*, 1923, 56, [B], 491—501).—In a previous communication (A., 1922, i, 1064), it has been shown that 4 : 4'-dipyridyl dibenzyl-iodide is reduced by 1 : 1'-dibenzyltetrahydro-4 : 4'-dipyridyl to

1 : 1'-dibenzyl-dihydro-4 : 4'-dipyridyl, which immediately unites with a second molecule of dipyridyl dibenzyl iodide to give a quinhydrone-like compound. More recently, Dimroth and Frister (this vol., i, 149) have isolated the parent substance of this quinhydrone, which they term dipyridylviolet chloride. In the present communication, this nomenclature is adopted, and a further series of tetra-alkyldipyridylviolet halides is described.



by the action of an alcoholic solution of 1 : 1'-dibenzyl-tetrahydro-4 : 4'-dipyridyl on an equimolecular quantity of dipyridyl dibenzylchloride. It can be preserved during some days when exposed to air. It is extraordinarily sensitive to air if dissolved in acetic anhydride or glacial acetic acid, but much more stable in chloroform, acetone, aniline, or, particularly, in pyridine. *Tetra*benzyl*dipyridylviolet bromide*, dark violet, oblique leaflets, is prepared in a similar manner. The substance is also prepared by the reduction of 4 : 4'-dipyridyl dibenzylbromide in alcoholic solution (90%) by zinc dust or magnesium powder, thus indicating that the blue colour observed during the treatment of dipyridyl dialkyl iodides with zinc dust is due to the quinhydrone, and not, as Weitz and König have supposed (A., 1922, i, 1186), to the halogen-free, 1 : 1'-dialkyl-4 : 4'-dipyridinium radicle.

[With VALENTIN DÖLLEIN.]—*Tetra*isoamyl*dipyridylviolet iodide*, dark violet leaflets, with a metallic reflex, is prepared by the action of zinc dust on 4 : 4'-dipyridyl diisoamyl iodide.

4 : 4'-Dipyridyl dibenzylchloride is reduced by chromous chloride to *tetra*benzyl*dipyridylviolet chloride*; the corresponding bromide is produced in unsatisfactory yield by the action of phenylhydrazine on 4 : 4'-dipyridyl dibenzylbromide.

The semiquinonoid character of *tetra*benzyl*dipyridylviolet bromide* and *iodide* is further established by the observation that a molecular proportion of either substance dissolved in glacial acetic acid absorbs an atomic proportion of oxygen.

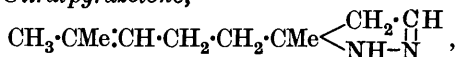
[With HEINRICH LUDWIG.]—2 : 6 : 2' : 6'-*Tetra*dimethyl*dipyridyl dibenzyl iodide*, obtained from its components at 150°, is isolated in a red, anhydrous and a yellow, hydrated form. It is converted by dibenzyltetrahydrodipyridyl into *tetra*benzyl*di*-2 : 6 : 2' : 6'-*tetra*dimethyl*dipyridylviolet iodide*, dark bronze-brown, oblique leaflets, m. p. about 170°. 2 : 6-Dimethylpyridine benzyl iodide is prepared from its components at 130° (corresponding *perchlorate*, long needles, m. p. 141°); it is reduced by sodium amalgam to *dibenzyltetrahydro*di-2 : 6 : 2' : 6'-*tetramethylpyridyl*, pointed prisms, m. p. 124°, after previous darkening.

[With GERHARD JUNGCK.]—Dimethyltetrahydrodicollidyl and dipyridyl dibenzyl iodide yield *tetra*benzyl*dipyridylviolet iodide* and methylcollidinium iodide. Collidinium methoperchlorate is

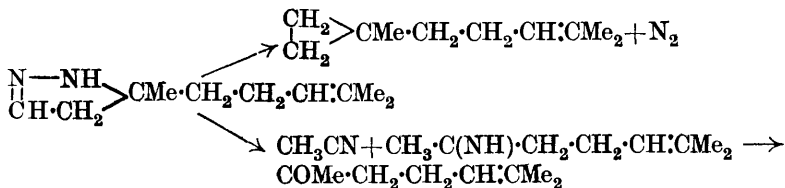
obtained by the action of silver nitrate dissolved in alcohol on 1:1'-dimethyltetrahydrodicollidyl and, after removal of the silver, addition of perchloric acid.

[With EBERHARD VOGT.]—By the introduction of a phenyl group in position 4, it was hoped to weaken the union of the γ -carbon atoms possibly to such an extent as to lead to the formation of the radicle. With this object, 4-phenylpyridine is converted into the corresponding *methiodide*, almost colourless crystals, which, however, is reduced by sodium amalgam and water to 4-phenyl-1-methyldihydropyridine, colourless needles, m. p. 36°, instead of the expected dipyridyl derivative. H. W.

The Conversion of Citral into the Hydrocarbon, $C_{10}H_{18}$, of the *cycloPropane* Series. N. KISHNER (*J. Russ. Phys. Chem. Soc.*, 1918, 50, 1—19; A., 1911, i, 1027; 1914, i, 129).—The hydrazone of citral is converted by distillation into the pyrazolone. The anomalous behaviour of citral in forming a semi-stable hydrazone, although it has a double bond in the $\alpha\beta$ -position to the carbonyl group, which seems usually to preclude the formation of hydrazones, giving in their place pyrazolones, is explained as being due to the space configuration of the citral, which approaches that of ring compounds, these giving stable hydrazones. *Citralpyrazolone*,

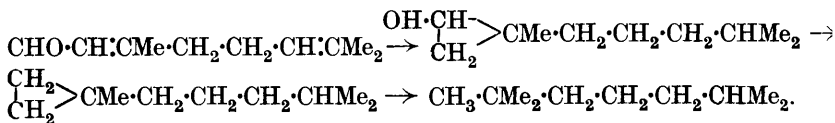


is obtained as an oil, b. p. 122°/12 mm., d_{20}^{20} 0.9213, n_{20}^{20} 1.4897, soluble in water, and very hygroscopic. The *phenylthiocarbamyl* compound, $\text{NHPh}\cdot\text{CS}\cdot\text{N}_2\text{C}_{10}\text{H}_{17}$, forms large prisms, m. p. 51°. The pyrazolone is unaffected by cold glacial acetic acid or by cold fuming hydrochloric acid, but on heating with the latter in a sealed tube at 100°, hydrazine hydrochloride is eliminated, and *p*-cymene obtained quantitatively. The *p*-cymene thus obtained is uncontaminated by other products, and this method is recommended for its preparation in a pure state. Citral itself gives the same product under these conditions, but the reaction is much slower, and it seems probable that the pyrazolone is converted directly into *p*-cymene, and not first into citral. The pyrazolone on distillation, in the presence of platinum catalyst, from alkali hydroxide, gives in the distillate, together with unchanged material, acetone, nitrile, methylheptanone, and 1-methyl-1-isohexylenylcyclopropane, $\text{C}_{10}\text{H}_{18}$, formed in the following way:



The hydrocarbon had b. p. 160°/735 mm., d_4^{20} 0.7744, n_D^{20} 1.4432. Its structure was deduced from its oxidation products, acetone, {a

ketone, and an acid. The *ketone*, $\begin{smallmatrix} \text{CH}_2 \\ | \\ \text{CH}_2 \end{smallmatrix} > \text{CMe} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CHMe}_2$, has m. p. 14.5—15°, b. p. 222.5°/749 mm., d_4^{20} 0.9406, n_D^{20} 1.4491 (*semicarbazone*, m. p. 149—151°). The *acid*, $\begin{smallmatrix} \text{CH}_2 \\ | \\ \text{CH}_2 \end{smallmatrix} > \text{CMe} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, has b. p. 219—222°/756 mm., d_4^{15} 0.9919, n_D^{15} 1.4444, and gives an *anilide*, m. p. 126—127°. Further evidence of the structure of the hydrocarbon is given by its reduction products, obtained by the action of hydrogen in the presence of a platinum catalyst. This results in a mixture of three parts of 1-methyl-1- β -methylpentyl-cyclopropane with five parts of a further reduction product, $\beta\beta\gamma$ -trimethylheptane, b. p. 150.5—151.5°/748 mm., d_4^{20} 0.7215, n_D^{20} 1.409. The reduction of the undistilled hydrazone, which has a citral-like structure, leads to the production of an isomeride of the latter, $\beta\epsilon$ -dimethyloctane. It is shown that the hydrocarbon obtained by Skita and Ritter (A., 1911, i, 272) by the Sabatier reduction of citral is not, as they stated, the $\beta\epsilon$ -dimethyloctane, but $\beta\beta\epsilon$ -trimethylheptane, the formation of which is thus explained:



R. T.

Bromo-derivatives of 4-Methylglyoxaline. FRANK LEE PYMAN and GEOFFREY MILLWARD TIMMIS (T., 1923, 123, 494—503).

4(5)-Nitroglyoxaline-5(4)-carboxylic Acid. A. WINDAUS and W. LANGENBECK (*Ber.*, 1923, 56, [B], 683—686).—The acid (cf. Windaus and Opitz, A., 1911, i, 752; Mörner, A., 1918, i, 198; *Z. physiol. Chem.*, 1918, 103, 80; Fargher and Pyman, T., 1919, 115, 219) may be obtained readily by the condensation of 5(4)-nitro-4(5)-methylglyoxaline with aldehydes and oxidation of the products by potassium permanganate.

4(5)-Nitro-5(4)-methylglyoxaline condenses with benzaldehyde in the presence of piperidine at 150—160° to yield 4(5)-nitro-5(4)-styrylglyoxaline, $\begin{smallmatrix} \text{N} \cdot \text{C}(\text{NO}_2) \\ | \\ \text{CH} - \text{NH} \end{smallmatrix} > \text{C} \cdot \text{CH} \cdot \text{CHPh}$, golden-yellow leaflets, decomp. above 220°; the corresponding *compound* from anisaldehyde crystallises in orange-yellow needles, m. p. about 296° (decomp.). The styryl derivative is converted by potassium permanganate in cold alkaline solution almost quantitatively into 4(5)-nitroglyoxaline-5(4)-carboxylic acid, almost colourless prisms, m. p. above 300° (decomp.). The acid loses carbon dioxide when heated at 150° and yields 4(5)-nitroglyoxaline. *Methyl-4(5)-nitroglyoxaline-5(4)-carboxylate* crystallises in colourless, lustrous leaflets, m. p. 212—213°; 4(5)-*nitroglyoxaline-5(4)-carboxyamide* forms almost colourless needles or prisms, m. p. 291°. Methyl nitroglyoxalinecarboxylate is hydrogenated in absolute alcoholic

solution in the presence of palladium black to the corresponding amino-ester, which is characterised as the *picrate*, $C_{11}H_{10}O_9N_3$, yellow needles, m. p. 235° (decomp.), and *hydrochloride*, $C_5H_8O_2N_3Cl$, m. p. about 210° (decomp.). 4(5)-Aminoglyoxaline-5(4)-carboxy-amide is prepared in a similar manner, and is characterised as the *picrate*, $C_{10}H_9O_9N_3$, small prisms, decomp. about 240° , and the *hydrochloride*, $C_4H_7ON_4Cl$. H. W.

Bromination of Glyoxaline-4-carboxyanilide. HAROLD KING and WILLIAM OWEN MURCH (T., 1923, 123, 621—629).

Some New Unsymmetrical Dialkylbarbituric Acids. I. Ethylalkylbarbituric Acids. M. TIFFENEAU (*Bull. Soc. chim.*, 1923, [iv], 33, 183—188).—The preparation and properties of some new ethylalkylbarbituric acids are described. *Ethyl-n-butylbarbituric acid* forms slender needles, m. p. 128° . It was obtained by condensing carbamide with *ethyl ethyl-n-butylmalonate*, b. p. 240 — $245^\circ/770$ mm. This ester on hydrolysis and subsequent heating of the free acid gives α -*ethylhexoic acid*, b. p. 220 — $224^\circ/770$ mm. Its *chloride* boils at 85 — $90^\circ/20$ mm., and its carbamide, α -*ethylhexoylecarbamide*, melts at 159° . *Ethylisobutylbarbituric acid*, needles, m. p. 174° , was prepared in the usual way from *ethyl ethylisobutylmalonate*, b. p. 234 — $240^\circ/760$ mm. This ester on saponification gave *ethylisobutylmalonic acid*, m. p. 107 — 108° , which by loss of carbon dioxide gave γ -*methyl- α -ethylvaleric acid*, b. p. $115^\circ/20$ mm. The *chloride* of this acid boils at 168 — 171° and the *amide* melts at 89° . Both the butyl- and isobutyl-ethylbarbituric acids are about three times as active as veronal. *Ethylisoamylbarbituric acid* forms leaflets, m. p. 154 — 155° . It is nearly as powerful a hypnotic as the butyl derivatives, but acts much more rapidly, and its effect is correspondingly less prolonged. It is obtained from *ethyl ethylisoamylmalonate*, b. p. 248 — 253° . *Ethylisoamylmalonic acid* melts at 116 — 118° , and is converted on heating into δ -*methyl- α -ethylhexoic acid*, b. p. 228 — 232° . The *chloride* of this acid boils at 188 — 192° , and the *amide* melts at 106 — 108° . To complete the series of alkylbarbituric acids, *di-n-butylbarbituric acid* was prepared. It melts at 153° .

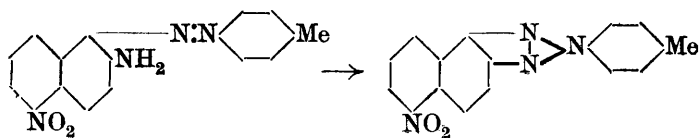
G. F. M.

Some New Unsymmetric Dialkylbarbituric Acids. II. Homologous Series. CH. SOMMAIRE (*Bull. Soc. chim.*, 1923, [iv], 33, 189—195).—The preparation of the following ethyl dialkylmalonates, free dialkylmalonic acids, and the dialkylacetic acids derived from them, and also the dialkylbarbituric acids obtained by condensation with carbamide, are described: *Ethyl methyl-n-butylmalonate*, b. p. 235 — 241° ; *methyl-n-butylmalonic acid*, m. p. 98° ; *methyl-n-butylbarbituric acid*, m. p. 181° ; *ethyl propyl-n-butylmalonate*, b. p. 248 — 253° ; *propylbutylmalonic acid*, m. p. 150 — 151° ; α -*propylhexoic acid*, d^0 0.914, its *chloride*, b. p. 192 — $195^\circ/767$ mm., and *amide*, m. p. 122 — 123° ; *propylisobutylbarbituric acid*, m. p. 153° ; *butylisobutylbarbituric acid*, m. p. 153° ; *ethyl methylisobutylmalonate*, b. p. 232 — 236° ; *methylisobutylbarbituric*

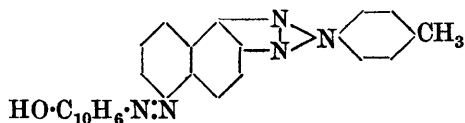
acid, m. p. 195°; γ -methyl- α -propylvaleramide, m. p. 121°; propylisobutylbarbituric acid, m. p. 164—165°; ethyl methylisoamylmalonate, b. p. 242—247°; methylisoamylmalonic acid, m. p. 131—132°; α , δ -dimethylhexoic acid, b. p. 120—130°/15 mm., giving a chloride, b. p. 69—71°/15 mm., and an amide, m. p. 103°; methylisoamylbarbituric acid, m. p. 187°; ethyl propylisoamylmalonate, b. p. 254—259°/76 mm.; propylisoamylmalonic acid, m. p. 143°; δ -methyl- α -propylhexoic acid, b. p. 238—245°, giving a chloride, b. p. 200—205°, and an amide, m. p. 117—118°; propylisoamylbarbituric acid, m. p. 134°; ethyl heptylmalonate, b. p. 273—275°; ethyl ethylheptylmalonate, b. p. 168—171°/15 mm.; ethyl heptylbarbituric acid, m. p. 118—119°. The maximum hypnotic activity observed by Tiffeneau (preceding abstract) with the C₁₀ and C₁₁ members of the barbituric acid series was not exceeded by any of the above homologues. The activity of the higher members seems to depend on the solubility, which diminishes rapidly with increasing number of carbon atoms. The influence of a branched chain on the solubility in water is anomalous. In the methyl series, the isobutyl group does not change the solubility as compared with the butyl group, in the ethyl series it somewhat reduces the solubility, in the propyl series it increases it slightly, and in the butyl series it considerably increases it. In all cases, an increasing number of carbon atoms decreases the solubility, with the sole exception of the methyl- and ethyl-butylbarbituric acids, the solubility of the former being only about one-half of that of the latter. G. F. M.

Constitution of Natural Muscarine. S. SCHELBA (*Atti R. Accad. Lincei*, 1922, [v], 31, ii, 518—520).—In order to ascertain if muscarine has the aldehydic structure usually assigned to it, the author treated, with the Angeli-Rimini aldehyde reagent, an extract prepared from *Agaricus muscarius*; no hydroxamic acid was, however, obtained, although the extract showed distinctly the physiological effect of muscarine. To obtain a definite decision on this question, the preparation of a larger quantity of muscarine is contemplated. T. H. P.

Preparation of a Series of Substituted α -Naphthylamines and of the Dyes derived from them. L. B. HOLLIDAY & Co., LTD., and GILBERT THOMAS MORGAN (Brit. Pat. 191797).—Triazoles derived from α -naphthylamine are obtained from 5-nitro- β -naphthylamine, which is the main product of the dehydration of β -naphthylamine nitrate, by coupling with diazotised *p*-toluidine, whereby 1-*p*-toluenazo-5-nitro- β -naphthylamine is obtained, and this compound on oxidation with chromic acid is converted into 6-nitro-2-*p*-tolyl- $\alpha\beta$ -naphthatriazole, according to the following scheme:



On reduction with stannous chloride, the corresponding 6-amino-1-p-tolyl- $\alpha\beta$ -naphthatriazole is formed. A similar series of reactions may be carried out with 8-nitro- β -naphthylamine. The amino-triazoles are capable of conversion into diazo-derivatives which couple readily with phenols, and the more reactive aromatic amines



to form azo-dyestuffs. Thus, for example, on coupling with β -naphthol a red azo-compound, 2-p-tolyl- $\alpha\beta$ -naphthatriazole-6-azo- β -naphthol, of the an-

nexed constitution is obtained.

The amino-triazoles can also be coupled with other diazo-compounds, for example, a brownish-red dyestuff, 7-p-nitrobenzene-azo-6-amino-2-p-tolyl- $\alpha\beta$ -naphthatriazole is obtained from the above amino-triazole and diazotised *p*-nitroaniline. The conversion of this substance, by oxidation with chromic acid, into a bis-triazole derivative proves its constitution as an ortho-amino-azo-compound.

G. F. M.

Adsorption of Uric Acid by Animal Charcoal, Suspensoid Colloids, and Proteins. K. HARPUDE (Z. ges. exp. Med., 1922, 29, 208—223; from Chem. Zentr., 1923, i, 90—91).—The adsorption of uric acid by animal charcoal follows the ordinary equation, $y/m = kc^{1/n}$. The temperature coefficient of adsorption is negative and inappreciable. Adsorption is increased in the presence of hydrochloric acid, decreased in presence of moderate concentrations of alkalis; with higher concentrations of alkalis adsorption is increased. In the presence of large quantities of neutral salts, adsorption is increased. Addition of sodium urate to a colloidal solution of ferric hydroxide produces, first, a marked turbidity and then, with larger quantities of sodium urate, flocculation, the sodium urate being adsorbed by the colloidal ferric hydroxide. Casein in 0.1*N*-alkali solution does not adsorb a neutral urate. In 0.1*N*-acid solution, however, sorption takes place and separation of the urate by ultra-filtration is not possible. The fixation differs in some respects from normal adsorption. The flocculation of casein chloride by neutral salts is facilitated by addition of uric acid. This is due either to a widening of the isoelectric zone or to flocculation before the isoelectric point is reached. Casein in acid solution is flocculated by uric acid directly. 0.373 Millimol. of uric acid flocculate 100 c.c. of 0.75% casein solution in 0.005*N*-hydrochloric acid. The corresponding value for flocculation by sodium chloride is 16.45 millimol., and by sodium sulphate 0.21 millimol. Serum-globulin behaves like casein. The effect of sorption of uric acid on the stability of globulin is less marked than in the case of casein solutions. Albumins show very little sorption of uric acid, which, in consequence, has no effect on their stability. The sorption of uric acid by proteins is held to be governed by intensity of electrical charge and is not a simple adsorption. A purely electrical explanation is, however,

*p**

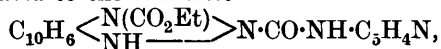
inadequate. Organ extracts from muscle, cartilage, and liver fix uric acid to varying extents, the greatest fixation being shown by liver extract, the least by cartilage extract. G. W. R.

The Formation of By-products in Diazotisation by Witt's Method. L. ELION (*Rec. trav. chim.*, 1923, 42, 145—183).—Diazotisation by Witt's method (A., 1909, i, 855) of six substituted anilines, all somewhat basic, showed that the reaction did not in any instance take place wholly in the normal manner. Five of the substances, 3:5-dibromo-4-aminobenzoic acid, 3:5-dibromo-4-aminobenzaldehyde, 3:5-dibromo-4-aminoacetophenone, 3:5-dichloro-4-aminobenzoic acid, 3:5-dibromo-2-aminobenzoic acid, yield, in addition to the anticipated product, a nitro-derivative, whilst the sixth, 3:5-dinitro-4-aminobenzoic acid, furnished a diazonium compound of such instability that it was decomposed by the addition of ice to its solution. The action of the nitric acid on the first four substances is to replace the group in the para-position to the amino-group by a nitro-group in a portion of the product: this takes place when the two ortho-positions with respect to the amino-group are occupied by bromine or chlorine, the groups replaced being carboxyl, acetyl, and the aldehyde group, respectively. In the case of 3:5-dibromo-2-aminobenzoic acid, the bromine atom in the para-position to the amino-group is replaced by the NO_2 -group, whilst when nitro-groups occupy both ortho-positions, as in 3:5-dinitro-4-aminobenzoic acid, the amino-group is not diazotised to hydrogen, but to hydroxyl, and the carboxyl group in the para-position is left unchanged. In order to study the formation of these by-products, the action of nitric acid on the original amines was investigated and the results showed that in each case in which nitration during diazotisation yields a by-product, the acid yielded a nitrated nitroamine. From 3:5-dibromo-4-aminobenzaldehyde two nitroamines were obtained, one of which contains the aldehydic group unchanged, whilst in the other this is replaced by the nitro-group; the author considers that the latter substance is obtained by secondary nitration. In the case of 3:5-dibromoanthranilic acid, an intramolecular rearrangement of bromine and the nitro-group of the ring takes place subsequently to nitration. With the exception of 3:5-dinitro-4-aminobenzoic acid, a small quantity of a diazonium compound was obtained in each experiment, probably due to the formation of nitrous acid from the nitric acid. The results of direct nitration of the amines suggest that the accessory reaction in diazotisation takes place in such a way that a portion of the original substance is first transformed into nitroamine, which is then diazotised and reduced, thus forming the by-product. The diazotisation of a nitroamine being essentially a reduction, an attempt to bring about this transformation by means of alcohol was made and treatment of 2:6-dibromo-4-nitrophenylnitroamine with alcohol resulted in the formation of 3:5-dibromonitrobenzene. The same change was also effected by Witt's method of diazotisation, which is also accompanied by denitration. The following substances do not

appear to have been described previously: 3:5-dichloro-4-amino-benzoic acid, prepared by chlorination of *p*-aminobenzoic acid, m. p. 291°; 3:5-dinitro-4-nitroaminobenzoic acid, yellow plates containing 1H₂O, softens at 80°, decomp. 135—136°; 3:5-dinitro-bromobenzene, obtained by diazotising 2:4-dinitro-6-bromoaniline, long, pale yellow plates, m. p. 77°. H. J. E.

The Azo-ester Reaction of 3-Aminopyridine. OTTO DIELS and GEORG BEHNEN (*Ber.*, 1923, 56, [B], 561—566).—It has been shown previously that strongly basic amines react with azodicarboxylic esters to give amides, whereas aliphatic amines generally yield stable additive products of differing types. 3-Aminopyridine is found to behave in the same manner as the strong bases, but in addition to diamides it also yields the ester amides of which representatives have not previously been obtained; they are remarkable for the extraordinary readiness with which the alkyl group of the carbalkoxy-residue suffers replacement.

Ethyl azodicarboxylate reacts vigorously with 3-aminopyridine in alcoholic solution, with the formation of *azodicarboxy-di-3-pyridyl-amide*, N₂(CO·NH·C₅H₄N)₂, pale yellow needles, m. p. 164° (decomp.). If the substances are allowed to react at -20°, *ethyl azodicarboxy-3-pyridylamidate*, C₅H₄N·NH·CO·N·N·CO₂Et, orange-yellow, coarse needles, m. p. 136—137° (decomp.), is obtained; the substance decomposes slowly when preserved, rapidly when treated with dilute acids. The corresponding *methyl* ester, orange-yellow needles, m. p. 113° (decomp.), is prepared from 3-aminopyridine and methyl azodicarboxylate in methyl-alcoholic solution. It is converted by crystallisation from ethyl alcohol into the ethyl ester, m. p. 136—137°, which is also obtained from methyl azodicarboxylate and 3-aminopyridine in the presence of ethyl alcohol. The ethyl ester is converted by a solution of methylamine in alcohol at -20° into *azodicarboxy-3-pyridylmethyl diamide*, C₅H₄N·NH·CO·N·N·CO·NHMe, red crystals, m. p. 137°, and by β-naphthylamine in the presence of pyridine into the *compound*, (β)NH₂·C₁₀H₆·(α)N(CO₂Et)·NH·CO·NH·C₅H₄N, colourless, lustrous leaflets, m. p. 182° (decomp.) [the *hydrochloride*, *perchlorate*, and *acetyl* derivative, C₂₁H₂₁O₄N₅, m. p. 232° (decomp.), are described]. The compound is oxidised by hydrogen peroxide in the presence of glacial acetic acid to the *substance*



dark brown needles, decomp. above 250°.

H. W.

Catalytic Hydrogenation of Alkyl-substituted Pyrroleazo-dyes. HANS FISCHER and FRIEDRICH ROTHWEILER (*Ber.*, 1923, 56, [B], 512—519).—Aminopyrroles have previously been very difficultly accessible substances. A number of them are now obtained by the catalytic hydrogenation of pyrroleazo-dyes. Since, however, the behaviour of certain of the compounds is scarcely that which would be expected of substances containing the amino-group, the constitutions are assigned to them with

reserve, since the possibility that an extension of the ring has occurred is not excluded.

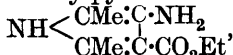
Reduction is effected in alkaline-alcoholic solution in the presence of platinum black. The formation of the hydrazo-compound takes place rapidly, after which further absorption of hydrogen proceeds much more slowly.

Reduction of 2 : 3 : 5-trimethylpyrrole-4-azobenzenesulphonic acid in alkaline solution leads to the production of 4-amino-2 : 3 : 5-trimethylpyrrole, $\text{NH} \begin{smallmatrix} \text{CMe}:\text{CMe} \\ \text{CMe}:\text{C}\cdot\text{NH}_2 \end{smallmatrix}$, colourless crystals, m. p. 186°

(decomp.), and sodium sulphanilate, which are separated from one another by taking advantage of the ready solubility of the base and the insolubility of the salt in alcohol. The amine gives a hygroscopic *hydrochloride*, prismatic crystals, m. p. 234° (decomp.), and a crystalline *picrate*, m. p. (indefinite) 210—230° (decomp.), after becoming black at 180°. It could not be acetylated, benzoylated, methylated with methyl sulphate, or caused to react with phenylcarbimide.

5-Amino-3-acetyl-2 : 4-dimethylpyrrole, $\text{NH} \begin{smallmatrix} \text{C}(\text{NH}_2):\text{CMe} \\ \text{CMe}=\text{CAc} \end{smallmatrix}$, rods, m. p. 223° (decomp.) after darkening and softening at 220°, is obtained similarly from 3-acetyl-2 : 4-dimethylpyrrole-5-azobenzenesulphonic acid; it gives a *picrate*, m. p. 175—190°, after darkening at 175°, according to the manner of heating.

Ethyl 4-amino-2 : 5-dimethylpyrrole-3-carboxylate,



is obtained in the form of the *hydrochloride*, colourless, rectangular leaflets or slender needles, m. p. 212° (decomp.) after previous darkening and softening, by the reduction of 3-carbethoxy-2 : 5-dimethylpyrrole-4-azobenzenesulphonate. The corresponding *picrate* has, according to the mode of heating, m. p. 185—195° after softening at 150°. The hydrochloride (as also 4-amino-2 : 3 : 5-trimethylpyrrole) does not appear to lose the amino-group when treated with hydrogen iodide and glacial acetic acid.

3-Acetyl-2 : 4-dimethylpyrrole-5-azobenzenesulphonic acid is obtained in almost quantitative yield by coupling 3-acetyl-2 : 4-dimethylpyrrole-5-carboxylic acid with diazobenzenesulphonic acid, the carboxyl group of the pyrrole being eliminated. In a similar manner, diazotised *p*-nitraniline gives 3-acetyl-2 : 4-dimethylpyrrole-5-*p*-nitroazobenzene, an orange-coloured substance, m. p. 198° (decomp.). 3-Carbethoxy-2 : 4-dimethylpyrrole-5-azobenzene, small, yellow needles, m. p. 127°, is obtained from its components in acetic acid solution; it gives a well-crystallised *picrate*, m. p. 156—158° (decomp.), and *styphnate*, m. p. 163° (decomp.). 2 : 4-Dimethylpyrrole-3-carboxylic acid couples with loss of carbon dioxide with diazobenzenesulphonic acid, *p*-nitrobenzenediazonium chloride, and *p*-dichlorobenzenediazonium chloride, to give crystalline dyes. A loss of the carbethoxy-residue from ethyl 2 : 4-dimethylpyrrole-3 : 5-dicarboxylate does not occur even under the energetic action

of diazotised picramide. The aldehyde residue of substituted pyrroles cannot be displaced by the azo-residue; the compounds investigated were ethyl 5-aldehydo-2:4-dimethylpyrrole-3-carboxylate, 3-acetyl-2:4-dimethylpyrrole-5-aldehyde, 2:3:5-trimethylpyrrole-4-aldehyde, ethyl 4-aldehydo-1-*p*-tolyl-2:5-dimethylpyrrole-3-carboxylate, and ethyl 4-hydroxy-5-aldehydo-2-methylpyrrole-3-carboxylate. H. W.

Oxidative Fission of Hydrazones and Derivatives of Oxhydrazine. MAX BERGMANN, REINHOLD ULPTS, and CHARLOTTE WITTE (*Ber.*, 1923, 56, [B], 679—682).—The isolation of reducing compounds of the sugar group from complex mixtures is frequently effected in the form of their hydrazones from which their regeneration is frequently a matter of difficulty. The possibility of oxidative fission by means of perbenzoic acid has been examined in the cases of simple anils and hydrazones.

Benzophenone is obtained in about 55% yield by the action of perbenzoic acid on an ethereal solution of benzophenonephenylhydrazone. Under similar conditions, benzylideneaniline yields much benzaldehyde and considerable quantities of nitrosobenzene. Oxidation of benzaldehydephenylhydrazone gives *benzaldehydephenylhydrazone oxide*, $\text{O} \begin{array}{c} \text{CHPh} \\ \diagup \\ \text{N} \cdot \text{NHPh} \end{array}$, pale yellow needles or prisms, m. p. 201° (corr. decomp.), which is a stable substance. It is decomposed by boiling glacial acetic acid with production of benzaldehyde and phenyl acetate, but the fission is by no means smooth, and large quantities of other substances are produced; a portion is isomerised to benzoylphenylhydrazine, thus showing that the carbon-nitrogen skeleton of the original material is preserved intact in the oxidation product. The oxide is decomposed by phenylhydrazine into dibenzoylphenylhydrazine, $\text{NHBz} \cdot \text{NBzPh}$, m. p. 176°, and much benzonitrile, by aniline into *p*-aminodiphenyl, m. p. 54°, and by dimethylaniline into benzamide.

Furfuraldehydephenylhydrazone is oxidised by perbenzoic acid in ethereal solution to *furfuraldehydephenylhydrazone oxide*, $\begin{array}{c} \text{CH} \cdot \text{CH} \\ \diagup \quad \diagdown \\ \text{CH} - \text{O} \end{array} \text{C} \cdot \text{CH} \begin{array}{c} \diagup \\ \text{N} \cdot \text{NHPh} \\ \diagdown \\ \text{O} \end{array}$, pale yellow or yellowish-brown crystals which appears to be considerably less stable than the corresponding derivative of benzaldehyde. H. W.

Colloid Chemical Characteristics of Albumin Fractions. Sensitisation and Protective Action of Hydrophilic Colloids. J. REITSTÖTTER (*Kolloid Z.*, 1923, 32, 47).—In opposition to the view held by Pauli, the author has shown that solutions of albumin cannot be submitted to prolonged dialysis without permanent changes taking place in the material. The changes can be detected by the effect of electrolytes on the solutions. Thus an albumin-ferric hydroxide sol, which has been submitted to electrodialysis through parchment membranes, is distinctly more sensitive to electrolytes than the pure ferric hydroxide sol. Albumin-ferric hydroxide sols are more sensitive to electrolytes than paraglobulin-

ferrie hydroxide sols. The paraglobulin from diphtheria and tetanus serum has a much greater negative charge than the paraglobulin from normal and anti-infection sera. Specific anti-substances have a definite charge which is always more negative than that of paraglobulin from normal sera. J. F. S.

Some Methods for the Preparation of Ultra-visible Albumin Sols and the Significance of these for Colloid Chemistry and Biology. A. FODOR (*Kolloid Z.*, 1923, 32, 103—107).—The author describes methods for the preparation of ultra-visible sols of albumin, globulin, and casein. By means of these sols it is shown to be possible to follow the change from the sol to the gel condition. The process consists, in the case of albumin, in the dehydration of the strongly solvated enhydrones of this protein, which are ultramicroscopically invisible, to such an extent that the particles become visible in a dark field illumination. This is achieved by diluting white of egg with ten times its volume of water, adding a crystal of thymol, and keeping for several months in an ice-chest. The solution thereby becomes very opaque, but there is only the smallest amount of coagulation. This is filtered and the filtrate placed in the field of an ultramicroscope which is illuminated by a paraboloid condenser, when relatively large aggregations which do not move markedly are visible. If the solution is now made faintly alkaline with sodium hydroxide, the aggregates are resolved into the primary particles which are in violent motion. If the solution is heated, the field becomes optically empty, but if the solution is kept for a week at 0°, the visible enhydrones are again apparent. J. F. S.

Nature of the Coagulation of Proteins by Alcohol and other Organic Substances. W. W. LEPESCHKIN (*Kolloid Z.*, 1923, 32, 100—103).—The nature of the coagulation of albumin by alcohol has been investigated. It is shown that the coagulation by alcohol is similar to the coagulation by heat, and that all factors which affect the heat coagulation have exactly the same effect on coagulation of proteins by alcohol. The addition of alcohol to albumin solutions brings about an acceleration of the velocity of the denaturisation, the amount of the acceleration being proportional to the amount of alcohol added. Such a denaturated product would be insoluble in water, as is found to be the case with the albumin coagulum after it has remained in contact with alcohol for a short time. J. F. S.

Conditions of Reversible and Irreversible Coagulation of Proteins by Salts. W. W. LEPESCHKIN (*Kolloid Z.*, 1923, 32, 44—46).—Solutions of albumin are coagulated reversibly by salts of the alkali metals, but irreversibly by salts of the alkaline-earth and heavy metals. Further, the coagulation by salts of the alkali metals is irreversible if it takes place in the presence of hydrochloric acid. The varying behaviour is due to the velocity with which the albumin in the various cases is denaturated. The presence of alkaline-earth and heavy metal salts and hydrochloric acid

accelerates the denaturation in various ways, which are explained in the paper, and so render the coagulation irreversible. J. F. S.

Relationship of Neutral Salts to Acid Albumins. SUSUMU MATSUMURA and JOHANN MATULA (*Kolloid Z.*, 1923, **32**, 37—42).—After a discussion of the views held by Pauli (A., 1909, i, 618) and Hardy (A., 1906, i, 121) on the mechanism of the reaction between neutral salts and solutions of acid proteins, the authors, who disagree with the views hitherto put forward, describe a number of parallel experiments on the action of hydrochloric acid and sodium chloride on solutions of the chloride of the protein obtained from horse-serum. The serum used had been preserved for several years under toluene and had deposited the whole of the globulin. The dialysed serum was mixed with equal volumes of 0.005*N*-, 0.01*N*-, and 0.05*N*-solutions of hydrochloric acid, respectively, and three solutions thus obtained in which the protein was not completely saturated, saturated, and over-saturated, with acid. These three solutions were treated with equivalent quantities of hydrochloric acid and sodium chloride at the ordinary temperature and at 100°. At the ordinary temperature, the coagulation of the protein takes place with much smaller concentrations of the salt than of the acid, whilst at 100° the same result is observed, but, further, in the case of hydrochloric acid, the amount of precipitation in hot solution is exactly the same as in cold solution, whereas with sodium chloride the amount of precipitate is greater in hot solutions than in cold. A further series of experiments on the electrical conductivity of protein chloride solutions to which hydrochloric acid and sodium chloride, respectively, have been added shows that the salt solution increases the specific conductivity from three to five times as much as the hydrochloric acid. The results indicate that the views put forward previously are inaccurate, and that the action of neutral salts consists in the first place in the formation of a poorly hydrated complex of the protein chloride and the

neutral salt, of the type $\text{NaCl} \cdot \text{R}^+ \begin{smallmatrix} \text{NH}_2 \cdot \text{HCl}^- \\ \text{CO}_2\text{H} \end{smallmatrix}$, whereby the electrolytic dissociation of the protein chloride is not markedly affected, but the viscosity is much reduced, and in the second place in the displacement of the ionisation of this complex which brings about the coagulation. J. F. S.

Precipitation of Serum-albumin by Copper Salts. SUSUMU MATSUMURA and JOHANN MATULA (*Kolloid Z.*, 1923, **32**, 115—118).—The authors have investigated the conditions under which solutions of cupric chloride cause the precipitation of serum-albumin solutions. It is shown that serum and albumin solutions which are entirely free from electrolytes are not precipitated by cupric chloride. Precipitation may be brought about by the presence of large quantities of neutral salts or by the presence of small quantities of alkalis. The nature of the precipitation in the two cases is different. In the first case, the amount of the precipitate increases with the amount of copper chloride added, whilst

in the second case the precipitation is restricted to a definite range of quantities of copper chloride, and with amounts beyond this it passes back into solution. The precipitate in the second case can also be brought back into solution by the addition of neutral salts, whilst in the first case the precipitate is insoluble both in excess of cupric chloride and neutral salt. Copper chloride solutions form positively charged complexes with dialysed albumin, in which the copper chloride is not united to the albumin molecule in the same place as the acid in acid albumins. J. F. S.

Reaction of Proteins with the Acids of Soaps and Fats. I. SUSUMU MATSUMURA (*Kolloid Z.*, 1923, **32**, 173—176).—The behaviour of solutions of sodium oleate with dialysed horse-serum has been investigated. It is shown that the whole of the proteins in sera, and also in egg-albumin, give precipitates when treated with soaps of the higher fatty acids. The precipitation is incomplete, but may be made complete by the removal of the free alkali, which retards the formation of the precipitate. The precipitates from dialysed sera which are soluble in sodium chloride solution may be brought permanently into solution by warming at 56°. On the other hand, sera which have been previously warmed at 56° are no longer precipitated by soap solutions. The soap precipitates, which are insoluble in sodium chloride, namely, those of serum-globulin and ovoglobulin, dissolve on warming, but on again cooling they are reprecipitated. J. F. S.

The Plant Albumin "Leucosin." HEINRICH LÜERS and MAX LANDAUER (*Biochem. Z.*, 1922, **133**, 598—602).—Leucosin, obtained from barley, and purified by the method of Osborne, shows the following distribution of its nitrogen: ammonia-N, 9.4%; melanin-N, 1.1%; hexone-base-N, 26%; monoamino-N, 63.1%. The results obtained using a shortened method of hydrolysis are also given and show agreement with those given by the longer process. W. O. K.

Physical Chemistry of the Globulins. I. Alkali and Alkaline-earth Globulinates. MONA ADOLF (*Koll. Chem. Beihefte*, 1923, **17**, 1—50).—A physico-chemical investigation of the portion of globulin which is insoluble in water. By electro-dialysis it is found possible to precipitate from human sera and exudations a globulin which is insoluble in water. This material did not change the electrical conductivity of pure water and contained 0.215% of ash and 0.047% of phosphorus. By means of solubility determinations of globulin in alkali and alkaline-earth hydroxide solutions, it is shown that these substances combine with globulin in equivalent quantities, and not in molecular quantities, as hitherto supposed, to form neutral salts. Globulin yields only one form of neutral salt with alkali, a property in which it differs from casein; this salt is not hydrolysed markedly. The power of globulin to combine with bases in an excess of strong alkali hydroxide solution is represented by 15×10^{-3} g. equivalent per g. of albumin, and is proportional to the amount of the latter

substance. The degree of hydrolysis of the albumin salt in aqueous solution is 24%, and the mean acid dissociation constant 1×10^{-10} . Weak bases apparently combine with less globulin, but if referred to isohydric concentrations with more globulin. The salts so formed are all more strongly hydrolysed. The same is true for all proteins hitherto investigated. The viscosity curve for a solution of constant albumin content but increasing alkali hydroxide concentration passes through a maximum both for strong and weak bases. The hydroxide concentration of the viscosity maximum and that at which the maximum combination takes place do not coincide, but the latter quantity corresponds with the maximum electrical conductivity of the protein salt. By measurements of the concentration of hydroxyl-ions and the viscosity, it is shown that the combination of globulin with the base is a time process, and is practically complete after twenty-four hours. The value of λ_{∞} for the neutral alkali globulinates has been deduced from electrical conductivity measurements, and the following values have been obtained for 25°: sodium globulinate, $\lambda_{\infty} = 100 \text{ ohms}^{-1}$; potassium and ammonium globulinate, 123—124 ohms^{-1} . From these values the mobility of the globulinate-ion is found to be 50. The valency of the negative globulin is found by the Walden-Ostwald rule to be 4. Three g. of globulin are neutralised by 1 millimol. of alkali hydroxide, and from this the equivalent weight of globulin is calculated to 3000, which indicates a molecular weight of 12,000.

J. F. S.

Antagonistic Behaviour of Albumin toward Globulin.

G. A. BROSSA (*Kolloid Z.*, 1923, **32**, 107—115).—Suspensions of globulin are peptised by negative colloidal solutions of dyes such as Congo-red and benzo-purpurin, and also by positive solutions of colloidal dyes such as night-blue. Of these sols, that obtained by peptising a suspension of globulin with Congo-red has been investigated. The Congo-red-globulin sol is extremely sensitive to electrolytes, and is coagulated by much smaller concentrations of electrolytes than the pure dye sol. The sensitiveness increases with increasing globulin content. The night-blue-globulin sol is also very sensitive. Albumin has a protecting action on the Congo-red-globulin sol, just as it has on the pure Congo-red sol. The antagonistic action of albumin and globulin is also manifested if the albumin or globulin in a serum is increased. A mixture of a Congo-red sol and a serum rich in globulin is much more sensitive than a mixture of a Congo-red sol and a serum rich in albumin. From this it is deduced that generally a serum which is richer in globulin than in albumin is more sensitive to electrolytes than one which is richer in albumin than in globulin for the same total protein content. This rule is found to be true when the globulin rich horse-serum is compared with the globulin poor rabbit-serum, and when pathological human-serum is compared with normal human-serum. From Kruyt's experiments (*ibid.*, 1922, **31**, 338), it follows that colloidal solutions of negative dyes such as alkali-blue, water-blue, Chicago-blue, as well as the positive dye night-

blue, are rendered more sensitive by the addition of tannin. Since in this case the increase in sensitiveness cannot be occasioned by the discharge of the colloid particles by the added substance, it is very questionable whether the discharge of the colloid particles causes the increase of sensitiveness in the present case. J. F. S.

The Hydrolysis of Edestin with Sulphuric Acid. J. S. JAITSCHNIKOV (*J. Russ. Phys. Chem. Soc.*, 1918, 50, 105—108).—Edestin is hydrolysed with sulphuric acid of various concentrations, varying the temperatures and the times of reaction. The reaction mixture is in each case neutralised with sodium hydroxide, and Fassbender's reagent added. The precipitate is analysed for nitrogen by Kjeldahl's method, and the amount of nitrogen found serves as a measure of the amount of unhydrolysed albumin. Increase in temperature and in H^+ -concentration have an accelerating effect on the hydrolysis, the influence of the former being more marked. R. T.

Identity of Hordein and Bynin. HEINRICH LÜERS (*Biochem. Z.*, 1922, 133, 603—604; cf. A., 1919, i, 603).—The equation given in the previous paper for the calculation of the histidine-nitrogen is incorrect. The recalculated values are now given. W. O. K.

The Products of Prolonged Tryptic Digestion of Casein. SIGMUND FRÄNKEL and KATHARINE GALLIA (*Biochem. Z.*, 1922, 134, 308—321).—Casein was digested with pancreatin for sixty days at 37°. A hot-water extract of the precipitate gave *d*-tyrosine anhydride and the mercuric sulphate precipitate of the filtrate contained tryptophan anhydride. On removal of mercury the filtrate was precipitated with phosphotungstic acid, and the filtrate from this on removal of foreign ions gave successive crops of crystals. The first crop was identified as *d*-tyrosine; it had a higher rotation, $[\alpha]_D + 17.9$, than any previously recorded value. The second and third crops consisted of *dl*-valin, and the fourth crop of *d*-valin. The formation of *d*-tyrosine is ascribed to a Walden inversion produced by an enzyme *Waldenase*. H. K.

The Oxygen-dissociation Curve of Blood, and its Thermodynamical Basis. W. E. L. BROWN and A. V. HILL (*Proc. Roy. Soc.*, 1923, [B], 94, 297—334).—On the assumption that the combination of oxygen or carbon monoxide with hæmoglobin in blood (as distinct from dialysed hæmoglobin) is a reversible chemical reaction of the following type: $H(\overline{Hb})_n + nO_2 \rightleftharpoons H(\overline{HbO_2})_n$ (cf. A., 1910, i, 288; A., 1922, i, 193), the authors have calculated, with the aid of the van't Hoff isochore, that the heat of reaction, q , of 1 mol. of hæmoglobin, $H(\overline{Hb})_n$, with n mols. of oxygen at constant volume is 19,000 cal. in the presence of carbon dioxide and 30,500 cal. in its absence. Direct estimations of the heat Q evolved when 1 mol. of oxygen combines, at constant volume, with hæmoglobin in blood have given a value of 14,400 cal. in the absence of carbon dioxide. The ratio q/Q is obviously equal to n ; hence $n = 305/144 = 2.1$ approximately. This agrees with the value

obtained independently from the shape of the dissociation curve and from other data, and is consequently regarded as confirmation of the theory of the reversible chemical combination of oxygen with hæmoglobin. The difference in the value of q in the presence and absence of carbon dioxide is due to the absorption of heat which occurs when carbon dioxide is expelled from its combination with base by the stronger acid, $H(\overline{HbO_2})_n$. Calculations of the acid dissociation constants of unsaturated hæmoglobin and carboxy-hæmoglobin [\overline{HHb}_n and $H(\overline{HbCO})_n$] have given values of 7.5×10^{-9} and 5×10^{-7} , respectively. E. S.

Tryptophan and Tyrosine Content of Hæmoglobin and other Blood Proteins. U. KIYOTAKI (*Biochem. Z.*, 1922, **134**, 322—335).—Globin prepared in a variety of ways contains 3.6% of tryptophan when estimated colorimetrically by Fürth and Lieben's application of the Voisenet reaction. In agreement with this, the amount of melanoidin formed by acid hydrolysis was 3.3%. The tryptophan is only liberated with difficulty from hæmoglobin, 18% being set free after three weeks' tryptic digestion with a highly active trypsin. The tyrosine content of globin was found to be between 3.5% and 4%, corresponding with one molecule of tyrosine for every molecule of tryptophan. In serum-albumin 5 mols. of tyrosine and in serum-globulin 2 mols. of tyrosine were found for every tryptophan molecule. H. K.

Hydrolysis of Yeast-nucleic Acid with Dilute Alkali at Room Temperature (Conditions of Steudel and Peiser). P. A. LEVENE (*J. Biol. Chem.*, 1923, **55**, 9—13).—Contrary to the results obtained by Steudel and Peiser (*A.*, 1922, i, 782), it has been found that, under the conditions used by these authors, the removal of guanylic acid from yeast-nucleic acid is incomplete. Moreover, the formation of the remaining three nucleotides occurs simultaneously with that of guanylic acid. E. S.

Determination of the Isoelectric Point of Gelatin. A Criticism of Patten and Kellems's Method. THOMAS SLATER PRICE (*T.*, 1923, **123**, 410—412).

Keratinisation. UBALDO SAMMARTINO (*Biochem. Z.*, 1922, **133**, 476—486).—Analyses have been carried out of the amino-acids of keratin from hair, nails, and from corns (of the foot). The cystine content, particularly, varies according to the source of the keratin. W. O. K.

The Origin of the Humin Formed by the Acid Hydrolysis of Proteins. VII. Hydrolysis in the Presence of Ketones. ROSS AIKEN GORTNER and EARL R. NORRIS (*J. Amer. Chem. Soc.*, 1923, **45**, 550—553; cf. *A.*, 1915, i, 726; 1916, i, 681; 1918, i, 84; 1920, i, 400, 450).—Fibrin was hydrolysed alone and in the presence of acetone and acetophenone, and the distribution of the nitrogen among the products was studied. Apparently the presence of ketones does not alter the nitrogen distribution as measured by

Van Slyke's method. Acid-insoluble humin formed during a protein hydrolysis does not apparently come from the interaction of a ketone and tryptophan. W. G.

The Specificity of Enzymes. RICHARD WILLSTÄTTER and RICHARD KUHN. I. **The Theory of Time Value Quotients.** (*Z. physiol. Chem.*, 1923, 125, 1—27).—A general discussion is given of the kinetics of enzyme action with special reference to the possible modes of action of accelerators and inhibitors. The question of the identity of enzymes in different preparations is considered, and the related question of the specificity of enzymes. A distinction is drawn between relative and absolute specificity, the first being a quantitative and the second a qualitative difference in their modes of attack on substrates. W. O. K.

Units of Enzymes. RICHARD WILLSTÄTTER and RICHARD KUHN (*Ber.*, 1923, 56, [B], 509—512).—A system of nomenclature is proposed in which the figures are directly proportional to the quantities and enzymatic concentrations of the preparations. The lipase unit is the quantity of enzyme which causes the fission of 2.5 g. of olive oil to the extent of 24% during one hour. The amylase unit is one hundred times the quantity of enzyme of $k=0.01$ and the peroxydase unit is equal to 1 g. of the purpurogallin number I. The lipase and amylase values are the number of units in 1 cg. The saccharase unit (*SE*) is the amount of enzyme in 50 mg. of material containing invertin of the time value I in accordance with the definition of O'Sullivan and Thompson. The purity of an invertin preparation (*SW*) is expressed by the reciprocal of the time-value, and thus denotes the number of saccharase units in 50 mg. substance. The relationship of the saccharase value to the inverting power as defined by von Euler and Svanberg is expressed by the equation: $SW=If/46.176$. The expressions for quantity and concentration are not universally applicable for invertin and other enzymes, since their behaviour towards sucrose is considerably influenced by the varying amounts of foreign matter with which they are associated. For the strict comparison of saccharase preparations of different origin the dissociation constants should be appended to the *SW* and *SE*. Invertins of different affinities are compared by calculation of the units measured in the usual manner, which is sufficiently exact for preparative work to an invertin of the medium affinity constant=50 ($k=0.020$). The "reduced saccharase unit" is calculated according to the formula $SE_{red}=S.E(n+k/n+0.02)$, in which n is the normality of the sucrose solution in which the constants of the reaction are estimated.

H. W.

The Nomenclature of Autolytic Enzymes. K. G. DERNBY (*Biochem. Z.*, 1922, 133, 432—433).—The author proposes to classify the proteolytic enzymes of plant or animal cells as primary proteases (pepsinases), secondary proteases (trypsinases), and tertiary proteases (ereptases), which act on protein in acid solution, on denatured protein and peptone in alkaline and neutral solution, and on peptides in alkaline solution, respectively. W. O. K.

A Comparison between the Chemical and Physiological Characteristics of Pepsin and Rennin. FREDERIC FENGER (*J. Amer. Chem. Soc.*, 1923, 45, 249—255).—Pepsin and rennin are proteins possessing widely different properties. Pepsin is coagulated by heat and is colloidal in nature, but rennin is a decomposition product of protein of the acid-albumin type, and is not precipitated on boiling. Pepsin may be dialysed without loss, but rennin readily diffuses through a parchment membrane. Proteolytic or peptic activity does not seem to be a part of the true physiological characteristics of the milk-curdling enzyme. Both enzymes are present in the stomach of the suckling calf, but in that of the adult hog only pepsin was found. W. G.

The Influence of Starch on Peptic Digestion. ANTON FISCHER (*Biochem. Z.*, 1922, 134, 360—362).—Contrary to statements in physiological literature, the addition of starch has no inhibiting action on the digestive action of pepsin. H. K.

The Specificity of Enzymes. II. Saccharase and Raffinase Activity of Invertase. RICHARD WILLSTÄTTER and RICHARD KUHN (*Z. physiol. Chem.*, 1923, 125, 28—92).—The influence of hydrogen-ion concentration on the hydrolysis of sucrose by invertase is apparently due to its action on the rate of decomposition of the compound of enzyme and substrate. This is shown by the fact that if the affinity constant $K = \frac{[\text{Enzyme}]}{[\text{Substrate}][\text{Enzyme-Substrate}]}$ be determined from measurements of the kinetics of the inversion, K is independent of the hydrogen-ion concentration. The affinity constant K does not vary with the degree of purity of the enzyme preparation, but is different in preparations made from yeasts of different sources, varying in the preparations tested from 0.016 to 0.040. If to one preparation there is added the solution obtained by heating another preparation so as to inactivate it, filtering from any coagulated protein, the affinity constant of this first preparation may be altered, in all the combinations tried a value of $K = 0.030$ being obtained.

Similar variations in the affinity constant of invertase for raffinose depending on the origin of the yeast have been found, and a comparison of the effects of invertase on raffinose and on sucrose leads to the conclusion that ratio of the affinity constants of the different preparations is constant, and likewise the ratio of the molar quantities of the two sugars hydrolysed by a given amount of invertase under optimum conditions, if interpolated to the value for infinite quantities of substrate. There appear to be strong indications that the saccharase and raffinase present in invertase are identical. W. O. K.

The Preparation of Highly Active Invertin and its Sulphur Content. H. VON EULER and K. JOSEPHSON (*Ber.*, 1923, 56, [B], 453—455).—The term invertin is applied to the natural group of enzymes obtained from yeast-cells or similar materials which causes the enzymatic inversion of sucrose and contains saccharase

as its main component. Highly active specimens ($If=182$) are readily obtained from "aged" autolysed yeast-juice by fractional precipitation and dialysis combined with adsorption by aluminium hydroxide and elution with potassium arsenate solution.

A specimen which has the value $If=182$ contains 0.38% of sulphur, corresponding with 0.48% S in a specimen having $If=230$. If this sulphur content is due to the presence of one atom of sulphur in the saccharase molecule, the combining weight of the latter is 6700, a value which is somewhat greater, but of the same order of magnitude as that derived from the analysis of silver saccharase.

H. W.

Saccharase. H. VON EULER and K. JOSEPHSON (*Ber.*, 1923, 56, [B], 446—452).—The preparation of highly active saccharase from autolysed yeast-juice is effected by a combination of the methods of fractional precipitation and dialysis with those of adsorption by aluminium hydroxide and elution with potassium arsenate. The parallelism between phosphorus content and activity ceases when the value of If exceeds about 100. The phosphorus content of the most active specimens ($If=210$ at 18°) is 0.15%, and is therefore considerably higher than the lowest value recorded by Willstätter (0.03—0.006%), whose specimens were obtained from "aged" autolysed juice with the aid of lead acetate (cf. Willstätter and Racke, A., 1922, i, 598; Willstätter, Graser, and Kuhn, A., 1922, i, 1200; Willstätter and Wassermann, this vol., i, 69). Analysis of the most highly active specimens gives ash=4.0%, C=45.58%, H=6.70%, N=12.7%, P=0.15%, As<0.1%.

The preparation of the silver compound of saccharase (von Euler and Josephson, A., 1922, i, 1076) has been repeated with highly active saccharase; it contains about 2% of silver, thus indicating a minimum molecular weight of about 5400 for the enzyme.

The methods of indicating the activity of saccharase preparations are described. The conversion of the inverting capacity (If) to the time values of O'Sullivan and Thompson (T., 1899, 57, 834) is effected by multiplication by the factor 58.6. H. W.

The Action of Quinine and Quinine Derivatives on Stomach Lipase. P. RONA and M. TAKATA (*Biochem. Z.*, 1922, 134, 118—130).—Stomach lipase (from the small stomach of a dog by Pavlov's method) is inhibited by quinine and its derivatives, quinidine, optoquin, eucupin, and vuzin, to an extent corresponding with their property of lowering the surface tension as measured by the drop number. The degree of inhibition depends on the hydrogen-ion concentration of the solution and therefore on the degree of dissociation of the quinine salt, and on the quinine concentration, but not on the concentration of the ferment. The quinine concentration-inhibition curve is an adsorption isotherm, the logarithm of the quinine concentration being proportional to the logarithm of the inhibition. H. K.

The Action of Quinine and of Atoxyl on Pancreatic Lipase. P. RONA and R. PAVLOVIĆ (*Biochem. Z.*, 1922, **134**, 108—117).—The action of pancreatic lipase is strongly inhibited by quinine, but not by atoxyl. Liver lipase, however, is very sensitive to atoxyl. If the logarithms of the quinine concentration be plotted against the logarithms of the degree of inhibition, a straight line is obtained. Sodium fluoride inhibits the action of pancreatic lipase slightly, that of liver and serum lipase strongly. H. K.

Pancreatic Enzymes. I. Determination of Pancreatic Fat Hydrolysis. RICHARD WILLSTÄTTER, ERNST WALDSCHMIDT-LEITZ, and FRIEDRICH MEMMEN (*Z. physiol. Chem.*, 1923, **125**, 93—131).—The activity of the lipase of the pancreas, unlike that of invertase, is dependent on its state of dispersion and on the colloidal material present in the solution containing it. In the case of invertase, these factors do not affect the activity, but only the stability of the preparations (cf. A., 1922, i, 1200). The activity of lipase is, of course, also dependent on the hydrogen-ion concentration, and so, as in the hydrolysis of triolein, acid is being constantly produced and the rate of the reaction thus being changed, direct measurement of the activity is not possible. The estimation of the activity may be carried out in three ways, (1) in an acid medium, of constant P_H of 4.7, this being approximately the P_H on adding oleic acid to water; (2) in an alkaline medium, the reaction being kept constant by the presence of a large amount of buffer solution, which, however, interferes to some extent with the activity; (3) in a medium alkaline at first, which, however, is allowed to become acid as the reaction proceeds. In the last case, the results are calculated from the observed course of the hydrolysis. As the activity of the enzyme solution depends on the other substances present, it is necessary, in order to obtain comparable results, to add activators, a suitable combination being calcium chloride and albumin.

If the activity of lipase adsorbed by various adsorbing surfaces be measured, it is found that the adsorbents fall into two groups, those which at most only slightly diminish the activity of the lipase (e.g., kaolin or aluminium hydroxide), and those which render the adsorbed lipase practically inactive (tristearin and cholesterol). It is suggested that, in the latter cases, the specifically active groups of the lipase molecule are held firmly by the surface, whilst in the former cases the active groups are free, and adsorption depends on other groups of the molecule. W. O. K.

Pancreatic Enzymes. II. Pancreatic Lipase. RICHARD WILLSTÄTTER and ERNST WALDSCHMIDT-LEITZ (*Z. physiol. Chem.*, 1923, **125**, 132—198).—Pancreatic lipase, as obtained by extraction of the pancreatic glands by glycerol, is mixed with amylase and trypsin. Lipase shows both acid and basic properties, and is adsorbed by aluminium hydroxide and by kaolin. Pancreatic amylase and trypsin, on the other hand, have no marked acid properties, and when in a pure condition they are not adsorbed by aluminium hydroxide. However, when mixed with lipase they

are adsorbed to some extent, but at most a very small amount of these is washed out by ammonium phosphate, which removes the lipase. On repeating the process, lipase is obtained free from amylase and trypsin. Amylase and trypsin may be separated by utilising the fact that the basic properties of trypsin are more marked, and that it is preferentially adsorbed from acid solution by kaolin.

Further purification of the lipase is effected by adsorbing on kaolin, and extracting with alkali phosphate. This may be followed by adsorption on cholesterol or tristearin, which are particularly selective in their adsorptive action. Very full details of these processes are given in the original paper. Only traces of the colour reactions of any known group of organic compounds are given by the purified lipase, which has been obtained in a concentration three hundred times that in dried pancreas. W. O. K.

Ferments and Light. I. Diastase. I. LUDWIG PINCUSSEN (*Biochem. Z.*, 1923, **134**, 459—469).—Diastase, independently of dilution, loses its activity on exposure to ultra-violet rays in a quartz tube, but not in sunlight. The destruction by light is greatest at a P_H of 4.6, which is the optimum reaction for diastatic activity, and is least between P_H 7 and 7.4. The presence of salt influences the rate of destruction by ultra-violet light, iodide increasing it. Sugars are without effect in ultra-violet light, although in presence of dextrose even sunlight is slightly effective. The effect of ultra-violet light is inhibited by glycine and starch. Temperature has apparently little effect. W. O. K.

The Action of Iodine on Diastase. L. BERZELLER and J. FREUD (*Biochem. Z.*, 1922, **133**, 493—501).—The action of saliva diastase is decreased by iodine, but it is not completely inactivated. Starch protects the diastase against the action of iodine. In the same way, the hydrolysis of starch by mineral acids is also inhibited by iodine. W. O. K.

The Action of Calcium on the Clotting of Milk by Rennin. P. RONA and E. GABBE (*Biochem. Z.*, 1922, **134**, 39—75).—An extensive series of experiments was carried out on the influence of calcium on the clotting of milk under specified conditions as regards dilution, time, temperature, and hydrogen-ion concentration. The course of fermentation was followed by observing the temperature at which samples removed at intervals were clotted by heat. If calcium chloride is added at the beginning of the fermentation, the time which elapses before clotting is the longer the higher the calcium content. Small concentrations of calcium stimulate the ferment action, but large concentrations inhibit it. If, however, the calcium chloride is added after the fermentation has been in progress some time, the period before clotting is prolonged. The conversion of caseinogen into casein is only complete at hydrogen-ion concentrations between P_H 6.0 and 6.4. H. K.

Experiments on Liver Catalase. PETER RONA and ARISTIA DAMBOVICEANU (*Biochem. Z.*, 1922, **134**, 20—38).—A series of experiments carried out on the catalase of calf's liver showed that the activity is not affected by the particular buffer mixture used, and that the optimum activity is exhibited over a broad range of P_H round about 7 and is only inhibited at P_H 11. If the ferment is in excess of the hydrogen peroxide, the reaction is unimolecular, but if the ferment is only sufficient to decompose 65 to 80% of the hydrogen peroxide, the reaction is bimolecular. Chloridion inhibits the fermentation, but a 0.0005 molar sodium hydrogen carbonate solution is sufficient to inhibit the action of a 0.154 molar sodium chloride solution. If, however, the ferment is in large excess over the peroxide, the inhibiting action of chloridion is not so noticeable. H. K.

Ferments and Light. II. Urease. I. LUDWIG PINCUSSEN and NAOSABURO KATO (*Biochem. Z.*, 1923, **134**, 470—475).—Urease gradually loses its activity on exposure to sunlight or to ultra-violet light, most rapidly apparently at the reaction optimum for the activity of the urease. W. O. K.

Synthesis of Carbamide with the Enzyme Urease. EDWARD MACK and DONALD S. VILLARS (*J. Amer. Chem. Soc.*, 1923, **45**, 501—505).—It is shown that, when concentrated solutions of ammonium carbonate and carbamate are used, the enzyme urease acts reversibly and increases the velocity of formation of carbamide, hastening the attainment of the equilibrium. A 1% solution of the enzyme will bring about equilibrium in a 10N-ammonium carbonate-carbamate solution, containing about equal amounts of each salt, in about ten hours at 55°, whereas with a 0.1% solution of the enzyme the reaction is only about one-third complete in ninety-eight hours and without any enzyme equilibrium would be attained only after about six hundred days at 55°. W. G.

The Action of Urease in the Decomposition of Carbamide. EDWARD MACK and DONALD S. VILLARS (*J. Amer. Chem. Soc.*, 1923, **45**, 505—510).—Experimental evidence is given to show that the transformation of ammonium cyanate into carbamide is not catalysed by the enzyme urease, but rather that the enzyme is slowly poisoned by the cyanate. When carbamide is hydrolysed, in the presence of urease, forming ammonium carbamate, which changes into the carbonate, there is simultaneous formation of ammonium cyanate from the carbamide. When considering the different stages possible in the transformation of carbamide into ammonium carbonate, it is shown by a process of elimination that the particular stage catalysed by the urease is the transformation of carbamide into ammonium carbamate. W. G.

The Urease of Fungi. A. GORIS and P. COSTY (*Compt. rend.*, 1923, **176**, 412—414).—A study of the urease of the higher fungi and in particular of *Boletus edulis*, Bull. This urease is not very sensitive to heat, only being destroyed at 76°. The optimum temperature is 30—38°. It is very sensitive to mineral and organic

acids. Of the organic acids studied, tartaric acid is the most injurious and acetic acid the least. The enzyme is less sensitive to alkalis, and it is able to resist a concentration of ammonium carbonate ten times as great as that of sodium carbonate, which destroys it. Of the neutral salts studied, those of calcium exert the greatest retarding action, and then, in descending order, those of sodium, potassium, ammonium, and magnesium. In general, antiseptics act very energetically on this enzyme. W. G.

Isomorphism in the Organo-metallic Series. V. Saturated Derivatives of Quinquevalent Metals and Metalloids. P. PASCAL (*Bull. Soc. chim.*, 1923, [iv], 33, 170—180).—A study was made of the temperatures of fusion and solidification of binary mixtures of oxides and sulphides of triphenylphosphine, triphenylarsine, and triphenylstibine, and the temperatures of the commencement and completion of solidification of the mixed substances in varying proportions are given in tables and curves. The results may be conveniently summarised by designating the types of binary mixtures obtained, arranged in the order of decreasing crystalline analogy, by (1), (2), (3), (4), where (1) is the formation of mixed crystals in all proportions, the curve being spindle-shaped; (2) mixed crystals in all proportions, curve with a minimum; (3) no mixed crystals, curve with a transition point, and (4) no mixed crystals, curve showing a eutectic point, and the following indicates the type to which each binary mixture belongs: $(PPh_3O, AsPh_3O)=1$, $(PPh_3S, AsPh_3S)=2$, $(PPh_3O, AsPh_3S)=4$, $(PPh_3S, SbPh_3S)=2$, $(PPh_3O, SbPh_3S)=4$, $(AsPh_3O, AsPh_3S)=2$, $(PPh_3S, PPh_3O)=2$, $(PPh_3S, AsPh_3O)=4$, $(AsPh_3O, SbPh_3S)=4$, $(AsPh_3S, SbPh_3S)=2$. It appears, therefore, that if in a pair of organo-metallic compounds the asymmetry of the central atoms is increased by the addition of oxygen in one and of sulphur in the other, the tendency to isodimorphism is increased. If, on the other hand, the central atoms are saturated by the same element—oxygen or sulphur—the tendency to isomorphism is increased. Binary mixtures in which the phenyl group of the phosphines was replaced by the $-OPh$, $-SPh$, and C_2H_5- groups, were also examined. The same relations of isomorphism were found to exist between the phosphate and thiophosphate as between the phosphine oxide and sulphide, but isodimorphism occurs when aliphatic groups are introduced into one of the constituents of the binary mixture, or when phenyl and oxyphenyl derivatives are mixed. G. F. M.

Substitution Factors of the Affinity Constants in the Group of the Arsinic Acids. RICHARD LORENZ and ELISABETH BREHMER (*Ber.*, 1923, 56, [B], 742—750).—The dissociation constants of a large number of substituted phenylarsinic acids have been measured, and from the results the authors have constructed a table of factors for the mathematical expression of the influence of various groups in differing positions in the molecule. The following data are recorded, Wegscheider's factors for the carboxylic acids being placed within brackets: *o*-Nitro, 1.41, 1.51* (103); *m*-nitro, 5.0, 5.5 (5.75); *p*-nitro, 5.3 (6.6); *o*-hydroxy,

0.42 (17.0); *m*-hydroxy, about 1.45* (1.45); *p*-hydroxy, 0.55 (0.48); *o*-methyl, 2.4* (2.00); *m*-methyl, 0.85* (0.86). The factors marked with an asterisk are based on experiments with acids containing an amino-group. The dissociation constant of phenylarsinic acid is 0.027. In general, the two tables exhibit a close similarity, the marked divergences occurring in cases where the substituent is in the ortho-position to the carboxyl or arsinic group.

The conductivity of a substituted arsinic acid depends therefore on that of the parent acid, on the nature and position of the substituent (the effect is the same on the arsinic as on the carboxyl group provided that the groups are not too close to one another, in which case an additional factor enters), and on the immediate mutual action between acid radicle and substituent. The latter action is more marked in the arsinic than in the carboxylic series. In the latter, an increasing influence of the substituent is invariably observed as it more closely approaches the carboxyl group; the mutual action of the groups is not sufficiently great to overpower the effect of propinquity. The anomalies in the conductivity of di-ortho-substituted carboxylic acids, however, show that such mutual influence does exist. Possibly it is more marked in the arsinic acids by reason of the relatively greater arsinic residue, $\text{O}:\text{As} \begin{smallmatrix} \text{OH} \\ \text{OH} \end{smallmatrix}$

and $-\text{C} \begin{smallmatrix} \text{O} \\ \text{OH} \end{smallmatrix}$.

H. W.

The Crystalline Form of some Organic Derivatives of Arsenic. G. GILTA (*Bull. Soc. chim. Belg.*, 1923, **32**, 19—26).—A detailed crystallographic examination of *p*-aminophenylarsinic acid and of the pentahydrate of its sodium salt (cf. A., 1922, i, 961). Acid: monoclinic [$a:b:c=1.393499:1:1.162276$, $\beta=101^\circ 20'$]. The effect of conditions on the predominant forms (including a twin) is discussed. Sodium salt pentahydrate: monoclinic [$a:b:c=2.181215:1:0.960163$, $\beta=91^\circ 4'$]; measurements are also given of a crossed twin. Tri- and di-hydrates of the sodium salt have been obtained but not measured. E. E. T.

Crystalline Form of Atoxyl [Sodium *p*-Aminophenylarsinate] and its Characterisation using the Microscope. J. MÉLON (*Bull. Acad. roy. Belg.*, 1922, [v], **8**, 150—158).—A detailed crystallographic examination of atoxyl ($+4\text{H}_2\text{O}$): monoclinic, $a:b:c=0.986590:1:1.251538$, $\beta=82.5^\circ$ (cf. A., 1922, i, 961, and preceding abstract). E. E. T.

Arsenated Benzophenone and its Derivatives. II. W. LEE LEWIS and H. C. CHEETHAM (*J. Amer. Chem. Soc.*, 1923, **45**, 510—515; cf. A., 1922, i, 187).—By means of the Friedel and Crafts' reaction dichloro-*o*-arsinobenzoyl chloride has been condensed with a number of aromatic hydrocarbons and aromatic ethers to give new benzophenone arsinic acids. These compounds are easily and quantitatively reduced in acetic acid solution by concentrated hydrobromic or hydriodic acids to derivatives of arsenious oxide. In some cases, the reaction goes further, coloured crystalline

dibromo- or di-iodo-arsines being formed. The latter are easily converted again into the oxide by hydrolysis with dilute sodium carbonate. If the arsinic acids or, better, the arsenious oxides are heated under a reflux condenser with phosphorous acid in alcoholic solution, arseno-derivatives are obtained. The following new compounds are described: *Dichloro-o-arsinobenzoyl chloride*, $\text{AsCl}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{COCl}$, *benzophenone-2'-arsinic acid*, 4-methylbenzophenone-2'-arsinic acid, $\text{C}_6\text{H}_4\text{Me} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{AsO}_3\text{H}_2$, 4-methoxybenzophenone-2'-arsinic acid, 4-ethoxybenzophenone-2'-arsinic acid, 4-phenoxybenzophenone-2'-arsinic acid, 4:4'-dibenzoylarsenobenzene, 2:2'-dibenzoylarsenobenzene, 2:2'-di-*p*-anisoylarsenobenzene, 4:4'-diethoxybenzoyl-2:2'-arsenobenzene, 4-methoxybenzophenone-2'-dibromoarsine, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{AsBr}_2$, m. p. 161° , 4-ethoxybenzophenone-2'-dibromoarsine, m. p. 152° , 4-methoxybenzophenone-2'-arsenious acid, 4-methoxybenzophenone-2'-dichloroarsine, m. p. 148° , 4-methoxybenzophenone-2'-di-iodoarsine, m. p. 137° , 4-ethoxybenzophenone-2'-di-iodoarsine, m. p. 151° , 4-methoxybenzophenone-4'-dichloroarsine, m. p. 152° , 4-methoxybenzophenone-4'-dibromoarsine, m. p. 136° , 4-methoxybenzophenone-4'-di-iodoarsine, m. p. 105° , 4-methoxybenzophenone-4'-arsinoacetic acid. *Acetophenone-p-arsinic acid* is obtained when *p*-aminoacetophenone is diazotised and the product is treated with a solution of sodium arsenite.

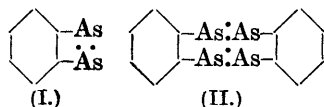
W. G.

Silver Salvarsan. WILLIAM HERBERT GRAY (T., 1923, 123, 635—642).

Aromatic Diarsinic Acids and their Reduction Products.

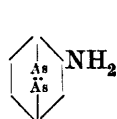
II. H. LIEB and O. WINTERSTEINER (*Ber.*, 1923, 56, [B], 425—433).—In a previous communication (Lieb, A., 1921, i, 696), it has been shown that *m*- and *p*-phenylenediarsinic acids are reducible by phosphorous acid in sealed tubes at an elevated temperature to yellow, amorphous substances of the composition $(\text{C}_6\text{H}_4\text{As}_2)_n$, the molecular weight of which could not be determined on account of their insolubility in all suitable media. It is now found that the reduction can be more conveniently effected in open vessels by hypophosphorous acid. With the object of obtaining sufficiently soluble compounds, the observations have been extended to a number of derivatives, none of which, however, fulfils the required conditions.

o-Phenylenediarsinic acid is converted by hypophosphorous acid (*d* 1.28) into *o*-arsenophenylene or *o*-diarsenobenzene (annexed formulæ I or II), an egg-yellow, amorphous precipitate.

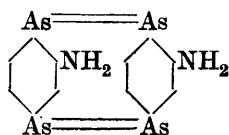


o-Nitroaniline is transformed by an equimolecular quantity of arsenic acid at 210° into a mixture of 3-nitro-4-aminophenylarsinic acid (cf. Mameli, A., 1909, i, 980; Bertheim, A., 1911, i, 1055) and di-3-nitro-4-aminophenylarsinic acid (Fargher, T., 1919, 115, 982). The former acid is converted by diazotisation and treatment with sodium arsenite in the presence of a little ammoniacal copper sulphate solution into 2(3)-nitrophenylene-*p*-diarsinic acid, colour-

less, pointed prisms, decomp. $239-243^{\circ}$; the corresponding *zinc* and *sodium* salts are described. The acid is reduced by sodium amalgam in the presence of methyl alcohol to 2(3)-*amino-p-phenylenediarsinic acid*, long, oblique prisms which can be obtained only with difficulty in the colourless condition; the *zinc* salt is described. The nitro-acid is transformed by hypophosphorous acid into *amino-*



(III.)



(IV.)

p-arsenophenylene or *diamino-p-diarsenobenzene* (annexed formula, III or IV), an ochre-yellow to brownish-red, amorphous powder, m. p. about $217-220^{\circ}$ after darkening at 205° ; the corresponding *hydrochloride* is a tile-red, amorph-

ous precipitate which decomposes gradually when heated above 220° .

2(3)-*Methyl-p-phenylenediarsinic acid* is prepared by the action of sodium arsenite on a diazotised solution of 4-amino-3-methylphenylarsinic acid; it crystallises in colourless leaflets which darken at 280° and decompose at 330° ; its properties are considerably affected by the presence of small amounts of organic and inorganic impurities, from which it is conveniently freed through its *magnesium* salt, a white, amorphous precipitate; the *sodium* salt ($+9\text{H}_2\text{O}$) and the amorphous *barium* salt, $\text{C}_7\text{H}_8\text{O}_6\text{As}_2\text{Ba}$, are also described. The acid is reduced by hydrogen sulphide to the *sulphide*, $\text{C}_6\text{H}_3\text{Me}(\text{AsS})_2$, a pale yellow, amorphous precipitate, and by phosphorous acid at 190° to *methyl-p-arsenophenylene* or *dimethyl p-diarsenobenzene*, a yellow, amorphous compound which is readily re-oxidised to the diarsinic acid.

H. W.

Physiological Chemistry.

Comparative Studies on Respiration. XXIII. The Effect of Adrenaline on the Production of Carbon Dioxide by Animals and by Plants. DOROTHY M. HUTCHINSON (*Amer. J. Physiol.*, 1922, 62, 192—196).—Carbon dioxide production was measured by the method of Osterhout (*J. Gen. Physiol.*, 1918, 1, 17). Adrenaline has similar effects on the respiration of frog's muscle and of radish seedlings. Stronger solutions (0.002 to 0.003%) cause a depression, followed by a return to normal, probably as the adrenaline is oxidised. Weaker solutions (0.002 to 0.005%) produce a rhythmic effect; the rate of carbon dioxide production falls, rises, then falls and rises again. CHEMICAL ABSTRACTS.

The Mineral Constituents of Blood. A. DESGREZ and J. MEUNIER (*Compt. rend.*, 1923, 176, 608—611).—A spectrographic analysis of the fractions obtained by crystallisation of the soluble portion of the ash of blood and of serum was made, the photographs being taken on panchromatic plates, and the salts heated in the

hydrogen flame. The first crystal fraction consisted mainly of sodium chloride with traces of potassium. In the next fractions, the potassium line 404 was very pronounced, and the presence of lithium was clearly indicated by the line 670. In the last fractions, the lithium line was as intense as the sodium line 568. The amount of lithium present was estimated at about 1/500 of that of sodium.

G. F. M.

Blood Studies in the Newborn. Morphological, Chemical, Coagulation, Urobilin, and Bilirubin. W. P. LUCAS, B. F. DEARING, H. R. HOOBLER, A. COE, M. R. JONES, and F. S. SMYTH (*Amer. J. Diseases Children*, 1921, **22**, 525—529).—The blood content of non-protein nitrogen, urea nitrogen, uric acid nitrogen, creatinine nitrogen, sugar, and carbon dioxide has been determined for the first twelve days of life. For this period, the calcium content of the whole blood, corpuscles, and plasma averaged, respectively, 8.8, 5.0, and 12.3 mg., respectively, per 100 c.c. for boys and girls together. During the first four days the coagulation time is definitely increased and the prothrombin element distinctly diminished. Urobilin or urobilinogen could not be found in the faeces. The estimation of bilirubin in plasma was carried out by adding 3 c.c. drop by drop to a solution of 30 c.c. of concentrated hydrochloric acid in 2 litres of 95% ethyl alcohol, and diluting to 25 c.c. On keeping, an emerald-green colour appears, developing greatest intensity in twenty-four hours. Comparison is made in a Hellige colorimeter with a wedge of gelatin, copper sulphate, and India ink, standardised with bilirubin. Eighty-two cases out of ninety gave a positive bilirubin reaction, the average curve beginning with 5 mg. of bilirubin per 100 c.c. of plasma, rising on the third day to 21 mg., and falling on the fourteenth day to 8 mg., although the actual quantities vary with different individuals.

CHEMICAL ABSTRACTS.

Physiology of the Glands. LIV. Proof of Adrenaline in the Arterial Blood of Animals. LEON ASHER and CARLO SCHNEIDER (*Biochem. Z.*, 1922, **133**, 373—390).—A biological proof is given of the presence of adrenaline in the general circulation.

W. O. K.

Production of Methæmoglobin by Narcotics. PH. ELLINGER and FRANZ ROST (*Arch. expt. Path. Pharm.*, 1922, **95**, 281—290).—The darkening of arterial blood which occurs during ether or chloroform narcosis is due to the formation of methæmoglobin.

E. S.

Blood Clotting. V. Alexander Schmidt's Thrombin. BERNHARD STUBER and MINORU SANO (*Biochem. Z.*, 1922, **134**, 239—249).—With a thrombin solution prepared by Schmidt's method and a fibrinogen solution prepared by Hammarsten's method a number of observations were made which the authors consider prove that the action of thrombin is a pure swelling process, the fibrinogen simultaneously losing its solvent and thereby clotting. Thrombin solution completely freed from protein by various pre-

cipitants or by dialysis cannot clot fibrinogen, and the smaller the protein content the longer is the period which elapses before clotting. Clotting time is dependent on the sodium chloride content of the fibrinogen, but is independent of its protein content. When thrombin and fibrinogen solutions of isotonic sodium chloride content were separated by a semipermeable diaphragm, clotting was observed to occur after many hours, even if the thrombin was replaced by gelatin or starch. This is interpreted as being due to the swelling of the partly denatured thrombin at the expense of the fibrinogen which loses its water and clots. H. K.

Blood Clotting. VI. Mode of Action of Thrombokinase. BERNHARD STUBER and MINORU SANO (*Biochem. Z.*, 1922, 134, 250—259).—Thrombokinase was prepared by Morawitz's method from liver. A high temperature and the presence of oxygen produce a feebly active product. The action of thrombokinase is attributed to its effect in lowering surface tension. On keeping, its solutions become more acid and lose activity, the maximum activity being observed over the range P_H 6 to 7. H. K.

Blood Clotting. VII. The Rôle of Calcium. BERNHARD STUBER and MINORU SANO (*Biochem. Z.*, 1922, 134, 260—268).—Oxalated plasma can be caused to clot by addition of strontium salts, but not by barium or magnesium. Calcium is therefore not essential. By means of Traube's viscostagonometer, the internal friction of plasma was determined with increasing oxalic acid content. Increase of the oxalic acid beyond the point of flocculation through neutralisation causes an increased internal friction, and hence an increased ionisation. The same is observed with citrated plasma, and in the region of high internal friction alcohol produces no precipitate. The results are interpreted on the basis that oxalated and citrated plasmas cannot clot owing to maximum ionisation of the fibrinogen-salt complex, and clotting by excess of calcium or strontium salts is due to a reversal of the ionisation of the complex. H. K.

Adsorption of Protein Degradation Products by the Blood-corpuscles in vivo and in vitro. B. SBARSKY (*Biochem. Z.*, 1923, 135, 21—31).—Using Bach's method (A., 1917, i, 375) for the estimation of degradation products of protein, the author has investigated the fate of the parenteral administration of erepton and diphtheria toxin to rabbits. No trace of protein degradation product was found in the blood immediately after intravenous injection of erepton (3.5 g.) or toxin (35 c.c.), either in the serum or in the blood, but if the blood is heated to boiling the protein degradation products are recovered quantitatively. The same applies to experiments in vitro. The injected peptones are therefore immediately adsorbed by the corpuscles and the first act in the process of immunisation is the adsorption of the toxins by the corpuscles. H. K.

The Glycogen Content of White Corpuscles. L. HABERLANDT (*Biochem. Z.*, 1922, 134, 405—406).—The author suggests

an explanation of de Haan's (A., 1922, i, 484) inability to find an increased glycogen content of the leucocytes of serum exudates after intraperitoneal administration of starch or glucose. H. K.

The Clinical Significance of the Estimation of Calcium in the Serum of Children, and Possible Errors in the Estimation. B. KRAMER, F. F. TISDALL, and J. HOWLAND (*Amer. J. Diseases Children*, 1921, 22, 560—564).—The blood-serum of normal children contains 10—11 mg. per 100 c.c., and that of normal adults 9·7—10·8 mg. Changes were observed only in cases of tetany and renal insufficiency, there being more or less distinct diminution of calcium in both cases. Sources of error in the estimation include the presence of calcium in the nitric and trichloroacetic acids, and even distilled water, and in the filter-paper, the solubility of calcium oxalate in water, and the fact that its precipitation must be accomplished in the presence of both magnesium and phosphates. The presence of magnesium in serum and plasma cannot normally be regarded as a serious source of error. Calcium oxalate is best precipitated from a liquid of p_H 5·2—6·2. CHEMICAL ABSTRACTS.

Antiphenolase (Antilaccase). A. BACH and W. ENGELHARDT (*Biochem. Z.*, 1923, 135, 39—45).—Rabbits were immunised by intravenous injections of a phenolase solution prepared from a fungus (*Lactarius vellereus*). The immune sera, produced, inhibited the oxidation of suitable substrates, guaiacol, or pyrogallol independently of the reaction of the medium, whereas normal sera failed to inhibit. The antiphenolase action is associated with the non-dialysable portion of the serum, and is completely destroyed by heating at 80° for thirty minutes. The question as to whether the antiphenolase action is due to a physical change of the immune sera or to production of a chemically defined anti-substances is undecided. H. K.

The Effect of Codeine on the Digestion of Meat by Dogs. EDWARD ZUNZ and ALEXIS DELCORDE (*Bull. Soc. chim. Belg.*, 1923, 32, 79—80).—Injections of codeine lengthen the stay, in the stomach, of cooked meat, which is less rapidly affected by the digestive juices. The effects are smaller than those produced by morphine and the other opium alkaloids. Codeine increases the proteoses and decreases the acid albumins in the stomach, similarly affecting the peptones and abiuretic compounds in the prepyloric portion. It does not, however, affect the subsequent contents of the small intestine, and has little effect on the amount of nitrogen present as ammonia-amine type. E. E. T.

The Influence of Various Quinine Derivatives on the Fermentative Function of the Organism. J. A. SMORODINZEV and A. N. ADOVA (*Biochem. Z.*, 1923, 135, 128—141).—The authors have investigated the effect of the addition of quinine monohydrochloride, quinine acid sulphate, quinine-urea dihydrochloride, urea nitrate, sulphate, and hydrochloride on the tryptic digestion of casein. The two quinine salts inhibit the action of trypsin, but the quinine-urea complex accelerates the reaction.

The urea salts at dilutions between $N/20$ and $N/80$ accelerate the digestion, but urea itself is without action. H. K.

Ferments of the Digestive Organs of the Bee. E. SARIN (*Biochem. Z.*, 1923, 135, 59—74).—The distribution of a number of ferments in various sections of the intestinal canal of the bee was examined. Catalase, lipase, amylase, invertase, pepsin, trypsin, and chymosin were found in the stomach, but not in the honey-stomach, the little intestine, or the colon, with the exception of catalase, which was found in the colon in the latter half of winter. Emulsin, lactase, and inulinase were absent in all cases. H. K.

The Invertase of the Intestinal Canal of the Bee. E. SARIN (*Biochem. Z.*, 1923, 135, 75—84).—Some further experiments (see preceding abstract) have been carried out on the invertase of the bee. In April and the late autumn, invertase appears to be absent from the bee's stomach, honey at this period consisting mainly of invert-sugar. For the preparation of an active invertase water is best, but the product does not keep well. An extract made with equal parts of glycerol and water retains its activity for eleven months. H. K.

Unit of Energetic Metabolism and Active Mass of the Organisms. EMILE F. TERROINE, A. FEUERBACH, and E. BRECKMANN (*Compt. rend.*, 1923, 176, 462—464).—Analyses of normal and starved subjects in the case of two species show that, although the weight of the animal may vary within wide limits, the nitrogen present expressed as a percentage of the body-weight is a constant. These results, when compared with those of other workers on animals of vastly different size, owing to the difference in species, show that the protein content of the species studied is practically identical. It is thus useless to attempt to establish any relationship directly and entirely between the intensity of metabolism and the protein content. W. G.

The Influence on Metabolism of some Purine and Pyrimidine Bases. F. P. UNDERHILL and H. F. FARRELL (*J. Metabolic Research*, 1922, 2, 107—111).—Solutions of caffeine, theobromine, uric acid, and of hypoxanthine when injected into fasting rabbits led to an augmented excretion of total nitrogen, creatine, and creatinine, indicating an increased protein katabolism.

CHEMICAL ABSTRACTS.

The Influence of Benzyl Benzoate on Nitrogenous Metabolism. G. T. PACK and F. P. UNDERHILL (*J. Metabolic Research*, 1922, 2, 73—105).—Investigations on dogs indicate that the therapeutic dose of benzyl benzoate for man is probably insufficient to disturb the normal nitrogenous metabolism; larger doses, however (*i.e.*, 0.5 c.c. per kg. of body-weight), cause an increase of protein katabolism in dogs. The total output of nitrogen is increased, marked creatinuria occurs, and conjugated glycuronates appear in the urine, but creatinine metabolism is unmodified. The changes are probably due to benzyl alcohol. Benzyl succinate produces

less change in the normal nitrogenous metabolism of the dog than the other benzene derivatives investigated. The katabolic processes which ensue after the administration of these benzene derivatives are discussed theoretically.

CHEMICAL ABSTRACTS.

Potassium in Animal Nutrition. I. Influence of Potassium on Urinary Sodium and Chlorine Excretion. HARRY G. MILLER (*J. Biol. Chem.*, 1923, 55, 45—59).—Experiments on pigs have shown that the increased excretion of sodium and chlorine which follows the administration of a single large dose of potassium salts is not maintained, even when the inclusion of potassium salts in the diet is continued.

E. S.

Potassium in Animal Nutrition. II. Potassium in its Relation to the Growth of Young Rats. HARRY G. MILLER (*J. Biol. Chem.*, 1923, 55, 61—78).—Rats maintained on diets containing less than approximately 0.1% of potassium showed failure of growth. Subsequent increases in the potassium content of the diet produced no permanent improvement.

E. S.

Hydrolysis of Higher Fats in Egg-secretion. OTTO GLASER (*Biol. Bull. Marine Biol. Lab.*, 1922, 46, 68—74).—*Arbacia* egg-secretion has the power to hydrolyse higher fats. Since whale oil, olive oil, and cetyl butyrate do not occur in sea urchin eggs, the lipase present must be non-specific. The lipolysin isolated by Woodward (cf. *J. Exp. Zool.*, 1918, 26, 459) appears to be, or contain, that enzyme which in unmodified egg-water is responsible for the hydrolysis of the higher fats.

CHEMICAL ABSTRACTS.

Chemistry of the Lung. Nucleic Acids of the Lung. UBALDO SAMMARTINO (*Biochem. Z.*, 1922, 133, 405—408).—A nucleic acid has been separated from lung tissue and purified by repeated precipitation as the copper salt. It has the formula $C_{33}H_{54}O_{24}N_{10}P_2$, and when hydrolysed with methyl-alcoholic hydrochloric acid yields adenine and guanine. No pentose could be detected.

W. O. K.

Production and Destruction of the Cholesterol of the Spleen during Aseptic Autolysis. SALVATORE MARINO (*Atti R. Accad. Lincei*, 1922, [v], 31, ii, 192—195).—The author confirms the observation of Abelous and Soula (*Compt. rend. Soc. Biol.*, 1920) that, during aseptic autolysis of the spleen, the cholesterol content at first increases and subsequently diminishes. The liver and brain show similar behaviour, but with the suprarenal and thyroid glands and the kidneys only destruction of the cholesterol occurs. These phenomena are functions of the temperature and time. It thus appears that, more than other organs, the spleen exerts a marked influence on the formation of cholesterol and on the metabolism of fats.

T. H. P.

Creatine Content of Muscle in Anaërobic Contraction. E. A. SPIEGEL and A. LÖW (*Biochem. Z.*, 1923, 135, 122—127).—The creatine content of the gastrocnemius muscles of frogs is not altered by stimulating them to exhaustion either in Ringer solution or in air or nitrogen.

H. K.

Acetaldehyde as an Intermediate Metabolic Product in Surviving Muscle. JULIUS HIRSCH (*Biochem. Z.*, 1922, 134, 415—423).—In the aqueous distillate from the muscles of frogs, acetaldehyde was detected by Rimini's colour reaction. By the use of a fixative, dimethylhydroresorcinol, acetaldehyde was isolated from the surviving muscles of carp and tench. The breakdown of carbohydrates or lactic acid in the animal body appears to be by way of acetaldehyde. H. K.

Manganese in Hair. J. McCRAE (*J. S. African Chem. Inst.*, 1923, 6, 18—19).—The ash from 2.5 to 10 g. of hair was evaporated to dryness with dilute nitric acid, and the residue extracted with boiling water acidified with the same acid. To the filtered extract a few drops of dilute silver nitrate were added and then a small quantity of concentrated ammonium persulphate. Depending on the quantity of manganese present, a more or less deep pink colour is developed. It was matched by dilution of *N*/2000 solution of potassium permanganate. Five samples of hair varying from fair to very dark were thus examined, and the quantity of manganese found to be of the order of 1 to 2 parts per million of hair. No relation with the colour was observed. The small proportion probably arises from the manganese in vegetable matter, which in turn is derived from that widely distributed in rocks and soil. T. S. W.

The Reduction of Nitro-groups by Living Tissues. N. WATERMAN and J. KALEFF (*Biochem. Z.*, 1923, 135, 174—181).—Lipschitz's results (*A.*, 1921, i, 203), on the reduction of *m*-dinitrobenzene by excised tissues and tumours, from which he draws important conclusions controverting the more direct results obtained by others with the Barcroft differential apparatus, are shown to be due to the use of impure *m*-dinitrobenzene, possibly containing thiophen derivatives. H. K.

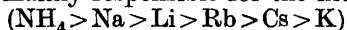
Calcium Content of Cats treated with Calcium. W. HEUBNER and P. RONA (*Biochem. Z.*, 1923, 135, 248—281).—The minimum content of calcium oxide of the muscles, liver, brain, and kidneys of normal cats lies between 5 and 7 mg. of the weight when fresh; of the heart and small intestine 11 mg., lungs 16 mg., and colon between 25 and 30 mg. After repeated subcutaneous administration of calcium chloride solution (2 to 5%) the only organ showing increased calcium content is the kidney. H. K.

The Inorganic Constituents of Marine Invertebrates. FRANK WIGGLESWORTH CLARKE and WALTER CALHOUN WHEELER (*U.S. Geol. Survey*, 1922, Professional Paper 124, 1—62).—Quantitative analyses have been made of the inorganic constituents of a large number of marine invertebrates, and of marine algae. The results of previous analyses by other workers are also quoted in the paper, and the general results are discussed in their bearing more particularly on geological problems. W. O. K.

Occurrence of Copper and Zinc in certain Marine Animals. HAZEL W. SEVERY (*J. Biol. Chem.*, 1923, 55, 79—91).—Estimations have been made of the copper and zinc content of sixteen

different marine animals. Zinc was present in every case. Copper, however, was absent, or practically so, from the mammals (whale, sea-lion), and also from the clam. E. S.

Is the Taste of a Salt due to the Ions or to the Whole Molecule? H. KIONKA and F. STRÄTZ (*Arch. exp. Path. Pharm.*, 1922, **95**, 241—257).—Results obtained with the chlorides, bromides, and iodides of the alkali metals and ammonia indicate that the kation is mainly responsible for the intensity



and the anion for the quality of the taste. Neither quality nor intensity is appreciably altered by the presence of tasteless colloids (starch). Sodium chloride has a pure saline taste; all the remaining salts examined have mixed tastes, amongst which no fewer than twenty-five distinct tastes have been distinguished. E. S.

Oxidation of Reduced Glutathione and other Sulphydryl Compounds. MALCOLM DIXON and HUBERT ERLIN TUNNICLIFFE (*Proc. Roy. Soc.*, 1923, [B], **94**, 266—297).—Experiments are described which show that the reduction of methylene-blue by reduced glutathione (this vol., i, 167), cystein, or thioglycollic acid are autocatalytic reactions in which the disulphide form of the sulphur compound acts as catalyst. This action is probably due to the formation of an additive compound between the sulphydryl and disulphide forms which is more active than the former alone. Acceleration of the reaction is also produced by surfaces such as glass-wool, kieselguhr, and platinum-black, provided care is taken to remove all traces of oxygen, and by direct sunlight. The oxidation of the sulphydryl compounds by atmospheric oxygen is similarly autocatalytic. In the cases of glutathione and cystein, the reaction velocity shows an optimum at P_{H} 7.4; this, however, is not characteristic of sulphydryl groups, since it is not shown by thioglycollic acid. E. S.

The Inorganic Phosphate content of Breast Milk of Mothers with Normal and with Rachitic Infants. L. VON MEYSENBURG (*Amer. J. Diseases Children*, 1922, **24**, 200—203).—Average samples of the milk of mothers of non-rachitic and rachitic infants contain, respectively, 2.5—6.2 (average 4) mg. and 2.7—5.7 (average 4.8) mg. of inorganic phosphate per 100 c.c. The serum of non-rachitic and rachitic infants contained, respectively, 4.1—5.8 (average 5) mg. and 2.2—4.1 (average 2.8) mg. of inorganic phosphate per 100 c.c. CHEMICAL ABSTRACTS.

Arginase. VII. Arginase in the Enteric Mucus and in the Enteric Secretion. ANTONINO CLEMENTI (*Atti R. Accad. Lincei*, 1922, [v], **31**, ii, 559—561).—By the method previously described (this vol., ii, 271) the author demonstrates the absence of arginase from the intestinal secretion of the dog, the conclusion being drawn that arginase is not, as is sometimes assumed, an extracellular digestive enzyme participating in the digestion of proteins in the intestinal tract. On the other hand, this enzyme occurs in the intestinal mucus of the dog or monkey, probably

because it plays a part in the synthesis of homogeneous proteins from the products of digestion of heterogeneous proteins, this process being necessarily accompanied by partial destruction or elimination of certain amino-acids.

T. H. P.

Behaviour of Cholesterol in the Blood and in the Kidneys.

LOTHAR TIETZ (*Frankfurter Z. Pathol.*, 27, 353—367; *Ber. ges. Physiol.*, 15, 93; from *Chem. Zentr.*, 1923, i, 176).—The elimination of cholesterol in the urine appears to be independent of the amount present in the blood. Occurrence of cholesterol in urine implies deposition of fat in the renal parenchyma.

G. W. R.

Elimination and Destruction of Uric Acid in the Human Body. HEINRICH CHANTRAINE (*Biochem. Z.*, 1922, 133, 613—625).—It appears that fluctuations in the mechanism of elimination rather than of production are responsible for the variations in the daily excretion of uric acid. If uric acid is administered as the sodium salt, no destruction seems to take place, and approximately the amount administered is eliminated in the urine during the next three or four days, in addition to the normal elimination.

W. O. K.

Analysis of the Urine Colouring Matters. III. Urochrome. M. WEISS (*Biochem. Z.*, 1922, 133, 331—349).—Urochrome does not exist primarily in the urine as such, but as urochromogen, derived apparently from the destruction of cells. Urochromogen is the cause of the Ehrlich diazo-reaction. When oxidised, which is easily effected by atmospheric oxygen in alkaline solution, it is converted into the coloured compound urochrome, or into uromelanin.

W. O. K.

Analysis of Urine Colouring Matters. IV. The Diazo-reaction of Urine and Urochromogen Excretion. M. WEISS (*Biochem. Z.*, 1922, 134, 269—291).—The red colour produced in urine by Ehrlich's reagent is due almost entirely to urochromogen.

H. K.

The Metabolism of Inorganic Materials in Diabetics. I. ROBERT MEYER-BISCH and PAUL THYSSSEN (*Biochem. Z.*, 1923, 135, 308—316).—In four cases of diabetes mellitus the authors have estimated the calcium, dextrose, sodium chloride, sulphuric acid (free and bound) content and the alkali reserve of the blood after administration of 50 g. of sodium hydrogen carbonate. In each case the alkali reserve fell off, the other quantities showing little alteration, except calcium, which remains constant in normal persons but sometimes exhibits a temporary depression in a diabetic.

H. K.

The Glycogen Content of the Tissues of Diabetic Animals and the Influence of Adrenaline thereon. A. I. RINGER, H. DUBIN, and F. H. FRANKEL (*Proc. Soc. Exp. Biol. Med.*, 1921, 19, 92—97).—Between the second and seventh day of glycosuria, the muscles of fasting dogs given daily injections of phloridzin were found to contain on an average 482, 306, 228, 155, and 138 mg.

of glycogen per 100 g. Despite continuous fasting and complete diabetes, the muscle-cells retained a certain amount of residual glycogen. The muscles of similarly phloridzinised dogs, which had also been injected with adrenaline on the second or third day of glycosuria, contained the following amounts of glycogen in mg. per 100 g. one, three, and five days, respectively, after the adrenaline injection: 0; 20, 33, 23, 39; 69. In the case of dogs rendered glycogen-free and given glycogenetic substances, such as glycine, alanine, propionic acid, and lactic acid, the resulting glycosuria was not comparable to that found in dogs not treated with adrenaline. It is concluded that fasting diabetic dogs possess the power of glycogen formation after that substance has been eliminated from the muscles by the administration of adrenaline, and that failure of glycosuria is not a criterion of the glycogenetic quality of a substance, when given to deglycogenised diabetic animals.

CHEMICAL ABSTRACTS.

Is there More Than One Kind of Rickets? P. G. SHIPLEY, E. A. PARK, E. V. MCCOLLUM, and NINA SIMMONDS (*Amer. J. Diseases Children*, 1922, 23, 91—106).—There are two main kinds of rickets. In the one, the calcium content of the blood is normal, or nearly so, and the inorganic phosphorus content low, whilst in the other the relation is reversed.

CHEMICAL ABSTRACTS.

Calcium and Phosphorus in the Serum in Relation to Rickets. J. HOWLAND and B. KRAMER (*Amer. J. Diseases Children*, 1921, 22, 105—119).—For the estimation of inorganic phosphates, the blood-serum should not be left in contact with the blood clot. The inorganic phosphorus content of the serum of sixteen non-rachitic children varied from 4 to 7.1 mg. per 100 c.c. (average 5.4 mg.). For partly or wholly breast-fed infants, the range was 5.6—7.1 mg. (average, 6.1 mg.). The calcium content of the serum of fourteen cases of rachitic infants without signs of latent tetany varied from 8 to 10.8 mg. per 100 c.c.; the phosphorus content 0.6 to 3.2 mg., in four cases the magnesium content being 1.8—2.5 mg. In some cases, the administration of cod-liver oil caused a decided increase in the amount of inorganic phosphorus.

CHEMICAL ABSTRACTS.

Calcium and Phosphorus Metabolism. I. The Excretion of Calcium and Phosphorus. II. The Metabolism of Calcium and Phosphorus in Rickets. S. V. TELFER (*Quart. J. Med.*, 1922, 16, 45—62; 62—72).—I. The excretion of calcium, phosphorus, and their fatty derivatives is interdependent, calcium being eliminated chiefly as the phosphate and to a less extent as insoluble soaps. The total amount of calcium and phosphorus eliminated is nearly proportional to the intake; a large part of the ingested calcium is not absorbed, and appears in the faeces as normal calcium phosphate, only a small fraction of the total calcium being excreted in the urine. There is no evidence that any appreciable amount of endogenous calcium or phosphorus is eliminated. In normal infants, 40% of the total phosphorus excreted appears in

the urine and 60% in the faeces, but with acid formation in the intestine a greater proportion is excreted in the urine. The degree of deviation of phosphorus to the urine is roughly proportional to the amount of fatty acids in the faeces, and, therefore, to the degree to which fatty acids had displaced phosphoric acid from its normal combination with calcium in the intestine. An excess of calcium restricts an increased amount of phosphorus in the intestine. When the fat and phosphorus intake was low, an excess of calcium rendered the urine free from phosphorus. The average daily faecal weight depends chiefly on the degree to which calcium soaps are formed, since these form a mechanical basis for the formation of faeces. When the intake of both fat and phosphorus is very deficient, calcium may be excreted as carbonate. No evidence was found of the absorption of calcium and phosphorus in excess of requirements, with re-excretion into the intestine.

II. In normal infants on a diet of cow's milk the retentions of lime and phosphate were approximately equal. An excess of phosphate is retained over the equivalent amount of lime required for bone formation. In rickets, there is diminished retention of lime and phosphate, the latter being possibly due to diminished fixation by the calcium. No negative retentions of lime or phosphate were found, so that it does not appear that bone softening in rickets is due to excessive decalcification.

CHEMICAL ABSTRACTS.

The Mechanism of the [Physiological] Action of Chlorates.

RUDOLF L. MAYER (*Arch. expt. Path. Pharm.*, 1922, 95, 351—377).—In the presence of either ferrous sulphate or hæmoglobin, potassium iodide is oxidised by potassium chlorate. In both cases, the reaction is similarly influenced by variations in acidity, temperature, and concentration. The author concludes that the reduction of chlorates in the blood is a catalytic reaction in which hæmoglobin acts as catalyst by virtue of the iron which it contains. Hæmoglobin also catalyses the oxidation of sodium sulphite by potassium chlorate; when the sulphite is completely oxidised, the production of methæmoglobin commences. The latter can be partly reduced if more sulphite is added immediately, but if time is allowed to elapse, the reduction is more incomplete. Apparently the methæmoglobin changes from an active to an inert form. E. S.

Pharmacology of Selenium and Tellurium. IV. Action of their Acids on Trypanosomes in vitro. FRITZ LEHMANN (*Biochem. Z.*, 1922, 134, 390—397).—High concentrations of selenium or tellurium are lethal to trypanosomes, but after one hour's exposure the following dilutions were not lethal: for tellurites 1:500, for tellurates 1:300, for selenites 1:500, and for selenates 1:100. It was not found possible to obtain exact figures of toxicity. H. K.

Toxicity and Actions of the Normal Butylamines. P. J. HANZLIK (*J. Pharm. Expt. Ther.*, 1923, 20, 435—449).—The pharmacological actions of mono-, di-, and tri-butylamines have been

studied. All are toxic, and act as cardiac depressants; on the smooth muscle of excised organs, however, they exert a stimulant action, thus resembling histamine. When placed in an atmosphere saturated with the vapours of mono- and di-butylamines, white rats rapidly succumb; tributylamine, on the other hand, is insufficiently volatile to produce this effect. E. S.

The Effect of the Parenteral Administration of some Amino-acids on the Respiratory Gas Exchange of the Dog. F. W. KRZYWANEK (*Biochem. Z.*, 1923, **134**, 500—527).—The parenteral administration of alanine and of glycine causes a rise in the respiratory quotient and a negative nitrogen balance. The results of the author and of other investigators are discussed at length. W. O. K.

Pharmacological Properties of some isoUrea Derivatives. STEWARD BASTERFIELD (*J. Pharm. Expt. Ther.*, 1923, **20**, 451—461).—The *O*-ethyl derivative of allophanic ester, $\text{NH}\cdot\text{C}(\text{OEt})\cdot\text{NH}\cdot\text{CO}_2\text{Et}$, m. p. 39° , when injected into rabbits produced a moderate depression, a rapid fall of body temperature, and an increased muscle tonus. No great physiological action was shown by other isourea derivatives. E. S.

The Chemical Defence Mechanism of the Fowl. JAMES H. CROWDLE and CARL P. SHERWIN (*J. Biol. Chem.*, 1923, **55**, 15—31).—Various substances were fed to fowls. Benzaldehyde, phenylpropionic acid, and cinnamic acid were excreted as ornithuric acid; *p*-hydroxybenzaldehyde as *p*-hydroxybenzoic acid; *m*-nitrobenzaldehyde probably as the anhydride of *m*-aminobenzoic acid; nitrobenzene as *m*-aminophenol; *o*-nitrophenylpropionic acid as *o*-nitrobenzoic acid, and *m*-aminobenzoic acid as *m*-acetamidobenzoic acid. The fowl employs, apparently, processes of oxidation, reduction, acetylation, and conjugation with ornithine for the detoxication of these compounds, but is unable to form carbamide-compounds or to furnish glycine for this purpose. E. S.

The Active Alkaloids of Ergot. H. H. DALE and K. SPIRO (*Arch. expt. Path. Pharm.*, 1922, **95**, 337—350).—The physiological actions of the two alkaloids ergotoxine, $\text{C}_{35}\text{H}_{41}\text{O}_6\text{N}_5$ (Barger and Carr, T., 1906, **94**, 89), and ergotamine, $\text{C}_{33}\text{H}_{35}\text{O}_5\text{N}_5$ (Spiro and Stoll, A., 1922, i, 47), isolated from ergot are qualitatively and quantitatively identical. E. S.

The Influence of the Parenteral Introduction of Protein on the Gas Metabolism. ALFRED LEIMDÖRFER (*Biochem. Z.*, 1922, **133**, 409—416).—Protein introduced parenterally into animals causes an increased oxidation in the tissues with a corresponding rise in temperature. W. O. K.

Effect of Pancreatic Extract (Insulin) on Normal Rabbits. F. G. BANTING, C. H. BEST, J. B. COLLIP, J. J. R. MACLEOD, and E. C. NOBLE (*Amer. J. Physiol.*, 1922, **62**, 162—176; cf. *Trans. Roy. Soc. Canada*, 1922, **16**, V, 1).—When injected subcutaneously

into normal rabbits, insulin causes a diminution of the sugar content of the blood within a few hours, the animal exhibiting signs of hunger and thirst, hyperexcitability, and apparent fear, convulsive seizures often supervening, the sugar content of the blood then usually being about 0.045%. Subcutaneous injections of dextrose act as an antidote to the convulsions and other symptoms. Post-mortem examination frequently discloses a peculiar mucigenous degeneration of the subcutaneous tissues of the abdominal wall. As a basis for the physiological assay of insulin, the authors suggest as one unit the number of c.c. which cause the blood-sugar of normal rabbits to fall to 0.045% within four hours. This dose is decidedly active in lowering the sugar content of the blood in diabetic patients.

CHEMICAL ABSTRACTS.

[Physiological] **Effect of "Arsylene."** S. KATZENELBOGEN (*Arch. internat. pharm. therap.*, 1922, **26**, 407—420; from *Chem. Zentr.*, 1923, i, 173).—Arsylene (sodium allylarsinate) is less poisonous than arsenious oxide. With single administration of a large dose, no simple alteration in the composition of the blood is observed. Daily doses of 0.015 g. per kg. of live weight produce slight decrease in erythrocytes, irregular variation in leucocytes, increase in lymphocytes, and occurrence of isolated nucleated erythrocytes. Daily doses of 0.001—0.002 g. per kg. produce irregular increase in erythrocytes and hæmoglobin. The resistance of erythrocytes against hæmolysis is not increased by "arsylene."

G. W. R.

Experimental Acid Poisoning. II. The Respiratory Gas Exchange in Acid Poisoning. A. LOEWY and E. MÜNZER (*Biochem. Z.*, 1923, **134**, 437—441).—The administration of hydrochloric acid to rabbits decreases the intake of oxygen as well as the output of carbon dioxide. The deleterious poisoning effects of the acid are therefore to be ascribed to a decrease in the rate of oxidation in the cell, as well as to the lowered capacity of the blood to transport carbon dioxide.

W. O. K.

Experimental Acid Poisoning. III. Does Methyl Alcohol Poisoning Lead to an Acidosis? A. LOEWY and E. MÜNZER (*Biochem. Z.*, 1923, **134**, 442—446).—In acidosis, there is a change in the dissociation constant of the blood. Methyl alcohol is said to be oxidised to formic acid in the body, and the abnormal amount of ammonium salts in the urine following methyl alcohol poisoning is said to be a result of the acidosis. It is now shown that if methyl alcohol is administered to dogs or rabbits, any acidosis so induced is too weak to alter the dissociation curve of the blood.

W. O. K.

A Study of Metabolism in Chloroform Poisoning. F. P. UNDERHILL and ROBERT KAPSINOW (*J. Metabolic Research*, 1922, **2**, 57—72).—Graham's hypothesis (*J. Exp. Med.*, 1915, **22**, 48) that in late poisoning with chloroform and with other alkyl halides the intoxication is due chiefly to the liberated hydrogen chloride was not confirmed. A diet yielding an alkaline ash when fed to

rabbits had no inhibiting effect on delayed chloroform poisoning. The excretion of chlorine by rabbits poisoned with chloroform was not increased in starvation. The only metabolic changes observed with the alkaline diet that could not be explained by the food were alterations in the creatinine, creatine, and total nitrogen excretion. These are probably the results of absorption of dead tissue following injury by chloroform. CHEMICAL ABSTRACTS.

Chemistry of Vegetable Physiology and Agriculture.

Influence of Copper on Lactic Fermentation. MARC FOUASSIER (*Compt. rend.*, 1923, 176, 606—608).—The influence exercised on lactic fermentation by contact with certain metals either previously to, or during the action of, the ferment was studied. Lamellæ of the following metals, zinc, aluminium, lead, silver, iron, nickel, copper, and tin, were placed in contact with sterilised milk, which was then inoculated with the lactic ferment, and observations were made of the increase in acidity. It was found that this increase was more rapid in presence of iron, much retarded by copper, and uninfluenced by the other metals. The inhibiting action of the metallic copper on the fermentation was just the same, whether the metal was present during the fermentation or whether the milk had previously been exposed for eight hours to the metal, which was then removed before inoculation. The antiseptic action of copper was further demonstrated by the gradual loss in activity of the ferment suspended in pure sterile water in presence of a piece of copper foil. G. F. M.

Bacteria which Split Nucleoprotein and their Importance for the Liberation of the Phosphorus Reserve in Surface Soils. ALFRED KOCH and ALICE OELSNER (*Biochem. Z.*, 1922, 134, 76—96).—Phosphates are liberated from nucleoproteins and their breakdown products by various soil bacteria (nucleobacter). Chalk is suitable to the liberation of inorganic phosphate, as it gives an alkaline reaction favourable to the bacteria. For analyses of inorganic phosphate in presence of organically bound phosphorus, ammonium molybdate was found suitable, and ultra-filtration was employed for removing bacteria from nutrient media before analysis. H. K.

The Chemotherapy of the Acridine Dyes in Experimental Tuberculosis. MAURICE I. SMITH (*J. Pharm. Expt. Ther.*, 1923, 20, 419—434).—Certain acridine derivatives, namely, acriflavine, proflavine, acridinium-yellow, and acridine-orange, inhibit to a marked degree the growth of the tubercle bacillus in vitro. The pathogenicity of the bacillus is not, however, altered, neither is the tuberculosis process in experimentally infected animals modified by injections of these substances. E. S.

Occurrence of *p*-Hydroxybenzaldehyde and *p*-Hydroxybenzoic Acid in the Bacterial Decomposition of Tyrosine, with Special Reference to Melanin Formation. KINSABURO HIRAI (*Biochem. Z.*, 1923, 135, 299—307).—By the prolonged action of *Proteus vulgaris* on *l*-tyrosine in Ringer's solution, *p*-hydroxybenzaldehyde and *p*-hydroxybenzoic acid were formed in small yield. In addition, after three weeks a black colouring matter was produced, but not if the medium contained glycerol. The production of this melanin is favoured by use of Henderson's phosphate mixture as a nutrient medium, or by the presence of platinum sponge. The melanin is amorphous, but is soluble in alkali, alcohol, glacial acetic acid, acetone, or ethyl acetate. Its production is probably due to a tyrosinase, as under parallel conditions it is not formed from tryptophan, phenylalanine, or leucine.

H. K.

Oxidation of Zinc Sulphide by Micro-organisms. W. RUDOLFS and ANDRÉ HELBRONNER (*Soil Sci.*, 1922, 14, 459).—A culture of organisms was isolated which were capable of oxidising zinc sulphide to sulphate without suffering injury from the soluble zinc salt. The addition of elementary sulphur to an impure culture increased the rate of oxidation of zinc sulphide. The "Lipman" sulphur oxidising bacteria produce sufficient sulphuric acid to dissolve zinc carbonate and silicate. The possibility of a biological process for utilising low-grade zinc blends is noted.

A. G. P.

Cell Respiration. I. The Respiration of Yeast-cells. P. RONA and K. GRASSHEIM (*Biochem. Z.*, 1922, 134, 146—162).—The optimum hydrogen-ion concentration, whether produced by phosphate or acetate buffer mixtures, for the respiration of yeast-cells (*Torula pulcherrima*) lies between P_H 4.5 and 6.6. Just outside these limits, the respiration falls off considerably. The oxygen consumption, using acetates as buffers, is about 30% more than when using phosphates, the most favourable concentration of the latter being one-third molar. The respiration is affected by the age of the yeast, for it falls off after seven days; it is not, however, affected by repeated freezing and thawing of the yeast-cells.

H. K.

The Transformation of Tertiary Amino-acids by Yeast. K. KURONO (*Biochem. Z.*, 1922, 134, 424—433).—When a large amount of sucrose was fermented by yeast in the presence of *dl*- α -amino- α -methyl-*n*-valeric acid, the products isolated were the same amino-acid exhibiting *laevo*-rotation, and methylpropylcarbinol also exhibiting *laevo*-rotation. The identity of this alcohol was proved by preparation of its α -*naphthylurethane*, m. p. 46°, by its oxidation to methyl propyl ketone, which gives a *p*-nitrophenylhydrazone, m. p. 112°. During the fermentation, it is therefore supposed that the degradation takes place via the ketone, $NH_2 \cdot CRR' \cdot CO_2H \rightarrow CORR' \rightarrow CHRR' \cdot OH$.

H. K.

The Behaviour of Pyruvic Acid and Acetaldehyde to Oxygenated Yeast. FRITZ LIEBEN (*Biochem. Z.*, 1923, 135, 240—247).—Pyruvic acid as its sodium salt is partly decomposed with evolution of carbon dioxide and partly utilised by the yeast-cells for body building, when shaken with yeast-cells in a stream of oxygen. Acetaldehyde under similar conditions is for the most part unchanged. Pyruvic acid can be quantitatively estimated by Fürth and Charnass's method if it be first of all reduced to lactic acid by zinc dust and hydrochloric acid. H. K.

The Oligodynamic Action of Metals. JOSEF SCHUMACHER (*Biochem. Z.*, 1922, 134, 398—404).—Pure methylene-blue reduced to leucomethylene-blue by sodium formaldehydesulphoxylate can be used for detecting silver in oligodynamic quantities. Water in which a silver coin has been boiled restores the blue colour instantaneously, and immersion of the coin in a leucomethylene-blue solution gives rise to blue layers over the coin, whereas the main bulk of the solution remains colourless. H. K.

The Influence of Hydrogen-ion Concentration on the Antiseptic Effect of Sublimate. GEORG JOACHIMOGLU (*Biochem. Z.*, 1923, 134, 489—492).—The antiseptic effect of mercuric chloride disappears in weakly alkaline reaction between P_H 7·8 and P_H 10·1, and appears to be most marked in weakly acid reaction between P_H 5·0 and P_H 6·6. W. O. K.

Formation of Oxygen from Carbon Dioxide by Protein-Chlorophyll Solutions. M. EISLER and L. PORTHEIM (*Biochem. Z.*, 1923, 135, 293—298).—The filtrate from a 95% alcoholic extract of grass was treated with four volumes of twenty-fold diluted horse-serum and the flocculated precipitate collected by centrifuging. The protein-chlorophyll mixture was dissolved in 0·85% sodium chloride solution, and using a differential blood-gas apparatus the solution in one bulb was exposed to bright sunlight in an atmosphere of carbon dioxide. The bulb exposed to sunlight exhibited an excess pressure which analysis showed was due to liberation of oxygen. H. K.

A New and Efficient Respirometer for Seeds and other Small Objects. GEORGE T. HARRINGTON and WILLIAM CROCKER (*J. Agric. Res.*, 1923, 23, 101—116).—After discussing various types of respirometers, previously advocated, the authors describe a new form of respirometer, a sketch of which is given in the original. With this apparatus, oxygen consumption and carbon dioxide production are determined in the same apparatus and for the same period of time, using the whole volume of air instead of a sample. The gaseous exchanges are determined at the end of an experimental period by means of a manometer, which is an integral part of the apparatus. The pressure readings are made the basis of direct calculations, both of oxygen consumed and of carbon dioxide given off. W. G.

Respiration of Apple Seeds. GEORGE T. HARRINGTON (*J. Agric. Res.*, 1923, 23, 117—130).—Using the respirometer previously

described (preceding abstract), the author has made a study of the respiration of apple seeds under different conditions.

The respiratory intensity of dormant apple seeds is low, but the intensity in the case of seeds capable of germination is higher and becomes very high with advancing germination, but soon falls if the germinated seeds are kept at too high a temperature. Removal of the outer seed coats increases the respiratory intensity and accelerates germination, but does not affect the respiratory quotient. At the ordinary temperature, the respiratory quotient corresponds with complete oxidation of fats or only slight increase in sugars. With rise in temperature, there is an increase in the respiratory quotient, causing impoverishment in easily oxidisable substances, and with fall in temperature there is a fall in the quotient and a storage of oxygen which probably leads to an increase in acids and sugars. With a relatively high rate of oxidation at high temperatures, there is a tendency for the seeds to become dormant. With advancing germination, the respiratory quotient becomes low, indicating the rapid transformation of fats and accumulation of sugars, but this is preceded by a brief initial rise, which indicates that oxygen-rich substances are being broken up more rapidly than they are replaced.

Respiratory intensity, respiratory quotients, and temperature coefficients are affected by the previous treatment of the seeds, being higher after treatment which tends towards after-ripening, and lower after treatment which induces deeper dormancy. W. G.

Ferment Formation in Germinating Plant Seeds. A. BACH and A. OPARIN (*Biochem. Z.*, 1922, **134**, 183—189).—The authors have estimated the content of respiratory ferments (catalase, peroxylase, oxygenase) and of hydrolytic ferments (amylase, protease) in germinating wheat grains and sunflower seeds. During germination, the content of ferments rises to a maximum in six to eight days except for catalase in wheat, which reaches its maximum in three to four days. The catalase content of sunflower seeds is greater than that of wheat, but the reverse is the case for the other ferments. H. K.

The Influence of Oxygen on the Formation of Ferments in Germinating Wheat Grains. A. OPARIN (*Biochem. Z.*, 1922, **134**, 190—193).—Increased partial pressure of oxygen has no influence on the formation of ferments (preceding abstract) with the exception of oxygenase, which is inhibited, but replacement by an inert gas such as hydrogen is inimical to all ferments except oxygenase. H. K.

Ammonia as Primary and End-product of Nitrogen Metabolism in Plants. D. N. PRIANISCHNIKOV (*Landw. Versuchs-Stat.*, 1922, **99**, 267—286).—The author further develops his earlier theories on the nitrogen metabolism of plants. In seedling plants receiving ammonium salts, the changes depend on the amount of carbohydrates present. Where, as in barley and maize, abundant carbohydrate is present, asparagine is formed and comparatively little ammoniacal nitrogen is found. Where, as in

lupines, the proportion of carbohydrate to protein is less, more ammoniacal nitrogen is found, and the formation of asparagine is depressed. By artificially decreasing the amount of carbohydrate, either by starvation or by removal of cotyledons or endosperm, plants rich in carbohydrate can be made to behave in the same way as those poor in carbohydrate. Similarly, by supplying dextrose to lupine seedlings, increased formation of asparagine and decrease in ammoniacal nitrogen may be induced. Asparagine is held to fulfil the same function in plant metabolism as carbamide in animal metabolism.

G. W. R.

The Chemical Mechanism of the Formation of Fat in the Living Cell. HUGO HAEHN and WALTER KINTTOF (*Ber.*, 1923, 56, [B], 439—445).—A preliminary communication. It has been suggested previously (HaeHN, *Z. tech. Biol.*, 1921, 9, 217) that acetaldehyde is an intermediate product in the conversion of carbohydrates into fats within the living cell, and that the process occurs in accordance with the scheme: dextrose \rightarrow pyruvic acid \rightarrow acetaldehyde \rightarrow aldol \rightarrow glyceryl ester. It is suggested that aldol is transformed into γ -dihydroxy-*n*-hexaldehyde or the corresponding unsaturated substance, which is converted by successive oxidation and reduction into sorbic and hexoic acids. Condensation of three molecules of the unsaturated aldehyde leads to the production of the carbon chain of oleic and stearic acids, whereas that of palmitic acid is derived from two molecules of hexaldehyde and one molecule of aldol. In the present communication, it is shown that the assumed intermediate products are assimilated by the cell, and that the presence of certain of them can be established by suitable methods.

Endomyces vernalis is grown in a normal culture solution which is replaced as soon as the mycelium is developed by pure solutions of acetaldehyde, pyruvic acid, or aldol, respectively, which are adjusted to P_H 6.8 by potassium hydrogen phosphate. In every case, the appearance of fat within the cells is noticed within twenty-four hours. Similar observations are recorded with maltose. The process of fat formation probably occurs in two phases, in the first of which the sugar is converted by zymase through pyruvic acid into acetaldehyde, probably in accordance with Neuberg's scheme of alcoholic fermentation; the hypothesis receives support from the observation that carbon dioxide is freely evolved, whereas the presence of ethyl alcohol cannot be detected. In the second phase, the synthesising enzymes, probably of the carboligase type, cause the formation of fat from the acetaldehyde.

The formation of acetaldehyde as intermediate product has been demonstrated by the aid of the sulphite process; in experiments in which the acetaldehyde is thus fixed, the production of fat is very small. The yields of acetaldehyde correspond approximately with those obtained by Neuberg in experiments with moulds.

For the estimation of fat, the mould is dried at 100° and cautiously heated in an iron crucible with water and solid potassium hydroxide. The molten mass is cooled, dissolved in water, and acidified

with sulphuric acid. The free fatty acids are extracted with light petroleum, dissolved in alcohol, and titrated with alcoholic potassium hydroxide solution; the results are expressed as triolein. H. W.

The Genesis of Peroxydase in Plants. Conditions determining Fission of Peroxydase from the Protoplasts and Liberation in the Cell-juice. W. PALLADIN and (FRL.) S. MANSKAJA (*Biochem. Z.*, 1923, 135, 142—157).—Using the colour reaction given by peroxydase with guaiacum-resin or guaiacol and hydrogen peroxide, peroxydase is found in the cell-sap, but also found in the protoplasts. During autolysis, the peroxydase is split off from the protoplasts, and especially so in the presence of salts. The results are interpreted in terms of Ehrlich's side-chain theory, the postulated existence of pro-ferments being unnecessary. Peroxydase is also found in the woody fibre of the beech. H. K.

The Constituents of Green Plants. XXIII. Malic Acid in Plants. HARTWIG FRANZEN and ERNST KEYSSNER (*Biochem. Z.*, 1923, 135, 183—216).—A critical review of the whole of the available literature on the occurrence of malic acid in plants leads to the conclusion that, contrary to general opinion, the wide distribution of malic acid is untenable. The proof of the identity of this acid is insufficient in numerous cases. H. K.

Identity of the Sugar Extracted from the Manna of the Carob Tree with Pinitol or Methyl-*d*-inositol. C. CHARAUX (*Bull. Soc. Chim. biol.*, 1922, 4, 597—600).—An exudation found on the trunk of the carob tree (*Ceratonia siliqua*, L.) yielded 84% of pinitol when extracted with alcohol. E. S.

The Prolamine of *Coix lacryma*, L. GISABURO HATTORI and SHIGERU KOMATSU (*J. Biochem. [Japan]*, 1922, 1, 365—369).—Kernels of *Coix lacryma*, L., gave: Water 12.33, ash 7.06, protein nitrogen 2.92, crude protein 18.68, crude starch 50.66, soluble non-nitrogenous matter 4.93, crude fat 4.69, and crude fibre 7.42%. Coicine was prepared by extracting the meal with 80% alcohol at 78° and after further purification formed a yellowish-brown powder containing 0.6% of ash. The distribution of nitrogen in the pure prolamine was determined by the method of Osborne and Harris (*J. Amer. Chem. Soc.*, 1903, 22, 323) as follows: Humin nitrogen 0.1%, ammonia nitrogen 3.32%, basic nitrogen 0.94%, non-basic nitrogen 0.23%, monoamino-nitrogen 5.50%, imino-nitrogen 6.95%, total nitrogen 16.84. Determinations of the amino-acids gave glutamic acid 20.65%, leucine 4.10%, tyrosine 1.46%, arginine 0.20%, histidine 1.88%, and lysine 0.76%. K. K.

The Influence of Hexamethylenetetramine and Formaldehyde on the Internal Morphology and the Chemistry of the Haricot Bean. E. NICOLAS and G. NICOLAS (*Compt. rend.*, 1923, 176, 404—407).—Both hexamethylenetetramine and formaldehyde in small doses are nutrients for the haricot bean. They cause, not only an increase in the weight of the plant (cf. this vol., i, 77) and a great development of leaf surface, but they are used, in addition,

for the differentiation and even lignification of the wood and of the pericycle, as well as for the formation of starch. W. G.

The Changed Content of Urea in the Ripening of the Fruit of *Lycoperdon*. NICOLAUS N. IVANOV (*Biochem. Z.*, 1923, 135, 1—20).—During ripening of *Lycoperdon gemmatum* (Puff-ball) there is a disappearance of carbohydrate (trehalose) and accumulation of nitrogen from 7.1 to 8.7%. The urea content increases during ripening, but disappears from the spores. The urea appears to be in the combined state, as it is not extracted by alcohol in an extractor, but is so by hot water. The urea probably functions as a reserve substance for the synthesis of arginine and purine bases, and for the production of ammonia used in building up tissue. H. K.

Microchemical Researches on Coumarin. ALBERT NAVEZ (*Bull. Acad. roy. Belg.*, 1922, [v], 8, 159—173).—From the fact that tannins can be localised by microchemical methods in *Melilotus albus* and *M. altissimus* in the same regions as the glucoside discovered by Bourquelot and Hérissé (A., 1920, i, 586), it is considered likely that the glucoside (coumarigenin), which is derived from dextrose and coumarin hydrocoumarate, is combined, in the plant, with a second glucoside, melilotannic acid, derived from melilotic acid and tannin. E. E. T.

Quantitative Composition of Coniferous Wood. ASTRID CLEVE VON EULER (*Cellulosechem.*, 1923, 4, 1—11).—The mineral constituents, the protein, and the fat-resin components are regarded as not belonging to the true wood substance, and the analytical results are calculated, with the exclusion of these, in terms of carbohydrates and lignin. To the lignin belongs the so-called "alcohol resin," which is regarded as a lignin derivative soluble in alcohol. This is estimated, after removal of the fat and oleo-resin by extraction for six hours in benzene, by a further extraction with 96% alcohol for twenty-four hours. It is extracted very slowly, and the dried alcoholic extract is not completely soluble in alcohol. In the estimation of the lignin by hydrolysis of the carbohydrates with 72% sulphuric acid, the result is always higher than when 40% hydrochloric acid is used, owing to the combination of sulphuric acid groups with the lignin. A correction of 5.7 units should be deducted from the lignin value found by the sulphuric acid method. By both methods, the acetyl group is eliminated from the lignin as the result of hydrolysis, and this is compensated by adding 2.0 units to the percentage of lignin found. All results are then calculated in terms of the pure wood substance, the "alcohol resin" being added to the insoluble lignin under the designation of lignin soluble in alcohol. The lignin value of the wood is not a specific constant, but varies within limits according to the origin of the sample. Recalculated on the above principle, the analysis published by Klason in 1921 becomes: Cellulose, 54.10; hemicelluloses comprising hexosans, 3.06, and pentosans 12.25; total carbohydrates, 69.40%; lignin, including the acetyl group, 30.60%. J. F. B.

Organic Chemistry.

The Pyridine Extract of Upper Silesian Coal : Preliminary Results. II. F. HOFMANN and P. DAMM (*Brenstoff-Chem.*, 1923, 4, 65—73; *ibid.*, 1922, 3, 73).—In the fraction of the "neutral oil" boiling above 300° at ordinary pressures, paraffins, other saturated hydrocarbons, and unsaturated hydrocarbons were found to be present. The first were for the most part separated by treatment with acetone in which they were much the least soluble. The last two could not be satisfactorily separated by liquid sulphur dioxide, but were so by means of methyl alcohol, in which the unsaturated hydrocarbons alone were soluble. The insoluble saturated hydrocarbons were treated with acetone at 0° and at -18° to separate any paraffins still present. Five hundred kg. of coal gave 42 kg. of pyridine extract containing 82 g. of paraffins, 332 g. of other saturated hydrocarbons, and 769 g. of unsaturated hydrocarbons. All the hydrocarbons were purified by recrystallisation and distillation at low pressures, alone and over sodium in a current of carbon dioxide. The unsaturated hydrocarbons received, in addition, treatment with methyl sulphate in which they were soluble.

There were identified in the paraffinoid portion: the hydrocarbons $C_{21}H_{44}$ to $C_{27}H_{56}$ inclusive. Evidence was obtained that a hydrocarbon separated by Pictet (A., 1916, i, 800) from a benzene extract of a coal, which he identified with Brodie's melene, was probably a mixture of the above paraffins. The other saturated hydrocarbons present appeared to be $C_{17}H_{30}$, $C_{17}H_{28}$, $C_{18}H_{28}$, $C_{19}H_{30}$, $C_{22}H_{36}$, $C_{23}H_{36}$, and $C_{24}H_{40}$, but these formulæ are given with reserve owing to the difficulty of deducing definitely the number of hydrogen atoms present in a molecule of these hydrocarbons from the analytical figures. They are probably partly reduced and partly substituted polynuclear aromatic hydrocarbons.

The unsaturated hydrocarbons were also difficult to place, determinations of the refractive index giving no satisfactory aid. The following appeared to be present: $C_{15}H_{20}$ (a partly reduced and alkyl-substituted naphthalene derivative), $C_{16}H_{20}$, $C_{17}H_{22}$, $C_{18}H_{22}$, $C_{19}H_{24}$ (partly reduced and substituted anthracene and phenanthrene, etc., derivatives), $C_{21}H_{26}$ (a partly reduced and substituted tetranuclear derivative. Methylanthracene, $C_{15}H_{12}$, was definitely isolated among these hydrocarbons. T. S. W.

The Preparation of True Acetylene Hydrocarbons. M. BOURGUEL (*Compt. rend.*, 1923, 176, 751—753).—The difficulties encountered in the preparation of pure acetylenes by the action of potassium or sodium hydroxide on halogen derivatives of saturated hydrocarbons are largely avoided by eliminating the hydrogen halide by means of finely powdered sodamide suspended in benzene or xylene. No isomerisation or polymerisation occurs, and the

true acetylene hydrocarbon is almost the sole product owing to the automatic formation of the sodium derivative, which after removal of the diluent is decomposed by the addition of ice and a mineral acid. The preparation of *n*-pentinene, $\text{C}_2\text{H}_5\cdot\text{CH}_2\cdot\text{C}\equiv\text{CH}$, b. p. $39\cdot6\text{--}40^\circ$, and of γ -phenylpropinene, $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{C}\equiv\text{CH}$, b. p. $69\cdot5\text{--}70^\circ/18\text{ mm.}$, by this method is described, and also of methyl propargyl ether, $\text{CH}_3\cdot\text{O}\cdot\text{CH}_2\cdot\text{C}\equiv\text{CH}$, b. p. 63° , from $\beta\gamma$ -dibromopropyl methyl ether, and ethyl propargyl ether, $\text{C}_2\text{H}_5\cdot\text{O}\cdot\text{CH}_2\cdot\text{C}\equiv\text{CH}$, b. p. $79\cdot5\text{--}80^\circ$, from the corresponding dibromopropyl ethyl ether. Phenylacetylene was obtained in a pure condition, b. p. $140\cdot5\text{--}141^\circ$, from styrene dibromide and sodamide. G. F. M.

Spinacene : its Oxidation and Decomposition. A. CHASTON CHAPMAN (T., 1923, 123, 769—779).

Compounds of Aluminium Bromide with Phosphorus Bromides and Organic Bromides. V. A. PLOTNIKOV (*J. Russ. Phys. Chem. Soc.*, 1916, 48, 1891—1896).—A compound, $\text{AlBr}_3\cdot\text{PBr}_5\cdot\text{EtBr}$, is obtained by the addition with cooling of a solution of phosphorus pentabromide in ethyl bromide to a similar solution of aluminium bromide. This compound is, unlike its constituents, stable above 150° , decomposition occurring at 230° , with evolution of hydrogen bromide and formation of some pentabromoethane. The complex is immediately decomposed by water, in which it is completely soluble, and the entire bromine content may be precipitated by silver nitrate, ethyl alcohol being identifiable in the solution. A similar compound, $\text{AlBr}_3\cdot\text{PBr}_3\cdot\text{EtBr}$, m. p. 160° (decomp.), may be obtained by substituting phosphorus tribromide for the pentabromide in the above reaction, whilst a third compound, $\text{AlBr}_3\cdot\text{PBr}_3\cdot\text{CMeBr}_2$, m. p. 134° , may be obtained by substituting ethylidene dibromide for ethyl bromide. Aluminium bromide and phosphorus pentabromide, if mixed in carbon disulphide solution, form a compound, $\text{AlBr}_3\cdot\text{PBr}_5$, decomposing at 100° . R. T.

The Structure of Complex Compounds. V. A. PLOTNIKOV (*J. Russ. Phys. Chem. Soc.*, 1916, 48, 1896—1905).—The structure of complexes of ethyl bromide with the bromides of aluminium and phosphorus, such as $\text{AlBr}_3\cdot\text{PBr}_5\cdot\text{EtBr}$ (preceding abstract), is discussed. The combination of molecules to form complexes is explained as being due to the action of electrons contained in the various atoms of the molecule, and the molecules combined together to form a complex exert a profound influence on each other. The result of this is to increase the reactivity of these groups, and, if molecules of water enter the complex, hydrolysis of its constituents takes place with abnormal rapidity and completeness. R. T.

The Isomeric Transformations of Halides of Alcohols, and of Sulphovinic Acids leading to the Regrouping of Carbon Atoms. A. E. FAVORSKI (*J. Russ. Phys. Chem. Soc.*, 1918, 50, 43—80).—Various examples of intramolecular rearrangement of organic compounds are studied, in particular those of halogen derivatives of hydrocarbons. From these, it is concluded that a

condition of strain may exist between carbon-carbon linkings, which may, in favourable circumstances, lead to dissociation. Such a tendency is weakest with triple linkings, and strongest with single ones. For saturated compounds, it is most marked in cyclic groupings, and with open-chain compounds between quaternary carbon atoms, *i.e.*, those joined to four others, as in tetramethylmethane or hexaphenylethane. Tertiary carbon atoms joined to other atoms multiply bound, will often undergo rearrangement, leading to the transposition of radicles. The mobility of radicles attached to tertiary carbon atoms depends, not only on the condition of strain of the bonds, but also on the degree of attraction between the radicles themselves.

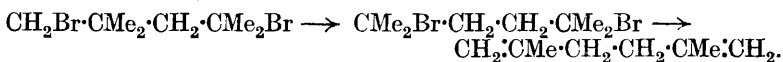
[With NADESHDA SAKARA.]—The acetate of $\beta\beta$ -dimethylbutyl alcohol has b. p. $152-153^\circ$ at 755 mm., and its *phenylurethane*, m. p. $65-66^\circ$. When oxidised, the alcohol yields small quantities of $\alpha\alpha$ -dimethylbutaldehyde, b. p. $102-104^\circ$, and of $\alpha\alpha$ -dimethylbutyric acid, b. p. $186-187^\circ/755$ mm., m. p. -13° . α -Bromo- $\beta\beta$ -dimethylbutane, b. p. $83-85^\circ/145$ mm., d_4^{20} 1.1958, prepared by heating the alcohol in a sealed tube at 100° with hydrogen bromide, undergoes isomeric change, which may occur in the following ways :



In order to decide which of these is produced, γ -bromo- γ -methylpentane, b. p. $82-83^\circ/145$ mm., d_4^{20} 1.2066, $R_G=37.67$, is synthesised by the action of hydrogen bromide on the product of the interaction of magnesium ethyl bromide with ethyl acetate. The other, β -bromo- β -methylpentane, b. p. $77-78^\circ/145$ mm., d_4^{20} 1.1807, $R_G=37.67$, is obtained in a similar way from the product of the interaction between magnesium propyl bromide and acetone. It is hence concluded that the action of hydrogen bromide on the alcohol is to produce the γ -bromo- γ -methylpentane. Alcoholic alkali hydroxide acts on this, to produce a mixture of hexenes as follows : $\text{CH}_2\text{Me}\cdot\text{CMe}\cdot\text{CHMe} \leftarrow \text{CH}_2\text{Me}\cdot\text{CMeBr}\cdot\text{CH}_2\text{Me} \rightarrow \text{CH}_2\text{Me}\cdot\text{C}(\text{CH}_2)\cdot\text{CH}_2\text{Me}$.

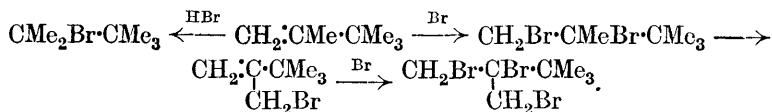
The first of these is the main product, γ -methylenepentane being present only in very small quantity.

[With N. SHIBAEV.]— $\alpha\delta$ -Dibromo- $\beta\beta\delta$ -trimethylpentane, under the influence of diethylamine, is transformed into diisobutenyl in the following way :



[With EUGÉNIE OPEL.]— $\beta\gamma\gamma$ -Trimethyl- Δ^a -butene, b. p. $75-80^\circ$, is prepared from β -hydroxy- $\beta\gamma\gamma$ -trimethylbutane by distillation with 50% sulphuric acid. When oxidised, it yields $\beta\gamma\gamma$ -trimethylbutane- $\alpha\beta$ -diol, m. p. $91-92^\circ$, which on further oxidation yields α -hydroxy- $\alpha\beta\beta$ -trimethylbutyric acid, m. p. $104-106^\circ$, and finally $\beta\beta$ -dimethylpropionic acid and formic acid. The hydrocarbon, on bromination in ethereal solution, gives a dibromide, $\text{C}_7\text{H}_{14}\text{Br}_2$, m. p. $38-39^\circ$, from which it is regenerated on distillation from zinc dust. Bromination in acetic acid solution gives the bromide

of β -bromo- $\beta\gamma$ -trimethylbutane, m. p. 150—151°, which on hydrolysis yields the same alcohol, so that bromination does not appear to cause any structural change. Bromination in ethereal solution also produces small quantities of a tribromide, $C_7H_{13}Br_3$, m. p. 50·5—52°, and of saturated and unsaturated monobromides. The formation of these is explained by the following scheme :



The dibromide, when heated for eight hours at 160° in a sealed tube with sodium ethoxide, gives a mixture of a hydrocarbon and a mixture of ethers, b. p. 145—148°. The hydrocarbon on oxidation gives a mixture of $\alpha\alpha$ -dimethylpropionic, formic, and $\beta\beta$ -dimethylbutyric acids, which points to it being $\delta\delta$ -dimethyl- $\Delta^{\alpha\beta}$ -pentadiene, b. p. 80—83°. This, when heated in a sealed tube at 100° with sodium, is converted into sodio- $\delta\delta$ -dimethyl- Δ^{α} -pentinene, which can be converted by the action of carbon dioxide into the sodium salt of $\delta\delta$ -dimethyl- Δ^{α} -pentinene- α -carboxylic acid. The free acid has m. p. 48—49·5°. The ether, b. p. 145—148°, is a mixture of two isomeric ethers, $CMe_3 \cdot CMe \cdot CH \cdot OEt$ and $CMe_3 \cdot C(CH_2) \cdot CH_2 \cdot OEt$, whilst the hydrocarbon is formed by an intramolecular rearrangement: $CH_2 \cdot C(CH_2Br) \cdot CMe_3 \rightarrow CH_2 \cdot CBr \cdot CH_2 \cdot CMe_3 \rightarrow CH_2 \cdot C \cdot CH \cdot CMe_3$.

[With SERGEI KAROLEV.]— $\beta\beta$ -Diphenylpropane- α -ol, b. p. 186—187°/15 mm., d_4^{20} 1·0968, is prepared by the reduction of $\alpha\alpha$ -diphenylpropaldehyde; the urethane has m. p. 148—149°, and the acetate, b. p. 182—183°/14 mm. Dehydration with potassium sulphate caused intramolecular rearrangement, with the production of $\alpha\beta$ -diphenylpropylene, $CH_3 \cdot CPh_2 \cdot CH_2 \cdot OH \rightarrow CH_3Ph \cdot C \cdot CHPh$.

R. T.

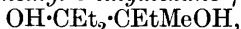
Catalytic Dehydration of Alcohols by Dilute Sulphuric Acid.

J. B. SENDERENS (*Compt. rend.*, 1923, 176, 813—816).—The dehydration of alcohols by sulphuric acid does not consist in a simple absorption of water, but is a catalytic action, and the large proportion or high concentration of acid required for the dehydration of certain alcohols is only for the purpose of raising the temperature to an extent sufficient for the catalytic reaction to proceed, and, as would be expected from this reasoning, the same results are obtained with either concentrated or diluted sulphuric acid, provided the proportions of acid and alcohol employed are such as to produce a reaction mixture of the same boiling point in each case. With propyl alcohol, for example, a mixture of 100 c.c. of alcohol and 75 c.c. of concentrated sulphuric acid boils at about 140°, and gives propylene almost exclusively, whilst 40 c.c. of acid gives a mixture boiling at 125°, and a yield of 30% of propyl ether is obtained with the propylene. Propyl alcohol with 200% of the dihydrate, $H_2SO_4 \cdot 2H_2O$, also gives a mixture boiling at about 135°, with propylene as the chief product, and with 60% of

the dihydrate the b. p. is 125° , and 38% of propyl ether is produced. A reaction mixture boiling at 125° is also obtained with the hydrate, $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$, mixed with a third of its volume of propyl alcohol, and the product consists of 40% of propyl ether, and a correspondingly diminished amount of propylene. Precisely analogous results were obtained with ethyl, *isopropyl* butyl, *isobutyl*, and *isoamyl* alcohols, the proportions of acid required to produce a certain result diminishing as the molecular weights and boiling points of the alcohols increase. Thus only a tenth of the quantity of $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ is required for the same volume of *isoamyl* alcohol as of propyl alcohol in order to produce the corresponding ether. G. F. M.

Preparation of Absolute Alcohol with Calcium Chloride and Lime. WILLIAM A. NOYES (*J. Amer. Chem. Soc.*, 1923, 45, 857—862).—An apparatus is described by means of which alcohol of 99.0—99.5% concentration may be prepared rapidly by the use of calcium chloride. An apparatus is also described for preparing absolute alcohol with lime. When absolute alcohol is distilled from an excess of lime, a little calcium is carried over, probably as calcium ethoxide. Metallic sodium is not suitable for the preparation of absolute alcohol, because (1) sodium ethoxide, alcohol, water, and sodium hydroxide form an equilibrium such that some water will always pass over with the alcohol, (2) sodium ethoxide is very sensitive to oxidation on exposure to the air. On distilling a concentrated alcoholic solution containing equimolecular proportions of water and calcium chloride, alcohol of 99.5% concentration, or stronger, passes over; on concentration of such a solution, a solid alcoholate, not a hydrate, separates when the boiling point reaches 95 — 100° , and there is an equilibrium between the alcoholate and the hydrate present. W. S. N.

The Preparation of Various Pinacones by the Action of Grignard Reagents on α -Hydroxymethyl Ketones. R. LOCQUIN and SUNG WOUSENG (*Compt. rend.*, 1923, 176, 682—684).—Pinacones of the general type, $\text{OH} \cdot \text{CRR}' \cdot \text{CR}'' \cdot \text{Me} \cdot \text{OH}$, where R, R', and R'' are alkyl groups, are obtained by the action of magnesium alkyl iodides on α -hydroxyl methyl ketones of the general formula $\text{OH} \cdot \text{CRR}' \cdot \text{CO} \cdot \text{CH}_3$, the preparation of which has been previously described (this vol., i, 302). Thus the interaction of 3 mols. of magnesium ethyl iodide on methyl α -hydroxy- α -ethyl-propyl ketone gave γ -methyl- δ -ethylhexane- $\gamma\delta$ -diol,



b. p. 103 — $104^{\circ}/11$ mm. From methyl α -hydroxy- α -propylbutyl ketone and magnesium methyl iodide β -methyl- γ -propylhexane- $\beta\gamma$ -diol, $\text{OH} \cdot \text{CPr}_2 \cdot \text{CMe}_2 \cdot \text{OH}$, b. p. 110 — $112^{\circ}/12$ mm., was obtained, whilst the same hydroxy-ketone and magnesium propyl iodide gave δ -methyl- ϵ -propyloctane- $\delta\epsilon$ -diol, b. p. 137 — $140^{\circ}/19$ mm. Magnesium methyl iodide and methyl α -hydroxyl- α -*tert*-butylethyl ketone gave $\beta\beta\gamma\delta$ -tetramethylpentane- $\gamma\delta$ -diol, $\text{CMe}_3 \cdot \text{CMe}(\text{OH}) \cdot \text{CMe}_2 \cdot \text{OH}$, b. p. 99 — $100^{\circ}/13$ mm. All these pinacones are viscous liquids or low-melting solids. They have no characteristic odour, and do

not furnish crystalline hydrates with water. On dehydration by heating with dilute mineral acids, they are converted into pinacolines.

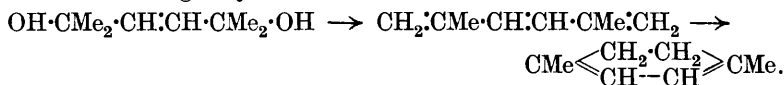
G. F. M.

Addition of Hydrogen to Acetylene Derivatives. VIII.

I. S. ZALKIND (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1830—1848).—When $\beta\epsilon$ -dimethylhexene- $\beta\epsilon$ -diol is reduced with hydrogen by the Sabatier process, using a palladium catalyst, two stereoisomeric ethylenic reduction products may be obtained, namely, the *cis*- and *trans*-isomerides of $\beta\epsilon$ -dimethyl- Δ^7 -hexene- $\beta\epsilon$ -diol,



One isomeride, the α -form, melts at $76\cdot5$ — 77° , whilst the β -isomeride has m. p. 69 — $69\cdot5^\circ$. The dehydration of these substances by sulphuric acid leads to the production of 2:3-dihydro-*p*-xylene in the following way:



The two isomerides are not interconvertible under the conditions of the catalytic reduction, but are formed side by side, the quantity of each isomeride in the reaction product being determined by the velocity with which the reduction is conducted. Thus if a large quantity of catalyst is used, the reduction proceeds rapidly to completion, giving as the main product the α -isomeride, whilst a slow reduction produces principally the β -form. Both isomerides are converted by heat or by mild dehydrating agents into the γ -lactone, the α -form suffering dehydration more readily. With phosphorus tribromide, they give an oily, unsaturated monobromide, $\text{C}_8\text{H}_{13}\text{Br}$. Bromination of the isomerides gives for each an oil and a crystalline compound, m. p. $98\cdot5$ — $99\cdot5^\circ$, both having the formula $\text{C}_8\text{H}_{16}\text{O}_2\text{Br}_2$. From the α -isomeride, the main product is the oil, which is obtained as a by-product from the bromination of the second form. It is probable that some conversion of the stereoisomerides is effected in each case by the hydrogen bromide liberated during bromination.

R. T.

Existence of Alkyl Chlorites. GIORGIO RENATO LEVI (*Gazzetta*, 1923, **53**, i, 40—42).—Attempts to prepare alkyl chlorites from either silver chlorite and ethyl halide or barium chlorite and methyl sulphate have proved unsuccessful, an explosive reaction usually taking place (cf. A., 1922, i, 527; ii, 567).

T. H. P.

Phosphorous Acid Esters. The Influence of the Character of the Groups R' , R'' , R''' on the Stability of the Molecular Complexes $\text{R}'\text{R}''\text{R}'''\text{C}\cdot\text{O}\cdot\text{PCL}_2$ and $\text{R}'\text{R}''\text{R}'''\text{C}\cdot\text{O}\cdot\text{P}(\text{OH})_2$. I. DAVID RUNCIMAN BOYD and GUY CHIGNELL (*T.*, 1923, **123**, 813—817).

The Action of Organomagnesium Salts on Sulphuryl Chloride; Preparation of Aliphatic Sulphonyl Chlorides and Bromides. E. CHERBULIEZ and O. SCHNAUDER (*Helv. Chim. Acta*, 1923, **6**, 249—257).—By the action of aromatic or aliphatic

organomagnesium compounds on sulphuryl chloride, sulphonyl chlorides or bromides can be obtained, provided that the solution of the Grignard compound is added to the sulphuryl chloride, the latter being present in excess throughout the reaction. In the aromatic series, the yields are poor, but in the aliphatic series they are from 25% to 35% of theory. The yields are lower at very low temperatures, -20° to -40° , at which the product is chiefly halogenated hydrocarbon, than at higher temperatures; the best yields of aliphatic sulphonyl compounds are obtained at $+10^{\circ}$. Magnesium benzyl chloride behaves as an aliphatic compound. The magnesium alkyl chlorides and iodides with sulphuryl chloride both give sulphonyl chlorides, but the magnesium alkyl bromides give sulphonyl bromides, which are new. *Methanesulphonyl bromide*, obtained in 21% yield from methyl bromide, is a colourless liquid with a pungent odour, b. p. $72-73^{\circ}/15$ mm., or 173° (decomp.) at the ordinary pressure. *Ethanesulphonyl bromide* (35% yield), from ethyl bromide, a colourless liquid with a pungent odour, has b. p. 80° at 13 mm., or 170° with rapid decomposition at the ordinary pressure.

The course of this reaction can be best explained by Meisenheimer and Casper's theory of the constitution of organomagnesium compounds (A., 1921, i, 654), in which it is assumed that they are co-ordination compounds. Assuming the co-ordination number

of magnesium to be 6, the intermediate compound $\text{Hal}-\text{Mg}\begin{matrix} \nearrow \text{R} \\ \searrow \text{SO}_2 \\ \nearrow \text{Cl} \end{matrix}$

may be formed. In favour of the formation of such an intermediate compound is the observation that, at low temperatures, when an iodide is used, the precipitation of the salt MgClI takes place very slowly. Such an intermediate compound would explain the formation of $\text{R}\cdot\text{SO}_2\text{Cl}$ or $\text{R}\cdot\text{SO}_2\text{Hal}$, according to the nature of the halogen. When this is bromine, in the aliphatic series $\text{R}\cdot\text{SO}_2\text{Br}$ is formed exclusively, but in the aromatic series a mixture of $\text{R}\cdot\text{SO}_2\text{Br}$ and $\text{R}\cdot\text{SO}_2\text{Cl}$ is obtained. At very low temperatures, a mixture of $\text{R}\cdot\text{Br}$ and $\text{R}\cdot\text{Cl}$ is formed. The formation of sulphinic acid and sulphone by the action of an organomagnesium compound on a sulphonyl chloride can be explained by the same hypothesis.

In the course of the reaction between organomagnesium bromides or iodides and sulphuryl chloride, free bromine or iodine is always formed, the proportion increasing at higher temperatures.

E. H. R.

Hydration of Acetic and Hydrochloric Acids and the Factors Determining the Activity of the Hydrogen-ion. W. C. McC. LEWIS, DORIS E. MERRIMAN, and T. MORAN (*J. Amer. Chem. Soc.*, 1923, 45, 702—712).—The activity of the hydrogen-ion (produced from acetic acid) in the presence of various amounts of sucrose has been experimentally determined at 30° . In the case of acetic acid, the activity of the hydrogen-ion can be completely accounted for by assuming acetic acid to be hydrated to the extent of three molecules of water for each molecule of acid,

and then identifying activity with the concentration of the hydrogen-ion per unit of free water space in the sucrose solution. The change in the activity of the hydrogen-ion (produced from hydrochloric acid) in the presence of sucrose cannot be accounted for by a space correction alone. In this case, the heat of dilution of the ion must be considered, and it is shown that by combining the two above factors it is possible to account for 80–90% of the observed activity; no definite conclusion is drawn as to the causes of the excess activity observed. It is pointed out, however, that the excess might be attributed to an increased ionisation of the acid, a modification of a suggestion originally made by Scatchard (A., 1922, i, 230). The average degree of hydration of hydrogen chloride in solution between 0.1*N* and 1.2*N* has been calculated by an examination of the kinetics of the inversion of sucrose by this acid, employing the data of Fales and Morrell (A., 1922, ii, 832). It is shown to be approximately 7. J. F. S.

Electrolysis of Acetic Acid with Commutated Direct Current. EMIL BAUR (*Z. Elektrochem.*, 1923, 29, 105–110).—Solutions of acetic acid of various concentrations and also solutions of potassium acetate in acetic acid have been electrolysed between bright platinum electrodes by means of commutated direct current. The products of electrolysis consist of carbon dioxide and hydrocarbons, the latter consisting of approximately equal volumes of ethane and methane. The results are discussed in connexion with the author's hypothesis of the optically sensitised photolysis.

J. F. S.

Separation of Methyl Oleate and Linoleate by Fractional Distillation. ÉMILE ANDRÉ (*Compt. rend.*, 1923, 176, 686–689).—The separation by fractional distillation under pressures of 1–3 mm. of mixtures of methyl oleate and linoleate was attempted, but the polymerisation which occurred during the long series of repeated distillations that was necessary proved a serious obstacle against the isolation of the higher boiling methyl linoleate in a pure condition. The highest iodine value obtained was 160, as compared with 172.7 for the pure ester. A certain quantity of fairly pure methyl oleate was, however, obtained having an iodine value of 92–95, by uniting the fractions with the lowest iodine values and redistilling. It is suggested that the addition of a small quantity of a phenolic substance (antioxygen) to the esters might facilitate the separation.

G. F. M.

The Course of the Reaction in the Acetoacetic Ester Synthesis. K. H. MEYER (*Z. angew. Chem.*, 1923, 36, 169).—Scheibler's view (*ibid.*, 6; cf. also this vol., i, 82) that, in the above synthesis, ethyl sodioacetate is first formed and reacts with a second molecule of ethyl acetate to give a salt-like condensation product, which is then decomposed by acids into alcohol and ethyl acetoacetate, was put forward by the author ten years ago (*Annalen*, 1913, 398, 49). Whilst in the latter case the explanation was based on analogy with ethyl sodiomalonate, Scheibler's work appears to afford experimental proof of it.

W. T. K. B.

Action of the Grignard Reagent on Keto-acids. PHILIP K. PORTER (*J. Amer. Chem. Soc.*, 1923, **45**, 1086—1087).—Lævulic acid reacts in ethereal solution with magnesium methyl iodide to give isohexolactone, and with magnesium ethyl bromide to give the lactone of γ -hydroxy- γ -methylhexoic acid, the yields being 31.5% and 35.1%, respectively. The yields of these compounds previously obtained, starting from ethyl lævulate, are 30—35% (Noyes and Marvel, A., 1917, i, 455) and 35% (Grignard and Moissan, A., 1903, i, 31), respectively. W. S. N.

The Hydroxy-acids Contained in an Oil from Grape Stones. ÉMILE ANDRÉ (*Compt. rend.*, 1923, **176**, 843—845).—The hydroxy-acids, the presence of which in oil of grape stones has previously been established (*ibid.*, 1921, **172**, 1296), were isolated from the other fatty acids which accompanied them by taking advantage of the partial insolubility of the hydroxy-acids in light petroleum when a relatively high proportion is present in the fatty acid mixture, and, secondly, of the greater solubility of the lithium salts of the hydroxy-acids, which results in their accumulating in the mother-liquors from the crystallisation of the lithium soap. By repeated alternate application of these two principles, 15—16% of the original material was separated as a viscous liquid, having saponification value 222, iodine value 69.2, and average molecular weight 252.2. It is concluded that the acetyl value of the oil of grape stones cannot therefore be attributed to ricinoleic acid, but rather to hydroxy-acids of lower molecular weight containing C_{14} to C_{16} . There would appear to be at least two such hydroxy-acids, one saturated, and the other having an ethylenic linking.

G. F. M.

Synthesis of an Acid of the Digitoxonic Acid Group. GÉZA ZEMPLÉN (*Ber.*, 1923, **56**, [B], 686—689).—An acid which closely resembles natural digitoxonic acid in structure and properties has been obtained by the condensation of crotonaldehyde with ethyl bromoacetate and oxidation of the product with perbenzoic acid.

Ethyl β -hydroxy- Δ^{γ} -hexenoate, $CHMe:CH:CH(OH)\cdot CH_2\cdot CO_2Et$, b. p. $86^{\circ}/0.5$ mm., is prepared by the addition of activated zinc to a well-cooled mixture of crotonaldehyde and ethyl bromoacetate. The success of the operation (which is fully described in the original) appears to be greatly dependent on details; replacement of zinc by magnesium leads to less satisfactory results. The ester is oxidised by perbenzoic acid in chloroform solution, and the product converted by barium hydroxide into *barium $\beta\gamma\delta$ -trihydroxy-n-hexoate*, which could not be caused to crystallise. The corresponding free acid does not exhibit any tendency towards crystallisation; it yields a *hydrazide*, $C_{12}H_{18}O_4N_2$, coarse, colourless crystals, m. p. 159° . H. W.

Preparation of Oxalic Acid from Acetylene. M. LUCRETIA KEARNS, L. HEISER, and J. A. NIEUWLAND (*J. Amer. Chem. Soc.*, 1923, **45**, 795—799).—Oxalic acid can be prepared by passing
r*

acetylene into dilute nitric acid (75% by volume), with mercuric nitrate as catalyst. An acetylene-mercury compound is first formed, which gives acetaldehyde with part of the nitric acid; the aldehyde is then oxidised to oxalic acid by the nitric acid. Oxalic acid is also formed by the action of (1) nitrogen oxides on acetylene, (2) nitrogen oxides on acetaldehyde, (3) acetaldehyde vapour on nitric acid.

Acetaldehyde can be obtained by passing (1) acetylene over dry mercuric nitrate, (2) nitrogen oxides over metallic mercury, and then passing acetylene over the resulting salt. The mercury salts may be regenerated, after reduction, by means of nitrogen oxides.

W. S. N.

The Decomposition of the Peroxides of Succinic, Fumaric, and Benzoic Acids by Heat and their Relation to the Behaviour of the Corresponding Salts on Electrolysis. FR. FICHTER and ALBERT FRITSCH (*Helv. Chim. Acta*, 1923, 6, 329—336).—In a previous paper (A., 1918, i, 369), it was suggested that in the Kolbe hydrocarbon synthesis by the electrolysis of salts of organic acids, unstable peroxides are formed intermediately and are decomposed by the relatively high temperature of the anode, forming the hydrocarbon. Confirmation of the theory is obtained from a study of the decomposition of peroxides of succinic, fumaric, and benzoic acids. Succinyl peroxide (purity about 86%) decomposes explosively when heated in a bomb, forming a mixture of gases containing 55.2% of carbon dioxide and 21.1% of ethylene, the volume ratio being 2.6:1 instead of the theoretical 2:1. Gentler decomposition by heating in boiling xylene gave a ratio 2.25:1. Electrolysis of succinates gave a very similar ratio, 2.4:1. Fumaroyl peroxide could only be obtained in a very impure form by the action of sodium peroxide on fumaroyl chloride in ice-water. When decomposed in the bomb it gave 67.6% of the expected yield of carbon dioxide and 10.6% of acetylene. Electrolysis of sodium fumarate gave 19.9% of the theoretical yield of acetylene. Benzoyl peroxide decomposed explosively when heated in a bomb at 180—200°, giving 80.2% of the theoretical yield of carbon dioxide and 39.1% of diphenyl. By the electrolysis of benzoates, no diphenyl is produced, because the oxidation potential needed for peroxide formation is higher than the nucleus can carry without itself being oxidised (cf. Fichter and Krummenacher, *loc. cit.*).

E. H. R.

Ketens. XLVI. Attempts to Prepare Diketens. H. STAUDINGER and W. KREIS (*Helv. Chim. Acta*, 1923, 6, 321—326).—It was hoped to prepare the diketen $\text{OC}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}$ from ethanetetracarboxylic dianhydride. This anhydride can be obtained by treating ethanetetracarboxylic acid with an ethereal solution of oxalyl chloride, or by the action of oxalyl chloride on the silver salt, as well as by the method of Philippi and Hanusch (A., 1920, i, 594). When heated under reduced pressure, the anhydride gives no trace of keten; with aniline, it gives a dianilide which, when heated, decomposes into carbon dioxide and succin-

anilide. When ethylenetetracarboxylic acid is boiled for several days, a new acid is formed, which appears to be *ethylenetricarboxylic acid*, m. p. 180—184°.

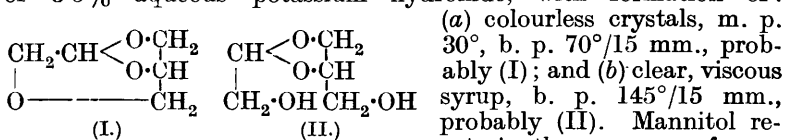
With oxalyl chloride, the tetracarboxylic acid or its silver salt decomposes, forming a brown, amorphous compound, which appears to be a polymerised form of a new *carbon suboxide*, CO:C:C:CO. A similar brown, amorphous substance is formed, together with diphenylacetic anhydride, by the action of diphenylketen on ethylenetetracarboxylic acid. *Dimethyldicarboxyglutaric dianhydride*

(annexed formula) was obtained by the action of diphenylketen in ethereal solution on dimethyldicarboxyglutaric acid. It forms colourless crystals, m. p. 126—127°. When heated, the anhydride decomposes without formation of any trace of a diketene.

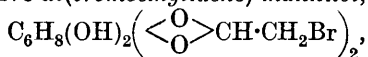
E. H. R.

Cellulose Chemistry. III. Bromoparacetaldehyde and Monobromoacetaldehyde. Preparation, Properties, and Utilisation for the Synthesis of Bromo- and Hydroxy-cyclic Acetals related to Polysaccharides. HAROLD HIBBERT and HAROLD SANFORD HILL (*J. Amer. Chem. Soc.*, 1923, 45, 734—751).—Bromoparacetaldehyde (cf. Helferich and Speidel, A., 1922, i, 6), which is prepared by the addition of bromine to cold paracetaldehyde in the presence of sunlight, breaks down on slow distillation into bromoacetaldehyde (*semicarbazone*, long, flat needles, m. p. 128°, decomp.), the polymerisation of which to the trimolecular compound occurs spontaneously, more rapidly in the presence of concentrated acids. The bromo-aldehyde has been used to prepare cyclic acetals, the essential structure of which is present in maltose, cellobiose, lævoglucozan, diamylose, and the cellulose unit.

The cold, crude product of bromination of paracetaldehyde reacts with α -bromohydrin, with formation of *bromoethylidene bromohydrin*, a heavy oil, b. p. 118—120°/10 mm., yield 56%, and with ethylene glycol with formation of *bromoethylidene glycol*, a heavy oil, b. p. 63—65°/12 mm.; the latter is also obtained in 42% yield when ethylene glycol is heated at 100° with a little sulphuric acid and the "crude syrup," obtained by extracting the crude bromination mixture by means of ether. Under similar conditions, trimethylene glycol reacts with the "crude syrup," yielding *bromoethylidene trimethylene ether*, b. p. 80—86°/12 mm. Similarly, glycerol, "crude syrup," and sulphuric acid give *bromoethylidene glycerol*, b. p. 137—140°/15 mm., alternative formulæ for which are suggested; this compound is decomposed by means of 3.5% aqueous potassium hydroxide, with formation of:



acetaldehyde to give *di(bromoethylidene)-mannitol*,



slender, white needles, m. p. 137—141°, but this is not produced from either the extracted syrup or the crude bromination mixture. It is shown that acetaldehyde and α -bromohydrin react in the presence of a trace of iodine to give *ethylidene bromohydrin*, a colourless oil, b. p. 168—169°.

W. S. N.

The Preparation of Mesityl Oxide. RENÉ LOCQUIN (*Ann. Chim.*, 1923, [ix], 19, 32—44).—A general survey of various methods shows that they may be grouped in two series, (a) those in which condensation and dehydration of two molecules of acetone are effected simultaneously, (b) those in which diacetone alcohol [*isohexane- β -one- δ -ol*] is obtained as an intermediate. The author considers that a simple standard method is required, and gives details of one based on condensation under the influence of sodium hydroxide solution and subsequent dehydration by means of oxalic acid. Only 20% of the acetone reacts, and from this portion a 75% yield is obtained; the remainder may be recovered unchanged.

H. J. E.

Some Constitutional Problems of Carbohydrate Chemistry.

JAMES COLQUHOUN IRVINE (T., 1923, 123, 898—921).—A lecture delivered before the Chemical Society on February 22nd, 1923.

The Influence of some Normal Salts on the Mutarotation and Specific Rotation of Dextrose. HANS MURSCHHAUSER (*Biochem. Z.*, 1923, 136, 66—70).—The velocity constants of the mutarotation of dextrose have been determined in the presence of a number of simple inorganic salts of the alkali and alkaline-earth metals and a few acetates in *N*-, 2*N*-, and 4*N*-concentrations of the salts. Of those examined, potassium chloride and bromide, like sodium chloride, retard the mutarotation, but hydrolysed salts of acetic acid accelerate it. The final value of the rotation of dextrose is influenced by the presence of salts, and twenty values are recorded ranging between $[\alpha]_D +47.4$ and 61.2, the former for 4*N*-potassium iodide and the latter for 4*N*-calcium chloride.

H. K.

Physico-chemical Studies on Biological Reactions. III.

Mutarotation of Sugars. PAUL HIRSCH and ANNA ELISABETH KOSSUTH (*Fermentforsch.*, 1922, 6, 302—339).—The use of Löwe's interferometer to follow the course of the mutarotation of dextrose and lactose shows that the refractive indices of solutions of these sugars prepared from the α -modifications undergo slight increase in the refractive index, whilst those of solutions of the β -modifications show slight decrease, during the period of mutarotation (cf. Schmoeger, A., 1892, 948; Stolle, A., 1901, i, 368, 507; Trey, A., 1904, i, 292; Rabe, A., 1911, i, 14). These results throw doubt on Hudson's theory, that mutarotation of the sugars is due to hydration or dehydration.

Gradual increase in refractive index occurs also during the conversion of succinic anhydride into the acid, and during the

resolution of trimeric formaldehyde into simple molecules in aqueous solution; the results obtained in the latter case support Auerbach and Barschall's view that this resolution is accompanied by hydration (A., 1905, i, 859; 1908, i, 131). T. H. P.

Fluoroacetyl Derivatives of Sugars. I. D. H. BRAUNS (*J. Amer. Chem. Soc.*, 1923, 45, 833—835).—*Fluorotetra-acetylglucose*, m. p. 108°, *fluorohepta-acetylcellulose*, m. p. 187°, and *fluorotriacetylxylose*, m. p. 87°, are prepared by the action of liquid hydrogen fluoride on the relevant acetyl sugar. The latter is placed in the receiver attached to a retort in which potassium hydrogen fluoride is heated. The operation takes thirty minutes. The methods of analysis are given. W. S. N.

Dextrose and Sucrose Monosulphates. V. T. SODA (*Biochem. Z.*, 1923, 135, 621—628; cf. A., 1922, i, 986).—By the action of chlorosulphonic acid in chloroform at -10° on dextrose (18% excess) in dry pyridine, dextrose monosulphate is formed, and can be isolated without the intervention of the acetyl derivative. The solvents are removed, and the aqueous solution of the syrup suitably treated with lead oxide, barium carbonate, and silver sulphate to remove chlorides and sulphates. The crude barium salt is precipitated by alcohol. The pure brucine salt, crystallised from acetone, has m. p. 183° and $[\alpha]_D^{20} -5.6$ (final value). The barium salt crystallises with $2C_2H_6O$; the anhydrous salt has $[\alpha]_D^{17} +32^{\circ}$. In a similar manner, sucrose gives *barium sucrose monosulphate dialcoholate*. The alcohol-free salt has $[\alpha]_D^{23} +37.6^{\circ}$. H. K.

Mannose from White Spruce Cellulose. E. C. SHERRARD and G. W. BLANCO (*J. Amer. Chem. Soc.*, 1923, 45, [4], 1008—1013).—Extraction of spruce wood flour by means of 2.8% sodium hydroxide solution gives no mannose, but the latter is formed when the alkali-extracted wood is hydrolysed by means of 5% hydrochloric acid. Moreover, an equal or even greater amount of dextrose is simultaneously produced, the total sugars formed being approximately equivalent to the cellulose removed. By the solution of cellulose in zinc chloride-hydrochloric acid solution or in Schweizer's reagent and reprecipitation, different amounts of mannose are removed. It is concluded that the mannose is not present as a mannan, and that either (1) if the mannose is not in true combination with the cellulose neither is part of the dextrose, or (2) both mannose and dextrose are loosely attached to the cellulose nucleus and hydrolyse with equal readiness. The latter alternative is probable, since mannose is found to be distributed in the α -, β -, and γ -portions of the cellulose. W. S. N.

Attempts to Prepare Isomeric Osazones. Dimorphism of Two Hydrazones of Galactose. OLOF SVANBERG (*Arkiv Kem. Min. Geol.*, 1922, 8, No. 25, 1—19).—Attempts to obtain a third (γ) form of glucosazone and of glucosephenylmethylhydrazone were unsuccessful. Glucosephenylmethylhydrazone is converted by phenylhydrazine into glucosazone. All the specimens of glucosazone obtained, from whatever source, melted at about 204—206°

(decomp.), and had initial $[\alpha]_D -104 \pm 2^\circ$ in pyridine solution, showing weak mutarotation. Glucose- α -phenylhydrazone melts at about 148° , and has initial $[\alpha]_D -87^\circ$ and final $[\alpha]_D -53^\circ$ in aqueous pyridine. Its mutarotation was studied between p_H 4.9 and 13.8, and was found to be accelerated both by alkalis and by acids. The m. p. of glucose- β -phenylhydrazone was found to be $115-116^\circ$, a lower value than that given by Behrend (A., 1907, i, 481). The mutarotation of this substance is accelerated by acids and retarded by alkalis. In weak acid, the negative rotation increases very rapidly at first, then passing through the equilibrium values given by the α -compound; the equilibrium solution probably contains the γ -form in addition.

Galactosephenylmethylhydrazone is converted by phenylhydrazine in pyridine-acetic acid solution into galactose-phenylhydrazone, the latter, in dilute acetic acid solution, being rapidly converted by phenylmethylhydrazine into the phenylmethylhydrazone. Galactosazone has initial $[\alpha]_D +121 \pm 2^\circ$ in pyridine solution. Galactose-phenylhydrazone and -phenylmethylhydrazone (cf. Votoček, A., 1921, i, 544) both exhibit dimorphism, which (at any rate, in the former case) cannot be correlated with constitutional differences. The phenylhydrazone crystallises from hot solutions in leaflets, from cooler ones in needles, which change into leaflets on keeping.

E. E. T.

The Hydrolysis of Maltose by Extract of Malt. L. MAQUENNE (*Compt. rend.*, 1923, 176, 804—806).—The reducing power of a preparation of malt extract to which maltose has been added increases in comparison with that of the malt alone up to a certain limit, which varies with the temperature. The maximum increase is attained at about 50° , whilst at 60° the increase is very small. These facts can be explained most naturally by the assumption that malt extract contains maltase in addition to amylase, and that the maltose is, by its action, partly hydrolysed to glucose. This observation will obviously throw doubt on the conclusions drawn from results obtained on the hydrolysis of starch by malt extract and based on the assumption that maltose was the sole product of hydrolysis (Maquenne and Roux, A., 1906, i, 327, 547; ii, 623).

G. F. M.

Carbohydrates. III. The Action of Phosphorus Pentachloride on Octa-acetylmaltose. PERCY BRIGL and PAUL MISTELE (*Z. physiol. Chem.*, 1923, 126, 120—129).—Octa-acetylmaltose reacts with phosphorus pentachloride at $104-105^\circ$ to form α -chloro- β (?)-trichloroacetylhexa-acetylmaltose, m. p. $132-133^\circ$, $[\alpha]_D^{15} +80.0^\circ$, which forms white needles, soluble in benzene, chloroform, ethyl acetate, acetone, or hot alcohol. On hydrolysis with methyl-alcoholic ammonia, maltose is obtained, isolated as maltazone, decomp. 206° . This shows that the maltose grouping is still intact.

W. O. K.

Starch. F. W. TIEBACKX (*Pharm. Weekblad*, 1923, 60, 338—339).—The phosphorus stated to be always present in starch is

probably contained in an ester group which is removed by gradual hydrolysis on keeping or warming; this explains the increase in conductivity and decrease in viscosity. S. I. L.

Hydrolysis of Starch by the System : Neutral Salts + Amino-acids + Peptone. HUGO HAEHN (*Biochem. Z.*, 1923, 135, 587—602).—A 1% solution of soluble starch was treated with various quantities of a mixture of *N*/10-solutions of sodium, potassium, and calcium chlorides, with the addition of alanine and leucine and albumose or Witte's peptone. After incubation for a day at 37°, the solutions were tested with iodine solution. In many cases, a disappearance of the blue starch iodide colour was observed and particularly with the mixture of salts, amino-acids, and peptone. The liquid reduced Fehling's solution. The author considers the experiments prove the chemical hydrolysis of starch without the intervention of living matter. H. K.

Solvents of some Cellulose Esters. ERNEST WALTER JOHN MARDLES (*J. Soc. Chem. Ind.*, 1923, 42, 127—136T).—The relative solvent power of single and mixed liquids for some cellulose acetates, nitrates, nitroacetates, and chloroacetates was determined by investigating the temperature at which precipitation occurred on cooling, or where this method failed by finding the amount of a non-solvent required to initiate precipitation. The solubility depends on the specific character of both the liquid and the cellulose ester; it has a high temperature coefficient, and many non-solvents may become solvents when suitably mixed with other solvents, and *vice versa*. In general the solvent power and degree of dispersion of the cellulose esters are highest under conditions which admit of the greatest molecular attraction between the dispersed phase and the dispersing medium. G. F. M.

Hydrolysis of Pectin. FRANK TUTIN (*Biochem. J.*, 1923, 17, 83).—Theoretical. The author replies to various criticisms of his suggestion that pectin probably is the dimethylisopropenyl ester of pectic acid. S. S. Z.

Lignin. WALTHER SCHRAUTH (*Z. angew. Chem.*, 1923, 36, 149—152).—Based on observations made by previous workers on the degradation and reduction products and derivatives of lignin, the author develops a theory of the constitution of this substance, which attempts to reconcile the conflicting deductions which have from time to time been made. It is suggested that the fundamental unit of the lignin molecule is formed by the condensation of three molecules of 5-hydroxymethylfurfuraldehyde, which is itself produced by the internal condensation of carbohydrates. The unit so formed will consist of a compact condensed ring system, of which three of the outer rings are furan nuclei, and the other three outer rings and the central ring benzene nuclei. Hence under conditions favouring the fission of the furan rings, benzene derivatives appear as degradation products of lignin, and of the humic acids, etc., which with the efflux of time are developed from the

lignin during coal formation. The theory is further developed to account for the formation of methoxyl groups, ligninsulphonic acids, condensation products from the above fundamental unit, and so forth.

G. F. M.

Transport Experiments with Electrometric [Ionisable] Derivatives of Hydroxylamine. WILLIAM A. NOYES and JAMES H. HIBBEN (*J. Amer. Chem. Soc.*, 1923, **45**, 355—359).—Qualitative transport experiments have been carried out with aqueous solutions of trimethylamine oxide, hydroxytrimethylammonium salts, methoxytrimethylammonium iodide, ethoxytrimethylammonium bromide, trimethyliodomethylammonium hydroxide, and ethoxytrimethylammonium hydroxide. The solutions in many cases contained 7% of gelatin, and the cathode liquid contained hydrochloric acid. It has been shown that in each case an hydroxy-, a methoxy-, or an ethoxy-group remains with the nitrogen as a part of the kation. The linking of these groups to the nitrogen must therefore be very different from that of the hydroxyl or other atom or group which travels toward the anode during the electrolysis. The resistance of the solutions of trimethylamine oxide hydrate and of ethoxytrimethylammonium hydroxide seems more consistent with the hypothesis that the hydroxyl-ion of these compounds is attached to the nitrogen by a principal valency of such a character that it is only slightly ionised, than with that of the unlocalised polar valency assumed by Lewis and Langmuir (*A.*, 1920, ii, 243).

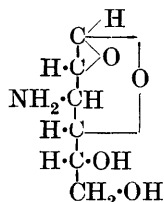
J. F. S.

Constitution of the Ampholytes, particularly the Amino-acids, and their Dissociation Constants. NIELS BJERRUM (*Z. physikal. Chem.*, 1923, **104**, 147—173).—A discussion of the constitution of ampholytes in which it is shown that the aliphatic amino-acids in an undissociated condition are present almost completely (about 95%) as salt-like double ions $^+\text{NH}_3\cdot\text{RCO}_2^-$. They are therefore not true amino-acids, but rather ammonium salts. The presence of hydrogen- or hydroxyl-ions in their solutions does not indicate that they are acids, but that hydrolysis of the salt has taken place. The constants k_a and k_b , by which the acid and basic character of the amino-acids has hitherto been represented, are not dissociation constants, but rather hydrolysis constants. The real dissociation constants, which give the strength of the acid and base within the neutralised amino-acid molecule, are $K_A = K_{\text{H}_2\text{O}} : k_b$ and $K_B = K_{\text{H}_2\text{O}} : k_a$, where $K_{\text{H}_2\text{O}}$ is the dissociation constant of water. The values of K_A and K_B are such that they are in keeping with the demands of the structural formula. From the nature of the acid and basic groups the values of K_A and K_B may be deduced if the influence of the other substituents is taken account of in the usual manner. That the amino-acids contain no free amino-group is confirmed by many chemical reactions, and many physico-chemical properties are in keeping with a salt-like nature rather than with an acid character. This is seen particularly in the fact that they increase the solubility of other

salts, and that they are more soluble in salt solutions than in water. Amongst the aromatic amino-acids, there are also double ions of the form $^+\text{NH}_3\cdot\text{R}\cdot\text{CO}_2^-$ and true amino-acids, $\text{NH}_2\cdot\text{R}\cdot\text{CO}_2\text{H}$, with free amino- and carboxyl-groups and this true acid may be present in amounts from 10% to 90%. In the case of the aromatic phenols, the double ion form is not present. From the dimensions of the dissociation constants of an ampholyte it is possible to deduce the ratio of the amounts of the two forms present. It is shown theoretically to be probable that for an ampholyte the product $K_A\cdot K_B$ cannot be smaller than $4K_{\text{H}_2\text{O}}$, that is $k_a\cdot k_b$ cannot be greater than $\frac{1}{4}K_{\text{H}_2\text{O}}$. From this it follows that the portions of an ampholyte present as anion and cation can never be more than 50%. A number of preliminary experiments confirming the above-mentioned results are recorded.

J. F. S.

Epiglucosamine. P. A. LEVENE and G. M. MEYER (*J. Biol. Chem.*, 1923, 55, 221—227).—When triacetylmethylglucoside- β -chlorohydrin (Fischer, Bergmann, and Schotte, A., 1920, i, 420) is heated with concentrated ammonia, methylepiglucosamine is obtained in the form of its *acetate*, m. p. 214° (corr.) after turning brown at 210° , $[\alpha]_D^{20} -130^\circ$ in 2.5% hydrochloric acid. The corresponding hydrochloride, long needles, has $[\alpha]_D^{20} -138^\circ$ in 2.5% hydrochloric acid. Methylepiglucosamine is readily hydrolysed by hydrochloric acid; the isolation of epiglucosamine has not, however, been accomplished owing to the ease with which this compound loses a molecule of water with the formation of *anhydroepiglucosamine*, which has been isolated in the form of its *hydrochloride*, $\text{C}_6\text{H}_{11}\text{O}_4\text{N}\cdot\text{HCl}$, m. p. (decomp.) 216° (corr.) after changing colour at 190° , $[\alpha]_D^{20} -172^\circ$ in 2.5% hydrochloric acid. That epiglucosamine is the first product of hydrolysis has been shown by the preparation from the reaction mixture of its *phenylosazone*, $\text{C}_{18}\text{H}_{22}\text{O}_3\text{N}_5$, long, lemon-yellow needles, m. p. 207° (corr.), $[\alpha]_D^{20} -41^\circ$ (initial) in a solvent composed of four parts of pyridine and six parts of 50% (by volume) methyl alcohol. Anhydroepiglucosamine

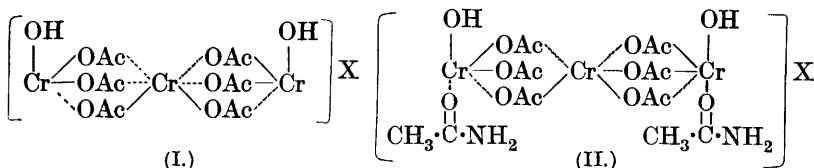


does not reduce Fehling's solution, but acquires this property on hydrolysis; on the basis of this behaviour, the annexed structure has been assigned to it. That the amino-group is in the γ -position both in this compound and in epiglucosamine follows from the preparation of the osazone of the latter (see above), which excludes the alternative β -position. The space arrangement of this group is, however, quite arbitrary. The configuration of epiglucosamine evidently depends on that of the β - and γ -carbon atoms.

E. S.

The Addition of Acid Amides to Ferric and Chromic Acetates. R. WEINLAND and HEINZ HACHENBURG (*Z. anorg. Chem.*, 1923, 126, 285—304).—Compounds formed from ferric or chromic chlorides by the addition of sodium acetate and weakly

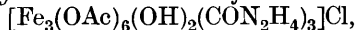
basic acid amides are described and formulæ suggested. The general type of the parent compound is shown by (I).



The central chromium atom is the only one exercising its full co-ordination number of 6: the others are co-ordinatively unsaturated and can presumably unite with one, two, or three molecules of an amide to give compounds of which II is typical. The compounds form coloured crystalline powders, brick red in the case of iron, and dark green in the case of chromium. The iron salts are easily soluble in cold water to garnet-red solutions, which are, however, unstable, so that recrystallisation from water is impossible. They are less soluble in alcohol, but decompose in this solvent on long heating. Addition of pyridine to the alcoholic solutions results in the formation of salts with complex kations containing pyridine and four iron atoms, but no amide.

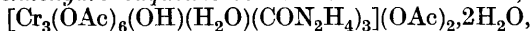
The chromium salts are more stable than those of iron; they are easily soluble in water, giving neutral solutions (in contrast to those of iron, which are weakly acid) which are quite stable, even when boiled. They are less soluble in alcohol than the iron compounds, the solutions being more stable.

Hexa-acetatodihydroxotricarbamidetriferrichloride,



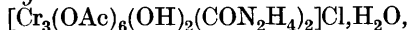
crystallises from an alcoholic solution of hexa-acetatodihydroxotri-ferrichloride and carbamide with $2\text{H}_2\text{O}$. The anhydrous salt is obtained by the addition of ether to the mother-liquor. The corresponding *perchlorate* crystallises in small tablets, the *nitrate* forms small, rhombic tablets, and the *chloroferrate* crystallises with H_2O in domed prisms.

* *Hexa-acetatohydroxoaoquetricarbamidetrichromidiacetate,*



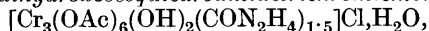
crystallises in green tablets from an aqueous solution of carbamide and the calculated quantity of the diacetate of the hexa-acetato-trichromibase.

Hexa-acetatodihydroxodicarbamidetrichromichloride,



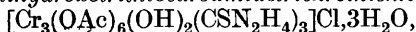
is prepared like the preceding compound, but using the chloride of the base; the corresponding *nitrate* crystallises with $3\text{H}_2\text{O}$ in right-angled tablets.

Hexa-acetatodihydroxosesquicarbamidetrichromichloride,



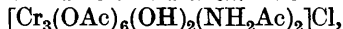
is obtained by the addition of the calculated quantity of carbamide to the preceding chloride.

Hexa-acetatodihydroxotri-thiocarbamidetrichromichloride,



crystallises in well-defined prisms; the corresponding *nitrate* ($2\text{H}_2\text{O}$) and *perchlorate* ($2\text{H}_2\text{O}$) were prepared.

Hexa-acetatodihydroxodiacetamidetrichromichloride,



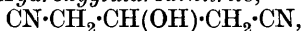
crystallises from an aqueous solution of the hexa-acetatodihydroxotrichromichloride and acetamide in anhydrous crystals and is converted by addition of lithium nitrate into *hexa-acetatodihydroxomonoacetamidetrichrominitrate*. It crystallises with $2\text{H}_2\text{O}$; the corresponding *perchlorate* crystallises with H_2O in prisms. H. H.

Hydrolysis and Polymerisation of Cyanamide. H. C. HETHERINGTON and J. M. BRAHAM (*J. Amer. Chem. Soc.*, 1923, 45, 824—829).—The behaviour of cyanamide in both acid and alkaline solution has been studied and the course of the reaction followed by determinations of both cyanamide and carbamide.

By the action of mineral or organic acids, or acid salts, cyanamide is hydrolysed to carbamide, without the formation of dicyanodiamide; the reaction is unimolecular, the velocity of hydrolysis increasing with increasing acid concentration within the limits studied. In alkaline solutions, cyanamide is hydrolysed to carbamide, as well as polymerised to dicyanodiamide, the reaction probably being due to the catalytic influence of the hydroxyl-ion.

Since the presence of acids does not bring about polymerisation, the latter cannot be explained on the equilibrium theory of Werner (T., 1915, 107, 715); the ionic theory suggested by Grube and Kruger (A., 1914, i, 152) is, however, quite satisfactory. W. S. N.

β -Hydroxyglutarodinitrile. R. LESPIEAU (*Compt. rend.*, 1923, 176, 754—756).— β -Hydroxyglutarodinitrile,



was obtained as a viscous liquid, b. p. $202\text{--}203^\circ/11\text{ mm.}$, by the action of saturated potassium cyanide solution on the chloronitrile, $\text{CH}_2\text{Cl}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CN}$, at a temperature not exceeding 70° . It has d_{25}^{22} 1.808 and n_D^{20} 1.4805. On saturating with hydrogen bromide, a crystalline mass, m. p. 230° , consisting of the *hydrobromide*, $\text{CN}\cdot\text{CH}_2\cdot\text{CHBr}\cdot\text{CH}_2\cdot\text{CN}\cdot\text{HBr}$, is formed, which when decomposed with potassium carbonate yields crystals of β -bromoglutarodinitrile, m. p. $87\text{--}88^\circ$. G. F. M.

Hydrocyanic Acid. An Ammono-carbonous Acid, an Ammono-formaldehyde, and a Formic Anammonide. EDWARD C. FRANKLIN (*J. Physical Chem.*, 1923, 27, 167—186).—A theoretical paper in which an attempt is made to show that hydrogen cyanide possesses simultaneously the properties of an ammono-carbonous acid, of a formaldehyde of the ammonia system, and of a compound related to ammonia as the unknown formic anhydride is to water. That hydrogen cyanide is an *ammono-carbonous acid*, $\text{H}\cdot\text{NC}$, is supported by the following reactions: its formation when carbon is heated in ammonia or a mixture of nitrogen and hydrogen; the action of nitrogen in converting sodium cyanide in the presence of sodium into sodium cyanamide; the formation of sodium cyanamide from sodium cyanide and sodium azide; the formation of sodium dicyanimide by the action of

cyanogen on sodium cyanide; the action of sodamide on carbon, carbon monoxide, and carbon dioxide; the reduction of sodium cyanamide and dicyanamide to sodium cyanide; the oxidation of sodium cyanide to sodium cyanate; the ammonolysis of ethyl carbylamine to ethylamine and hydrocyanic acid; the oxidation of methylcarbylamine to methylcarbimide; and the reduction of hydrogen cyanide to methylamine. That hydrogen cyanide is an *ammono-formaldehyde* is supported by its polymerisation to form compounds of unknown constitution; its condensation to form aldol-like products; its formation of additive compounds with hydrogen sulphites, hydroxylamine, hydrazine, and phenylhydrazine, and by the fact that the relation between hydrogen cyanide and methylamine is the same as that of an aldehyde to an alcohol. That it is *formic anammonide* is shown by the fact that hydrogen cyanide bears an analogous relation to formamide, formamidine, and the formimido-esters, respectively, as acid anhydrides do to acids.

J. F. S.

Magnesiumamine. I. GIUSEPPE ODDO and EMANUELE CALDERARO (*Gazzetta*, 1923, 53, i, 64—74).—To the compound obtained by treating an organo-magnesium compound, such as magnesium ethyl iodide, in ethereal solution with dry ammonia the authors give, in accordance with the nomenclature proposed by Oddo (A., 1912, i, 721), the name magnesiumamine. This product, like Grignard compounds, contains a molecule of ether, its composition being expressed by $\text{NH}_2 \cdot \text{MgX} \cdot \text{Et}_2\text{O}$. Magnesiumamine may be regarded as analogous to sodamide, better termed sodamine, but, unlike the latter, is obtainable easily and with constant properties. In the action of ammonia on magnesium ethyl iodide, the ethane liberated corresponds with only one of the hydrogen atoms of the ammonia: $\text{MgEtI} + \text{NH}_3 = \text{NH}_2 \cdot \text{MgI} + \text{C}_2\text{H}_6$. Like Grignard compounds, magnesiumamine forms with pyridine an *additive* compound, $\text{NH}_2 \cdot \text{MgI} \cdot 2\text{C}_5\text{H}_5\text{N}$.

Magnesiumamine reacts with acid chlorides giving the corresponding amides, the three stages of the reaction with benzoyl chloride being: $\text{NH}_2 \cdot \text{MgI} + \text{Ph} \cdot \text{COCl} = \text{NH}_2 \cdot \text{CPhCl} \cdot \text{OMgI}$, the latter $+ \text{NH}_2 \cdot \text{MgI} = \text{MgClI} + \text{MgIO} \cdot \text{CPh}(\text{NH}_2)_2$, and the latter $+ \text{H}_2\text{O} = \text{MgI} \cdot \text{OH} + \text{NH}_3 + \text{NH}_2\text{Bz}$. With ethyl benzoate, magnesiumamine reacts, giving dibenzamide, together with a small proportion of benzamide: $2\text{Ph} \cdot \text{CO}_2\text{Et} + \text{NH}_2 \cdot \text{MgI} = \text{NBz}_2 \cdot \text{MgI} + 2\text{EtOH}$ and $\text{NBz}_2 \cdot \text{MgI} + \text{H}_2\text{O} = \text{NHBz}_2 + \text{MgI} \cdot \text{OH}$; similarly, the reaction between potassamide and benzoyl chloride yields a mixture of benzamide and dibenzamide. Magnesiumamine reacts readily with ethyl phthalate, giving phthalimide, and in ethereal solution unites easily with benzonitrile or nitrobenzene, which are regenerated when the products formed are treated with water.

With benzaldehyde, magnesiumamine reacts in two ways, one of the reactions, which yields mainly hydrobenzamide, being analogous to that between aldehydes or ketones and Grignard compounds, and the other to that between sodamide and aromatic aldehydes: (I) $\text{Ph} \cdot \text{CHO} + \text{NH}_2 \cdot \text{MgI} = \text{NH}_2 \cdot \text{CHPh} \cdot \text{OMgI}$; $3\text{NH}_2 \cdot \text{CHPh} \cdot \text{OMgI} =$

$\text{MgI}\cdot\text{OH} + \text{NH}_3 + \text{MgIO}\cdot\text{CHPh}\cdot\text{NH}\cdot\text{CHPh}\cdot\text{NH}\cdot\text{CHPh}\cdot\text{OMgI} \rightarrow \text{OH}\cdot\text{CHPh}\cdot\text{NH}\cdot\text{CHPh}\cdot\text{NH}\cdot\text{CHPh}\cdot\text{OH} \rightarrow \text{CHPh}\cdot\text{N}\cdot\text{CHPh}\cdot\text{N}\cdot\text{CHPh}$.
 (II) $\text{Ph}\cdot\text{CHO} + \text{NH}_2\cdot\text{MgI} = 2\text{H} + \text{NHBz}\cdot\text{MgI} \rightarrow \text{Ph}\cdot\text{CO}_2\text{NH}_4 + \text{MgI}\cdot\text{OH}$.
 Magnesylamine and benzophenone yield an additive compound, which gives benzophenone when treated with water.

With acetylacetone, magnesylamine reacts with great readiness, yielding 2 : 5-dimethylpyrrole : $\text{CH}_2\text{Ac}\cdot\text{CH}_2\text{Ac} + 2\text{NH}_2\cdot\text{MgI} = 2[\cdot\text{CH}_2\cdot\text{CMe}(\text{NH}_2)\cdot\text{OMgI}] \rightarrow 2[\cdot\text{CH}_2\cdot\text{CMe}(\text{NH}_2)\cdot\text{OH}] \rightarrow \begin{matrix} \text{CH}\cdot\text{CMe} \\ \text{CH}\cdot\text{CMe} \end{matrix} > \text{NH}$.

An analogous reaction occurs when acetylacetone is heated in a sealed tube at 150° with a slight excess of alcoholic ammonia (Paal, A., 1885, 1206).

The compound formed from magnesylamine and nitrobenzene gives, with pyridine, a yellow precipitate, consisting of the *additive* compound, $\text{MgI}\cdot\text{O}\cdot\text{NPh}(\text{NH}_2)\cdot\text{O}\cdot\text{C}_6\text{H}_5\text{N}$. T. H. P.

Action of Acetylene on Zinc Ethyl. J. F. DURAND (*Compt. rend.*, 1923, 176, 992–993).—*Zinc acetylide* is formed according to the equation $\text{C}_2\text{H}_2 + \text{ZnEt}_2 = \text{ZnC}_2 + 2\text{C}_2\text{H}_6$ when acetylene is passed into a solution of zinc ethyl in light petroleum. It is a white substance, decomposed by water with formation of zinc hydroxide, and giving with ammoniacal cuprous chloride a red precipitate of copper acetylide. It is unstable in air, and becomes yellow on warming, owing to the formation of zinc oxide. G. F. M.

Preparation of Dialkyl Mercury Compounds from the Grignard Reagent. II. Relative Stability of the Carbon-Mercury Linking in Dialkyl Mercury Compounds. C. S. MARVEL and H. O. CALVARY (*J. Amer. Chem. Soc.*, 1923, 45, 820–823; cf. A., 1922, i, 329).—The reaction between the Grignard reagent and mercury halides has been applied to the production of dialkyl mercury compounds containing secondary and tertiary alkyl groups. The action of heat and of acids indicates that the carbon-mercury linking in $\text{CR}_3\text{-Hg}$ is less stable than that in $\text{CHR}_2\text{-Hg}$, and this in turn less stable than that in $\text{CH}_2\text{R-Hg}$. Mercury di-*sec*.-butyl reacts in alcoholic solution with aqueous hydrochloric acid to give *mercuric sec.-butyl chloride*, m. p. 30.5° , and with aqueous hydrobromic acid to give *mercuric sec.-butyl bromide*, m. p. 39° . The Grignard reagent from *sec*.-octyl bromide reacts with mercuric chloride in ethereal solution to give *mercury di-sec.-octyl*, yield 52%, which decomposes when heated, with formation of free mercury; when the above Grignard reagent is treated with mercuric bromide, *mercuric sec.-octyl bromide*, m. p. 98° , is produced. The action of mercuric bromide on the Grignard reagent from *tert*.-butyl bromide leads to *mercury di-tert.-butyl*, b. p. $78\text{--}82^\circ/5$ mm. with decomp.; if an excess of mercuric bromide is used, *mercuric tert.-butyl bromide*, m. p. 106° , decomp., is formed. Similarly, *mercury di-tert.-amyl*, b. p. $80\text{--}84^\circ/5$ mm., decomp., and *mercuric tert.-amyl bromide*, m. p. 82° , have been obtained.

The indices of refraction of various liquid mercury dialkyl compounds are given.

It is noted that the order of stability towards concentrated

hydrochloric acid is (1) mercury di-*n*-butyl, (2) mercury di-*sec*-butyl, (3) mercury di-*tert*-butyl. Similarly, mercury di-*n*-propyl is more stable than mercury di-*isopropyl*. The same order of stability towards heat is noted. W. S. N.

The Problem of Substitution in the Benzene Nucleus and the Thomson-Lewis-Langmuir Theory of Co-valence. RONALD FRASER and JAMES ERNEST HUMPHRIES (*Chem. News*, 1923, 126, 161—168).—An attempt is made to account for the directive influence of substituents already present in the benzene nucleus in terms of the Thomson-Lewis-Langmuir theory of co-valence. The development of the theory is based on three postulates: (1) the tendency of a disintegrated octet is towards further disruption; and of a nearly completed octet towards completion; (2) the tendency towards octet stability of an atom with nearly completed octet is greater than the tendency to octet instability of an atom with disruption only incipient; (3) the more nearly a group approaches octet stability, the greater the ease of replacement at that point. It is considered that there can be all grades of octet stability between that exhibited in truly polar compounds, where an atom surrounded by a complete octet can exist as a free ion, and that present in typically non-polar compounds. It is shown that an ortho-para-directive substituent, X, has the atom which is linked to the nucleus in a state approaching octet stability; hence the electrons are drawn into X, making the nuclear carbon atom, C¹, to which it is linked, positive and the ortho- and para-carbon atoms, C² and C⁴, negative. A meta-directive substituent, Y, however, such as NO₂, SO₃H, etc., has the atom linked to the nucleus in a state of incipient octet disruption; it is therefore positive, C¹ becomes negative, and the meta-carbon atom, C³, is also negative, on the principle of induced alternate polarities. Since a negative carbon atom tends to deprive its attached hydrogen atom of its electron, it is evident that a hydrogen atom attached to a negative carbon atom is in a condition favourable for substitution. It follows that a positive substituent such as NO₂, SO₃H, etc., is meta-directive, and a negative substituent such as halogen is ortho-para-directive. The terms positive and negative here have the opposite significance to that which they generally carry. Benzene substituents arranged according to the Hollemann series follow a descending order of octet stability. It is shown that a group which favours substitution in the meta-position should favour replacement in the ortho-para-positions, as is well known to be the case. A labile group is one that tends to complete its octet, and is therefore attached to a positive carbon atom. The lability of such a group will be increased by a group such as NO₂ in the ortho- or para-position. The entering group should be of greater octet stability than the one replaced. The theory also explains the loosening effect of ortho-para-directing groups or substituents in the meta-position. On similar lines to the above, the effects of two and three substituents in the benzene ring on the position taken up by an additional substituent are considered. E. H. R.

The Benzene Formula of Lely. S. C. J. OLIVIER (*Chem. Weekblad*, 1923, 22, 143—144; J. D. VAN ROON (*ibid.*, 144); H. A. J. SCHOUTISSEN (*ibid.*, 145); H. G. DERX and P. H. HERMANS (*ibid.*, 145—147).—Polemical. Replies to Lely (this vol., i, 99).
S. I. L.

Reaction of Nitrosyl Chloride on Toluene. E. V. LYNN and HELEN L. ARKLEY (*J. Amer. Chem. Soc.*, 1923, 45, [4], 1045—1047; cf. A., 1919, i, 245; 1922, i, 417).—Although nitrosyl chloride is unaffected by benzene, it reacts readily with toluene in the sunlight, giving crystals of benzaldoxime hydrochloride; phenyl-nitrosomethane is presumably the initial product, but is evidently very unstable, since no blue coloration is produced. W. S. N.

Separation of Xylenes. H. T. CLARKE and E. R. TAYLOR (*J. Amer. Chem. Soc.*, 1923, 45, 830—833).—The literature dealing with the preparation and separation of the xylenes is contradictory and misleading.

Fractional distillation, selective sulphonation, crystallisation of the sulphonic derivatives, and selective hydrolysis of xylenesulphonic acid all lead to a partial separation of the three xylenes, but none of these processes alone is entirely suitable for the isolation of *o*-xylene and *p*-xylene.

A satisfactory procedure is described in which the above processes are combined [cf. *J.S.C.I.*, 1923, 394A].
W. S. N.

A New Synthesis of Cumene and *p*-Cymene. L. BERT (*Compt. rend.*, 1923, 176, 840—842).—Cumene and *p*-cymene were obtained by the action of 1 mol. of magnesium phenyl bromide, and magnesium *p*-tolyl bromide, respectively, on an ethereal solution of 1 mol. of isopropyl sulphate, according to the scheme $\text{PhMgBr} + \text{SO}_4(\text{CHMe}_2)_2 \rightarrow \text{CHMe}_2\text{Ph} + \text{MgBrSO}_4 \cdot \text{CHMe}_2$. The yield of cumene, b. p. 151—152°/720 mm., amounted to 10%, and approximately the same for *p*-cymene, b. p. 173—175°/720 mm. The substances were each identified by the preparation and isolation of the respective barium sulphonates.
G. F. M.

Primary Tar Oil. R. WARRINGTON and E. MOEHRLE (*Brennstoff-Chem.*, 1923, 4, 81—84).—Oil from primary tar was freed from phenols and bases, and fractionated under reduced pressure. Unsaturated compounds were removed by dilute sulphuric acid, with which, as they were highly unsaturated, they readily combined. The percentage loss was noted, and the purified residue treated with cold concentrated sulphuric acid to separate aromatic compounds as sulphonic acids, which were afterwards decomposed by steam. The residue consisted of paraffins and naphthenes, which are very difficult to separate, but some success was achieved by the use of fuming nitric acid which attacked the latter. The following compounds were proved to be present in the oil: a homologue of indene, ψ -cumene, durene, naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, 1 : 6-dimethylnaphthalene. Indications were obtained of the presence of decahydronaphthalene,

dodecahydrodiphenyl, perhydrofluorene, and perhydroacenaphthene. Comparisons are made with coke-oven tar oil. T. S. W.

Nature of the Hydrocarbons Present in Primary Tar Light Oils. F. SCHÜTZ (*Brenstoff-Chem.*, 1923, 4, 84).—Hydrocarbons are the chief constituents of primary tar light oil—the following series occurring with very few gaps in the homologues: Paraffins, C_nH_{2n+2} ; olefines, C_nH_{2n} ; diolefines, C_nH_{2n-2} ; cyclic diolefines, C_nH_{2n-4} ; aromatic hydrocarbons, C_nH_{2n-6} ; reduced aromatic hydrocarbons (naphthenes). The chief constituents of primary coal tar "benzine," the light oil fraction boiling up to 150° , are aromatic hydrocarbons, then come the olefines in much smaller amounts, whilst only very small quantities of paraffins and other hydrocarbons are present. In researches on "benzines" from other tars (Fischer and Gluud, A., 1919, i, 379), little or no benzene was found, pentane and hexane chiefly being isolated. The cause of the difference may lie in the origin of the coal, or more probably in the method of distillation employed.

T. S. W.

Occurrence of Ketones and Aldehydes together with Sulphur Compounds in Primary Tar Light Oil. F. SCHÜTZ (*Brenstoff-Chem.*, 1923, 4, 84; cf. *J. Soc. Chem. Ind.*, 1923, 175A).—The 30—75° fraction of the light oil from primary tar contains about 14% of acetone, corresponding with 0.5 to 1 kg. per ton of coal. Acetaldehyde, paracetaldehyde, acetonitrile, methyl mercaptan, dimethyl sulphide, and carbon disulphide are present in smaller amounts.

T. S. W.

The Basic Properties of the Nitro-group. ÉMILE CHERBULIEZ (*Helv. Chim. Acta*, 1923, 6, 281—286).—When an equimolecular mixture of nitrobenzene and sulphuric acid monohydrate is cooled to -10° to -20° , after some delay the liquid crystallises in very pale green needles, m. p. 11° , having the composition $C_6H_5 \cdot NO_2 \cdot H_2SO_4$. That the crystals are really those of a compound is shown by the fact that crystallisation of the equimolecular mixture cannot be induced by crystals of either nitrobenzene or of sulphuric acid, but is started at once by a crystal of the new compound. By water and by solvents not miscible with sulphuric acid, the compound is split into its constituents, but it can be crystallised by cooling from an ethereal solution. Further evidence that compounds are formed between nitro-derivatives of hydrocarbons and sulphuric acid is afforded by the observation that nitromethane, nitrobenzene, and the three nitrotoluenes when dissolved in sulphuric acid increase its electrical conductivity. This increase in the case of *p*-nitrotoluene, which has the greatest effect, is about half as great as the increase caused by the weakly basic 1 : 2 : 4-dinitroaniline. It is therefore considered that mononitro-derivatives of hydrocarbons are very weak bases forming salt-like compounds with strong acids. In the dinitro-derivatives, this basic character has disappeared, for the dinitrobenzenes diminish the conductivity of sulphuric acid. Perchloric acid

in 70% aqueous solution has a powerful solvent action on nitro-compounds, possibly due to the formation of a loose compound between the acid and the nitro-group. E. H. R.

Preparation of Potassium and Sodium Arylsulphoniodo-amides. ELWYN ROBERTS (T., 1923, 123, 849—853).

Preparation of a New Chloroethyl Ester [β -Chloroethyl Toluene-*p*-sulphonate], and the Treatment of Phenols, Alcohols, and Amino-compounds therewith. BRITISH DYE-STUFFS CORPORATION, LTD., WILLIAM HENRY PERKIN, and GEORGE ROGER CLEMO (Brit. Pat. 193618).— β -Chloroethyl toluene-*p*-sulphonate is obtained in good yield as a colourless syrup by boiling toluene-*p*-sulphonyl chloride with ethylene chlorohydrin for three hours. It boils at 210°/21 mm., and condenses readily with phenols, aromatic alcohols, and amines to give ethers, substituted diamines, etc. Thus on heating with phenol in presence of sodium hydroxide β -chloroethyl phenyl ether, $\text{OPh}\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl}$, a pleasant smelling oil, b. p. 217—220°, is obtained as the main product, together with diphenylethylene ether, $\text{OPh}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OPh}$, in lesser amount. Similar β -chloroethyl ethers are obtained from the cresols and naphthols. The chloroethyl ethers react readily with amines, giving β -phenoxyethyl derivatives of these bases. Thus β -naphthyl- β -chloroethyl ether gives with dimethylamine β -naphthyl- β -dimethylaminoethyl ether, of which the hydrochloride, m. p. 185°, has a local anæsthetic action. Benzyl alcohol on treatment with β -chloroethyl toluene-*p*-sulphonate and sodium hydroxide gives benzyl β -chloroethyl ether, b. p. 95—110°/16 mm. This substance also reacts readily with amines, for example, from diethylamine benzyl β -diethylaminoethyl ether is obtained. β -Chloroethyl toluene-*p*-sulphonate reacts with amines in presence of sodium carbonate; on heating with aniline, for example, a mixture of diphenylethylenediamine, and diphenylpiperazine is obtained, whilst with methylaniline the main product is diphenyldimethylethylenediamine, $\text{NMePh}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NMePh}$, and some methyl- β -chloroethylaniline, b. p. 124°/10 mm., is obtained. β -Chloroethyl toluene-*p*-sulphonate also reacts with *m*-nitrophenols and with aminophenols, yielding chloroethyl ethers, but the amino-group must previously be protected by acetylation. *o*-Acetamidophenyl β -chloroethyl ether forms long prisms, m. p. 97—98°.

G. F. M.

New Type of Synthesis. I. Reaction between Halogen-Alkyl Sulphonates and Organomagnesium Halides. HENRY GILMAN and N. J. BEABER (*J. Amer. Chem. Soc.*, 1923, 45, 839—842).—A preliminary study has been made of the reaction between various organomagnesium halides and halogen-alkyl esters of toluene-*p*-sulphonic acid. In all cases the MgX group is replaced by the halogen-alkyl group (cf. Ferns and Lapworth, T., 1912, 101, 273).

The following compounds were obtained with β -chloroethyl-toluene-*p*-sulphonate: β -Chloroethylbenzene, yield 36%, from

bromobenzene; γ -chloropropylbenzene, 59%, from benzyl chloride; β -chloroethylphenylacetylene, 75%, from phenylacetylene, and β -chloroethyl benzoate, 5%, from the benzoate PhCO_2MgBr . γ -Chloropropylbenzene was obtained in 31% yield from bromobenzene and γ -chloropropyl toluene-*p*-sulphonate, b. p. 216—219°/17 mm., d_4^{20} 1.2674, n_D^{20} 1.5230. W. S. N.

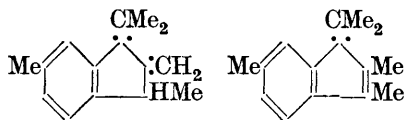
Sodium Toluene-*p*-sulphochloramide ("Chloramine"), and Its Effect on certain Organic Substances. N. O. ENGFELDT (*Z. physiol. Chem.*, 1923, 126, 1—28).—The action of hypochlorite solutions on various organic substances has already been investigated by the author (cf. A., 1922, i, 812), and similar experiments have now been carried out with "chloramine." Fats and carbohydrates are found not to react with "chloramine." Amino-acids react very similarly, qualitatively and quantitatively, as with hypochlorite. Hippuric acid, on the other hand, is not affected by the reagent, to which the $-\text{CO}\cdot\text{NH}-$ linking appears to be resistant. In accordance with this, proteins and peptones are much less affected by the reagent than by hypochlorite. Free ammonia and certain aldehydes also react with it to a much less extent. W. O. K.

Syntheses in the Indene Series. IV. A. P. ORÉKHOV [with V. SCHAPIR] (*J. Russ. Phys. Chem. Soc.*, 1916, 48, 1820—1826).—2:3-Diphenylindene is synthesised by the dehydration with phosphoric oxide of $\alpha\beta\gamma$ -triphenylpropane- $\alpha\beta$ -diol, m. p. 159—160°, prepared by the action of magnesium benzyl chloride on benzoin. Dehydration with acetyl chloride gives a 35% yield of the diphenylindene together with a 50% yield of monoacetate of the diol, m. p. 176—177°, which is the sole product of the action of acetic anhydride. R. T.

Syntheses in the Indene Series. V. A. P. ORÉKHOV (*J. Russ. Phys. Chem. Soc.*, 1916, 48, 1827—1829).—The method of the synthesis of indenenes from substituted bromopropanes by the elimination of hydrogen bromide, is applied with success to the synthesis of indones. The dibromide of benzylidenedeoxybenzoin. $\text{COPh}\cdot\text{CPhBr}\cdot\text{CHPhBr}$, is heated at 140—145°. A copious evolution of hydrogen bromide takes place and an 89% yield of 2:3-diphenyl-1-indone is obtained. R. T.

Azulene. ROLAND E. KREMERS (*J. Amer. Chem. Soc.*, 1923, 45, 717—723).—The isolation of azulene, b. p. 135.6°/1.1 mm., 167—168.4°/11 mm., from oil of milfoil (cf. Sherndal, A., 1915, i, 82, 702) has been slightly modified and the absorption spectrum plotted. The hydrocarbon, b. p. 130—140°/20 mm., produced by complete reduction by means of hydrogen and palladium, has the formula $\text{C}_{15}\text{H}_{28}$ (cf. Sherndal, *loc. cit.*; also Augspurger, *Science*, 1915, 42, 100), and is dicyclic. Reduction may also be effected, at least partly, by means of sodium amalgam, but not by aluminium amalgam. Azulene forms ill-defined additive products with bromine, nitrogen trioxide, and nitrosyl chloride, and apparently

forms also a sodio-derivative from which the hydrocarbon is regenerated by means of hydroxylic reagents. The oxidation of azulene (for which the annexed formulæ are proposed) by means of alkaline potassium permanganate, leads to carbon dioxide, acetone, acetic acid, and (probably) methylphthalic acid.



W. S. N.

The Binary Eutectics between Naphthalene, Iodoform, and Iodine. A. M. VASILIEV (*J. Russ. Phys. Chem. Soc.*, 1916, 48, 1779—1785).—The melting points and the composition of the binary eutectic mixtures of naphthalene, iodoform, and iodine are determined, in order to test the accuracy of a theory put forward by Flavitzki (A., 1906, ii, 152). According to this theory, where t_1 , t_2 , and t_3 are the melting points of three substances, of molecular weight M_1 , M_2 , and M_3 , t_{1-2} , t_{2-3} , and t_{3-1} , the melting points of the eutectic mixtures obtained from each pair, and $n_{1-2}M_1 + M_2$, $n_{2-3}M_2 + M_3$, and $n_{3-1}M_3 + M_1$ are the compositions of these eutectics, the following expressions are obtainable: $[n_{1-2}^2 M_1(t_1 - t_{1-2})]/[M_2(t_2 - t_{1-2})] = \alpha$, $[n_{2-3}^2 M_2(t_2 - t_{2-3})]/[M_3(t_3 - t_{2-3})] = \beta$, $[n_{3-1}^2 M_3(t_3 - t_{3-1})]/[M_1(t_1 - t_{3-1})] = \gamma$.

According to Flavitzki, the product $\alpha\beta\gamma$ should be equal to unity. The results obtained for the systems naphthalene-iodoform, iodoform-iodine, and iodine-naphthalene are in satisfactory agreement with this hypothesis, $\alpha\beta\gamma$ being 1.113.

R. T.

Action of Benzylidenemethylamine on certain Aromatic Nitro-derivatives. MICHELE GIUA (*Gazzetta*, 1923, 53, i, 53—56).—The author has investigated the action of benzylidenemethylamine on 2 : 3 : 4- and 2 : 4 : 5-trinitrotoluenes, and 1-chloro- and 1-bromo-3 : 4 : 6-trinitrobenzenes. These compounds contain a labile nitro-group, and the last two also a labile halogen atom, which, however, is replaced less readily than the nitro-group. The reaction of the labile nitro-group with benzylidenemethylamine is similar to that with methylamine, and is expressed by the equations: $\geq C \cdot NO_2 + CHPh \cdot NMe + H_2O = \geq C \cdot NHMe + Ph \cdot CHO + HNO_2$ and $CHPh \cdot NMe + HNO_2 = Ph \cdot CHO + CH_4O + N_2$. With the chloro- and bromo-trinitrobenzenes, the halogen atom also is replaced by NHMe if excess of the base is employed.

The hydrolysis of various bases, such as benzalazine, the phenylhydrazones, and benzylideneaniline by nitrohalogen compounds containing only the halogen atom in a labile condition was observed by Ciusa (A., 1906, i, 962), but these bases are not hydrolysed by nitro-compounds containing only a labile nitro-group. No hydrolysis of acetoxime, benzophenonephenylhydrazone, or benzylideneaniline occurs when these bases are heated with 2 : 3 : 4- or 2 : 4 : 5-trinitrotoluene, additive compounds being formed with the last two bases.

The interaction of benzylidenemethylamine and 2 : 3 : 4-trinitrotoluene yields 4 : 6-dinitromethyl-*m*-toluidine (cf. Brady and

Gibson, T., 1921, **119**, 98); that of benzylidenemethylamine and 2 : 4 : 5-trinitrotoluene, 2 : 4-dinitromethyl-*m*-toluidine (Brady and Gibson, *loc. cit.*), and that of benzylidenemethylamine and 1-chloro-3 : 4 : 6-trinitrobenzene, 4 : 6-dinitrodimethyl-*m*-phenylenediamine (cf. Blanksma and Meerum Terwogt, A., 1902, i, 715).

5-Bromo-2 : 4-dinitromethylaniline, $C_6H_2Br(NO_2)_2 \cdot NHMe$, prepared from 1-bromo-3 : 4 : 6-trinitrobenzene and benzylidene-methylamine, forms yellow crystals, m. p. 149—150°. T. H. P.

Action of Methyl Sulphate on Diphenylamine and on Diphenylmethylamine. CHARLES STANLEY GIBSON and DUDLEY CLOETE VINING (T., 1923, **123**, 831—837).

Reactions of Strongly Electropositive Metals with Organic Substances in Liquid Ammonia Solution. I. Preliminary Investigations. CHARLES A. KRAUS and GEORGE F. WHITE (*J. Amer. Chem. Soc.*, 1923, **45**, 768—778; cf. following abstract).—The action of sodium on solutions of various substances in liquid ammonia has been investigated, without, however, any generalisation being reached.

With the exception of triphenylmethane, which forms a sodio-derivative (cf. Schlenk and Thal, A., 1913, i, 1205), hydrocarbons and ethers are unaffected by sodium in ammonia solution; alcohols and phenols form alkylloxides and phenoxides, respectively, with liberation of hydrogen. Aldehyde-ammonia forms a similar sodio-derivative, but the behaviour of benzaldehyde has not been fully investigated. The thiophenols form ammonium salts with liquid ammonia, and these are converted by sodium into the sodium salts with formation of hydrogen and regeneration of ammonia. In a similar manner, acetic acid (ammonium salt) gives sodium acetate and hydrogen. Sodium apparently forms an additive product with acetone, or with acetone and ammonia; this is decomposed by water. Propyl iodide gives rise to propane, *n*-hexane, and *n*-propylamine; *tert*-amyl iodide is converted into *sec*-pentane. Ethylene chloride and sodium apparently react quantitatively in liquid ammonia solution in accordance with the equation: $C_2H_4Cl_2 + 2Na \rightarrow C_2H_4 + 2NaCl$. Acetylene dibromide and sodium probably react as follows: $C_2H_2Br_2 + 2Na \rightarrow C_2H_2 + 2NaBr$; $C_2H_2Br_2 + 4Na \rightarrow 2NaBr + C_2Na_2 + H_2$; $C_2H_2 + 2Na \rightarrow H_2 + C_2Na_2$. *o*-Chlorotoluene is converted into toluene and *o*-toluidine, *p*-chlorotoluene into toluene and *p*-toluidine; both reactions are probably to be expressed as follows: $2C_6H_4MeCl + 2Na + NH_3 \rightarrow C_6H_5Me + C_6H_4Me \cdot NH_2 + 2NaCl$. Similarly, dichlorobenzene gives benzene and *o*-phenylenediamine: $2C_6H_4Cl_2 + 4Na + 2NH_3 \rightarrow C_6H_6 + C_6H_4(NH_2)_2 + 4NaCl$. Nitrobenzene is reduced successively to azoxybenzene, azobenzene, hydrazobenzene, and aniline, or their sodio-derivatives. α -Bromonaphthalene is partly converted into naphthalene, whilst from phenylthiocarbimide aniline and diphenyl (traces) are produced. Sodium benzene-sulphonate gives rise to benzene, traces of diphenyl, and sodium sulphite; phenyl sulphide gives benzene and sodium sulphide.

From the product of the action of ammoniacal sodium on benzyl chloride or benzonitrile, no definite compound has been isolated.

W. S. N.

Reactions of Strongly Electropositive Metals with Organic Substances in Liquid Ammonia Solution. II. Action of Sodium on Phenyl Halides in Liquid Ammonia. GEORGE F. WHITE (*J. Amer. Chem. Soc.*, 1923, **45**, 779—784; cf. preceding abstract).—Sodium (1 atom) reacts with a phenyl halide (1 mol.) in liquid ammonia with formation of benzene and secondary and tertiary phenylamines, together with sodium halide and occasional traces of aniline, phenylcarbylamine, and sodium cyanide. The fundamental equations are: $6\text{PhCl} + 6\text{Na} + \text{NH}_3 = 3\text{C}_6\text{H}_6 + \text{NPh}_3 + 6\text{NaCl}$; $4\text{PhCl} + 4\text{Na} + \text{NH}_3 = 2\text{C}_6\text{H}_6 + \text{NPh}_2 + 4\text{NaCl}$; and as side-reactions: $2\text{PhCl} + 2\text{Na} + \text{NH}_3 = \text{C}_6\text{H}_6 + \text{NH}_2\text{Ph} + 2\text{NaCl}$. The benzene is a primary product, sodium phenyl not being produced. Benzene distils readily, and chlorobenzene and toluene distil slowly, from liquid ammonia mixtures. Diphenylamine and triphenylamine are partly miscible in the solid state, the limits of miscibility being approximately 13% and 75% of triphenylamine. A liquid phase containing 21% of triphenylamine is in equilibrium with the eutectic mixture at 43.6°. The formation of triphenylamine is favoured by dilution of the reaction mixture with light petroleum. Aniline and diphenylamine form sodio-derivatives in liquid ammonia solution.

W. S. N.

The Synthesis of Optically Active Asparagines. O. E. LUTZ (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1881—1887).—Various optically active *N*-substituted asparagines are synthesised by the action of aromatic amines on *l*-bromosuccinamic acid. In this way, aniline gives *l*-phenylasparagine, m. p. 147—148°, anisidine gives *l*-anisylasparagine, m. p. 135°, and *m*-toluidine gives *l*-m-tolylasparagine, m. p. 160—161°. These substances slowly lose their *l*-rotatory power if kept for some time with mineral acids. R. T.

β -Arylamino-ethanols. ROGER ADAMS and J. B. SEGUR (*J. Amer. Chem. Soc.*, 1923, **45**, 785—790).— β -Aminoethanols have been synthesised as follows: (1) the condensation of β -chloroethyl chloroformate with a primary amine in benzene solution, with formation of a β -chloroethyl carbamate; (2) the action of aqueous or alcoholic sodium or potassium hydroxide (1 mol.) on the β -chloroethyl carbamate, to give an oxazolidone; (3) the action of aqueous or alcoholic sodium or potassium hydroxide (4 mols.) on the oxazolidone. The last two reactions may be carried out in a single operation.

The following compounds are described. β -Chloroethyl *o*-tolylcarbamate, white needles, m. p. 45°, b. p. 209—210°/37 mm. β -Chloroethyl *p*-tolylcarbamate, white crystals, m. p. 61°. β -Chloroethyl *o*-chlorophenylcarbamate, white needles, m. p. 56.5—57°. β -Chloroethyl *p*-chlorophenylcarbamate, white needles, m. p. 62—63°. β -Chloroethyl *p*-ethoxyphenylcarbamate, white needles, m. p. 94°. 3-*o*-Tolyl-2-oxazolidone, straw-coloured oil, b. p. 180—185°/3 mm. 3-*p*-Tolyl-2-oxazolidone, white needles, m. p. 91°. 3-*o*-Chloro-

phenyl-2-oxazolidone, straw-coloured oil, b. p. 185—188°/3 mm. 3-*p-Chlorophenyl-2-oxazolidone*, white needles, m. p. 118·5—119°. 3-*p-Phenetyl-2-oxazolidone*, white crystals, m. p. 96°. β -*Anilinoethyl alcohol*, an oil, b. p. 280—285°/755 mm. or 167—170°/19 mm. β -*o-Toluidinoethyl alcohol*, an oil, b. p. 145—150°/3 mm. β -*p-Toluidinoethyl alcohol*, a straw-coloured oil, b. p. 153—155°/4 mm., and white plates, m. p. 42—43°. β -*o-Chloroanilinoethyl alcohol*, a straw-coloured oil, b. p. 148—152°/3 mm. β -*p-Chloroanilinoethyl alcohol*, white needles, m. p. 77—77·5°. β -*p-Phenetidinoethyl alcohol*, white crystals, m. p. 68·5—69°.

It is shown that the physiological properties of 3-*p*-phenetyl-2-oxazolidone are very similar to those of phenacetin. W. S. N.

Decomposition of Aryl Formamides. Preparation of Substituted Carbamides. A. MAILHE (*Compt. rend.*, 1923, 176, 689—691).—The catalytic decomposition of arylformamides, for example, formanilide, by alumina at 400° results mainly in the formation of aniline and carbon monoxide. Dehydration occurs to a relatively small extent with production of benzonitrile according to the scheme $\text{H}\cdot\text{CO}\cdot\text{NHPh} \rightarrow \text{H}_2\text{O} + \text{PhNC} \rightarrow \text{PhCN}$. The water produced also reacts to a slight extent with the carbylamine to give aniline and carbon monoxide, and with the formanilide to give aniline and formic acid, which in its turn is resolved into carbon dioxide and hydrogen. Contact with nickel at 340—350° also causes resolution of formanilide into aniline and carbon monoxide, but at 400—410° with rapid passage of the vapours, the aniline interacts with unchanged formanilide to give diphenylcarbamide: $\text{H}\cdot\text{CO}\cdot\text{NHPh} + \text{PhNH}_2 \rightarrow \text{H}_2 + \text{CO}(\text{NHPh})_2$, which crystallises in the outlet tubes and in the condensate. The formotoluidides behave in a perfectly analogous manner; *di-o-tolylcarbamide*, m. p. 243°, *di-m-tolylcarbamide*, m. p. 203°, and *di-p-tolylcarbamide*, m. p. 241°, were thus prepared. G. F. M.

New Method of Preparing Tetra-substituted Carbamides. A. MAILHE (*Compt. rend.*, 1923, 176, 903—905).—The catalytic decomposition by nickel at 400° (cf. preceding abstract) of formo-*o*-xylylidide, m. p. 97°, gives *di-o-xylylcarbamide*, $\text{CO}(\text{NH}\cdot\text{C}_6\text{H}_3\text{Me}_2)_2$, m. p. 236°, whilst formo-1-methyl-3-ethylphenyl-6-amide, m. p. 151°, yields *s-dimethylethylphenylcarbamide*, m. p. 215°. The formyl derivatives of secondary aromatic amines react in a precisely analogous manner giving tetra-substituted carbamides together with hydrogen, and carbon monoxide and dioxide, and a certain amount of regenerated amine according to the equations: $\text{NMePh}\cdot\text{COH} = \text{CO} + \text{NHMePh}$, and $\text{NMePh}\cdot\text{COH} + \text{NHMePh} = \text{H}_2 + \text{CO}(\text{NMePh})_2$. Thus methylformanilide, a yellow viscous liquid, b. p. 286°, gives a mixture of methylaniline and *diphenyldimethylcarbamide*, $\text{CO}(\text{NMePh})_2$, b. p. 245—246°. Ethyl-*o*-toluidine gives a *formyl* derivative, b. p. 272°, which is similarly catalysed to *di-o-tolyl-diethylcarbamide*, b. p. 258—260°, and 1-methyl-3-ethylphenyl-6-amine gives a *formyl* derivative, m. p. 141°, which is catalysed to *dimethylethylphenyldiethylcarbamide*, $\text{CO}(\text{NEt}\cdot\text{C}_6\text{H}_3\text{MeEt})_2$, a yellow liquid, b. p. 295°. G. F. M.

The Constituents of Lignite Tars. Lignite Tar Creosote Oils. R. AVENARIUS (*Z. angew. Chem.*, 1923, **36**, 165—168).—These oils are composed of phenols and small quantities of carboxylic acids, the latter occurring almost exclusively in low-temperature tars. Lignite itself has been shown to contain both phenols and acids (Hoffmann, *Z. angew. Chem.*, 1921, **34**, 217; Erdmann, *ibid.*, 309, also *J. Soc. Chem. Ind.*, 1921, 570A). The carboxylic acids, extracted with sodium carbonate, undergo decomposition when distilled at atmospheric pressure and even to some extent on distillation under diminished pressure. They are readily converted into their methyl esters and these submitted to fractional distillation under diminished pressure, although here, as in the case of the free acids, a sharp separation is impossible. Fractions boiling within ranges of 10° were collected separately and analysed. The results show that the acids are monobasic and contain a decreasing percentage of hydrogen with increasing molecular weight. The lower fractions comprised mainly acids of the type $C_nH_{2n-2}O_2$, whilst the higher contained also those of the type $C_nH_{2n-4}O_2$. The presence of esters of unsaturated acids was shown by the behaviour of the fractions towards potassium permanganate and bromine. Treatment with the latter, followed by distillation, destroyed the esters of the unsaturated acids, leaving unaltered those of the acids of the type $C_nH_{2n-2}O_2$. The latter appeared to be saturated naphthenic acids (*e.g.* the esters $C_7H_{13}\cdot CO_2Me$ and $C_8H_{15}\cdot CO_2Me$, boiling at $103\text{--}106^{\circ}/13$ mm. and $127\text{--}133^{\circ}/12$ mm., respectively, are found in the mixture of esters after treatment as above).

The crude phenols, containing water, were submitted to repeated fractional distillation under diminished pressure and the individual fractions treated, in absolute ethereal solution, with carbamyl chloride, whereby crystalline carbamic and allophanic esters were obtained. The former were fractionally crystallised from light petroleum or benzene (they are hydrolysed by boiling water), whilst the allophanates, which were insoluble in the above two solvents, were crystallised from dilute methyl alcohol. These esters were identified both by analysis and by comparison with the carbamates and allophanates of a number of homologues of phenol, synthesised specially for the purpose.

By these means phenol itself was found to be absent, whilst the occurrence of *m*-cresol and *p*-xylenol was proved. The aromatic, unlike the aliphatic, carbamic esters decompose in the neighbourhood of their m. p. When distilled, the original phenol and cyanic acid are produced, part of the latter polymerising and remaining in the distillation flask as cyanuric acid. This is a useful method for recovering phenols from their carbamic esters. A similar difference exists between aromatic and aliphatic allophanates. Thiophenols were found in the creosote oil, mainly in the higher fractions. The following esters were synthesised for reference: Phenyl carbamate, colourless needles, m. p. 143° . *o*-Tolyl carbamate, colourless needles, m. p. 155° . *m*-Tolyl carbamate,

colourless, lance-like crystals, m. p. 115—116°. *p*-Tolyl carbamate, colourless needles, m. p. 154°. *m*-4-Xyllyl carbamate, colourless needles, m. p. 156°. *p*-Xyllyl carbamate, colourless, star-like clusters of needles, m. p. 113—114°. *o*-4-Xyllyl carbamate, needles, m. p. 123—133°. ψ -Cumyl carbamate, colourless needles, m. p. 151—152°. All these esters melt to clear liquids which become cloudy on further heating. *Allophanic* esters: *phenyl*, short, colourless needles, m. p. 178°. *p*-Tolyl, colourless needles, m. p. 199—200°. *m*-4-Xyllyl, colourless needles, decomp. at about 220°. *p*-Xyllyl, colourless needles, m. p. 203°. *o*-4-Xyllyl, needles, m. p. 183°. ψ -Cumyl, colourless needles, m. p. 213°. W. T. K. B.

Stereochemistry of Cyclic Alcohols, Aldehydes, and Carboxylic Acids. A. SKITA (*Annalen*, 1923, 431, 1—30).—Use has been made of the method already described (A., 1922, i, 534) to determine the configurations of the six methylcyclohexanols, the hexahydro-*o*-toluic acids and the hexahydro-*p*-toluic acids, but the configuration of the only known form of hexahydro-*m*-toluic acid remains undecided.

[With H. HÄUBER and R. SCHÖNFELDER.]—The reduction of *o*-cresol by means of colloidal palladium and hydrogen in neutral solution gives an 80% yield of 1-methylcyclohexan-2-one, together with traces of *cis*-1-methylcyclohexan-2-ol. Continued reduction under similar conditions of the ketone or of *o*-cresol leads to an 81% yield of *trans*-1-methylcyclohexan-2-ol, which is also produced in 81% yield when the ketone is reduced by means of sodium in moist ethereal solution. The reduction of *o*-cresol or of the ketone by means of palladium-hydrogen in acetic acid solution leads to a 75% yield of the *cis*-alcohol (above), which is converted by means of fuming hydriodic acid into *cis*-2-iodo-1-methylcyclohexane, yield 64%. This iodo-compound reacts with magnesium and carbon dioxide in ethereal solution to give a poor yield of *cis*-1-methylcyclohexane-2-carboxylic acid, which is also formed by the reduction of *o*-toluic acid by means of palladium-hydrogen in acetic acid solution, yield 83%. Incidentally, cyclohexane-carboxylic acid is prepared in 83% yield from benzoic acid by the same method. The *trans*-alcohol (above) yields the *trans*-iodo-derivative, from which *trans*-1-methylcyclohexane-2-carboxylic acid is prepared, in 20% yield. The ethyl ester of the *cis*-acid is reduced by means of sodium and alcohol in 38% yield to *cis*-1-methylcyclohexyl-2-carbinol, which is oxidised by means of chromic acid in acetic acid solution to *cis*-2-aldehydo-1-methylcyclohexane, yield 35%. Similarly, the ethyl ester of the *trans*-acid yields the *trans*-carbinol and the *trans*-aldehyde. The *cis*-acid is quantitatively converted into the *trans*-acid by treatment with gaseous hydrogen chloride.

trans-1-Methylcyclohexan-4-ol results from the reduction of *p*-cresol in neutral solution; in acid solution, the *cis*-alcohol is formed. From these, the *trans*-iodo- and the *cis*-iodo-derivatives, respectively, are formed by the action of fuming hydriodic acid; both iodo-compounds lead, however, to the same *trans*-1-methyl

cyclohexane-4-carboxylic acid. This acid is also produced by the action of gaseous hydrogen chloride on the mixture of *cis*-acid and *trans*-acid which is formed by the catalytic reduction of *p*-toluic acid in acid solution. The reduction of the amide of *p*-toluic acid by means of palladium-hydrogen in acid solution gives a 96% yield of the amide of *cis*-1-methylcyclohexane-4-carboxylic acid, which is converted by means of nitrous acid into the *cis*-acid; the latter, being unstable, is esterified before purification. The ethyl ester of the *trans*-acid, from which the *trans*-amide is prepared, and the ethyl ester of the *cis*-acid, both give, on reduction by means of sodium and alcohol, *trans*-1-methylcyclohexyl-4-carbinol in 38% yield; from this the *trans*-aldehyde is obtained on oxidation by means of chromic acid in acetic acid solution; yield 25%.

m-Cresol gives *cis*-1-methylcyclohexan-3-ol on reduction in acid solution, *trans*-1-methylcyclohexan-3-ol in neutral solution. Both these alcohols lead, by the action of hydriodic acid, to the same iodo-derivative, which is converted by treatment with magnesium and carbon dioxide in ethereal solution into the only known form (liquid) of 1-methylcyclohexane-3-carboxylic acid; the latter is also produced by the catalytic reduction of *m*-toluic acid in acid solution. The reduction of the ethyl ester of the acid by means of sodium and alcohol leads to 1-methylcyclohexyl-3-carbinol, which gives the corresponding aldehyde on oxidation.

A *heptanaphthenecarboxylic acid* from Balachany petroleum, b. p. 190—192°, *amide*, m. p. 126°, has been shown to be different from any of the five known hexahydrotoluic acids.

It is shown that the physical constants of the compounds dealt with conform, with few exceptions, to Auwers's generalisation (A., 1920, i, 721).

The following compounds are new. *cis*-1-Methylcyclohexan-2-ol, b. p. 169·5—170·5° (corr.), and its *phenylurethane*, m. p. 95°. *Phenylurethane* of *trans*-1-methylcyclohexan-2-ol, m. p. 105°. *cis*-2-Iodo-1-methylcyclohexane, b. p. 96°/30 mm. *cis*-1-Methylcyclohexyl-2-carbinol, b. p. 188—189°; its *benzoate*, an oil. *cis*-2-Aldehydo-1-methylcyclohexane, b. p. 70°/24 mm., *semicarbazone*, m. p. 137—138°. *trans*-1-Methylcyclohexyl-2-carbinol, b. p. 192—192·5°, *benzoate*, an oil. *cis*-1-Methylcyclohexan-4-ol, b. p. 173·5—173·8°, *phenylurethane*, m. p. 98°. *Phenylurethane* of *trans*-1-methylcyclohexan-4-ol, m. p. 124—125°. *trans*-1-Methylcyclohexyl-4-carbinol, b. p. 197·5—198·5°, *benzoate*, an oil. *trans*-4-Aldehydo-1-methylcyclohexane, b. p. 75—76°/24 mm., *semicarbazone*, m. p. 183°. *Phenylurethane* of *cis*-1-methylcyclohexan-3-ol, m. p. 91°. *Phenylurethane* of *trans*-1-methylcyclohexan-3-ol, m. p. 76°. 1-Methylcyclohexyl-3-carbinol, b. p. 198—199°, *benzoate*, an oil. 3-Aldehydo-1-methylcyclohexane, b. p. 95°/35 mm., and its *semicarbazone*, m. p. 175·5°.

W. S. N.

The Fusion Curves of Binary Mixtures of α -Nitronaphthalene with the three Dihydroxybenzenes and of the Dihydroxybenzenes with Each Other. PIERRE SENDEN (*Bull. Soc. chim. Belg.*, 1923, 32, 97—102).—A study of the fusion curves of binary

mixtures of α -nitronaphthalene, quinol, resorcinol, and pyrocatechol leads to the conclusion that no compounds are formed between any two of these substances. H. J. E.

The Methylating and Sulphonating Action of Methyl Sulphate on Phenols in the Absence of Water. L. J. SIMON and M. FRÉJACQUES (*Compt. rend.*, 1923, 176, 900—902).—The action of methyl sulphate on phenol at 100—120° in the absence of water and alkali gives rise to numerous products owing to the superposition of a sulphonating action on the normal methylating action of this reagent. Both the phenol and the anisole formed from it are in part converted into sulphonic acids, and a proportion of the latter is methylated, so that the reaction mixture contains the free sulphonic acids of both phenol and anisole and their methyl esters, together with methyl hydrogen sulphate and sulphuric acid, and methyl ether is evolved, according to the equations: $\text{PhOH} + \text{Me}_2\text{SO}_4 = \text{PhOMe} + \text{MeHSO}_4$; $\text{PhOMe} + \text{Me}_2\text{SO}_4 = \text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{H} + \text{Me}_2\text{O}$; $\text{PhOH} + \text{Me}_2\text{SO}_4 = \text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{H} + \text{Me}_2\text{O}$; $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{H} + \text{Me}_2\text{SO}_4 = \text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{Me} + \text{MeHSO}_4$; $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{H} + \text{Me}_2\text{SO}_4 = \text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{Me} + \text{MeHSO}_4$. Treatment of anisole by methyl sulphate in the same way gives the same products but in different proportions, and the formation of phenol-sulphonic acid shows that a demethylating action occurs to some extent. A similar series of products was obtained from the cresols. The methyl sulphonates are crystalline substances, which distil at 150—160°/1—2 mm. Methyl phenolsulphonate melts at 95°, methyl anisolesulphonate at 30°, the corresponding derivatives from *o*-cresol at 93° and 58° respectively, and from *p*-cresol at 70° and 70° respectively. The methyl sulphonates are themselves methylating agents, readily giving substituted methylamines with primary amines such as aniline and *o*-toluidine, and methyl ethers with phenols in presence of an alkali. G. F. M.

The Reactions of Esters with Organomagnesium Derivatives. V. G. L. STADNIKOV (*J. Russ. Phys. Chem. Soc.*, 1916, 48, 1870—1874; cf. A., 1914, i, 954; 1916, i, 259, 260; 1917, i, 136).—Ethyl formate is allowed to react with magnesium phenyl bromide in the presence of a small quantity of iodine. The products of this reaction are benzhydryl ethyl ether and dibenzhydryl ether. The formation of these substances is due to the formation of some benzhydryl iodide, which reacts with the bromomagnesium ethoxide produced in the first part of the reaction giving the mixed ether, or with bromomagnesium benzhydryloxyde to give the simple ether. The formation of benzhydryl iodide as an intermediate product of the reaction is proved by the formation of tetraphenylethane in the following reaction. Iodomagnesium benzhydryloxyde is prepared from excess of magnesium, benzhydryl, and iodine, ethyl formate is added, and the solution boiled. A number of tarry products are formed, from which tetraphenylethane (formed by the elimination of iodine from two molecules of benzhydryl iodide) is separated. The reaction between magnesium α -naphthyl bromide and ethyl formate gave a quantity of tarry matter from

which some ethyl di- α -naphthylmethyl ether is isolated. This is formed in the same way as the corresponding diphenyl substance in the previous experiment. R. T.

The Reactions of Iodomagnesium Alkylloxides with Esters. II. G. L. STADNIKOV (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1875—1881); cf. A., 1915, i, 975).—Iodomagnesium menthyl oxide is formed by the action of menthol on magnesium methyl iodide, and an excess of ethyl formate is added. After boiling for twenty hours, menthyl formate is separated from the reaction mixture. Iodomagnesium triphenylcarbinyl oxide is prepared from triphenylcarbinol and magnesium methyl iodide. To this ethyl formate and a little iodine are added, and the mixture is boiled for forty hours. A variety of products results, from which triphenylcarbinyl peroxide is isolated, produced by the action of atmospheric oxygen on the hexaphenylethane formed by the elimination of iodine from two molecules of triphenylcarbinyl iodide. A larger yield of the peroxide is obtained by repeating the previous reaction in the presence of excess of magnesium, and at the same time some ethyl triphenylcarbinyl ether is formed. Iodomagnesium benzhydrioxide is prepared by the action of benzhydrol on magnesium methyl iodide, and is boiled for thirty hours with ethyl formate. In the reaction products, tetraphenylethane, formed from two molecules of benzhydriol iodide by the elimination of iodine, is found, together with dibenzhydriol ether and benzhydriol ethyl ether, formed by the interaction of iodomagnesium ethoxide with benzhydriol formate. On repeating this reaction, using an excess of magnesium, an increased yield of tetraphenylethane is obtained, proving that benzhydriol iodide is an intermediate product in the formation of the ethers. The same reaction was repeated, using ethyl acetate instead of ethyl formate, and resulted in the production of tetraphenylethane and of a quantity of tarry matter from which no identifiable product was isolated.

R. T.

β -Hydroxyarylethylamines. O. HINSBERG (U.S. Pat. 1432291).—The following β -hydroxyarylethylamines are prepared by interaction of aminoacetal with phenols in the presence of sulphuric, hydrochloric, or acetic acid: From phenol, β -di-*p*-hydroxyphenylethylamine, m. p. about 95°; from thymol, di-4-hydroxy-3-isopropylphenylethylamine, colourless needles, m. p. 220°. From *m*-aminophenol, β -hydroxy- β -2-amino-4-hydroxyphenylethylamine, flakes. From pyrocatechol, β -hydroxy- β -di-*o*-hydroxyphenylethylamine, m. p. 190°. From pyrogallol, β -hydroxy- β -trihydroxyphenylethylamine, very unstable. From gallic acid, β -hydroxy- β -trihydroxycarboxyphenylethylamine, which is not precipitated when ammonia is added to an aqueous solution of the hydrochloride. Methylaminoacetal and pyrocatechol yield β -hydroxy- β -di-*o*-hydroxyphenylmethylethylamine and $\beta\beta$ -di-*o*-hydroxyphenylmethylethylamine, which can be separated by fractional crystallisation of the hydrochlorides, the former (adrenaline) being the non-crystallising portion. *N*-Diisamylaminoacetal and pyrogallol yield β -hydroxy- β -trihydroxy

phenylethyl-diisoamylamine which is precipitated in flakes by the addition of ammonia to a solution of the hydrochloride. $\beta\beta$ -*Di-2-hydroxynaphthylethylamine*, from aminoacetal and β -naphthol, has m. p. about 124°. Interaction of sodium α -naphthol-8-sulphonate and aminoacetal, followed by addition of hydrochloric acid and washing with water, yields a *product*, m. p. above 250°.

CHEMICAL ABSTRACTS.

Naphthenic Acids Derived from Japanese Petroleum. YOSHIO TANAKA and SHOICHIRO NAGAI (*J. Amer. Chem. Soc.*, 1923, **45**, 754—756; *J. Chem. Ind. Japan*, 1922, **25**, 1031—1044).—By acidifying the waste lyes from the Akita petroleum refinery, a crude mixture of petroleum acids is obtained. Neutral impurities are removed by converting the crude acids into the potassium salts and extracting the aqueous-alcoholic solution by means of light petroleum. The acids are reprecipitated by acidification, and alkyl-sulphuric acids removed by distilling the mixture under reduced pressure after the addition of copper oxide. The distillate is again converted into the potassium salts and the aqueous solution extracted by means of light petroleum. The crude acid produced on acidification is fractionally distilled and the fraction b. p. 170—220°/9 mm. is converted into a mixture of methyl esters. These are then separated by repeated fractional distillation. *Methyl tridecanaphthenate*, b. p. 124—126°/9 mm. or 262—263°/760 mm., d_4^{15} 0.9622, n_D^{15} 1.4663; *methyl tetradecanaphthenate*, b. p. 135—137°/9 mm. or 277—278°/760 mm., d_4^{15} 0.9644, n_D^{15} 1.4686, and *methyl pentadecanaphthenate*, b. p. 147—149°/9 mm. or 296—297°/760 mm., d_4^{15} 0.9659, n_D^{15} 1.4728, are colourless liquids, possessing a fruity odour. The pure naphthenic acids are obtained as colourless, odourless liquids by hydrolysis of the esters by means of 2*N*-alcoholic potassium hydroxide solution. *Tridecanaphthenic acid*, b. p. 167—169°/9 mm., d_4^{15} 0.9916, n_D^{15} 1.4784; *tetradecanaphthenic acid*, b. p. 178—180°/9 mm., d_4^{15} 0.9930, n_D^{15} 1.4807, and *pentadecanaphthenic acid*, b. p. 191—192°/9 mm., d_4^{15} 0.9941, n_D^{15} 1.4848, have no iodine number, and are not discoloured on exposure to the air.

W. S. N.

Decomposition of Aminobenzoic Acids by Boiling Water. L. MCMASTER and R. L. SHRINER (*J. Amer. Chem. Soc.*, 1923, **45**, 751—753).—*o*-Amino- and *p*-amino-benzoic acids, but not *m*-aminobenzoic acid, are decomposed by boiling water into aniline and carbon dioxide; the reaction is unimolecular, the ortho-acid decomposing twice as fast as the para-acid. Both *o*-aminobenzoic acid and *p*-aminobenzoic acid are slightly volatile in steam, whilst *m*-aminobenzoic acid is not.

W. S. N.

Catalysis and Steric Hindrance. G. VAVON and A. HUSSON (*Compt. rend.*, 1923, **176**, 989—991).—The catalytic hydrogenation by means of platinum black of cinnamic acid derivatives was studied from the point of view of steric hindrance. The method adopted consisted in mixing 1 mol. proportion of the substance to be studied with 1 mol. of pinene, and after the fixation of 1 mol.

of hydrogen the proportion of the cinnamic acid derivative hydrogenised compared with the total amount of the mixed substances hydrogenised was determined by an observation of the change of rotation produced. The results obtained were strictly in accordance with the theory of steric hindrance, as is seen from the following figures which express the percentage which the dihydrocinnamic acid derivative forms of the total substances hydrogenised: *Series 1.* Cinnamic acid 57, β -methylcinnamic acid 26, α -methylcinnamic acid 22, $\alpha\beta$ -dimethylcinnamic acid 19. *Series 2.* Methyl cinnamate 63, methyl β -methylcinnamate 45, ethyl α -methylcinnamate 26. *Series 3.* Ethyl cinnamate 58, ethyl β -methylcinnamate 31, methyl α -methylcinnamate 22. *Series 4.* Methyl cinnamate 61, ethyl cinnamate 56, isobutylcinnamate 50, cyclohexylcinnamate 40.

G. F. M.

Ketens. XLIV. Inorganic Substituted Ketens. H.

STAUDINGER and H. SCHNEIDER (*Helv. Chim. Acta*, 1923, 6, 304—315).—It was to be expected that ketens with inorganic substituent groups such as halogen or hydroxyl would be comparatively stable substances, but this proves not to be the case. Halogen atoms decrease the stability and deepen the colour of ketens. Dichloroketen apparently cannot exist, chloroethylketen is very unstable, bromomethylketen is somewhat more stable and can be isolated. Oxygen-substituted ketens are extremely unstable; the existence of phenoxyethylketen and of diphenoxyketen have been established, but they could not be isolated.

Diphenylacetic-bromoethylmalonic anhydride decomposes at 88—89°. By distilling this at 15 mm., *bromoethylketen* was obtained as a reddish-brown, very unstable liquid, b. p. -40° at 0.03 mm. With aniline, it gives *bromoisobutyranilide*, m. p. 97—98°; with alcohol, it gives ethyl α -bromoisobutyrate. *Ethoxymethylmalonic acid* has m. p. 112° ; with diphenylketen, it forms *diphenylacetic-ethoxymethylmalonic anhydride*, m. p. 86° . No trace of ethoxymethylketen could be obtained by heating the anhydride. *Diethoxymalonic acid* has m. p. 159° (decomp.); *diphenylacetic-diethoxymalonic anhydride* melts with slight decomposition at 101 — 102° ; it gave no diethoxyketen when heated. *Ethyl phenoxyethylmalonate*, b. p. 170 — $180^{\circ}/12$ mm., was obtained by boiling ethyl bromoethylmalonate with sodium phenoxide solution; *phenoxyethylmalonic acid* forms crystals, m. p. 106° ; *diphenylacetic-phenoxyethylmalonic anhydride* crystallises in long needles, decomposing at 94° . Phenoxyethylketen could not be obtained directly from this, but its formation was proved by heating the anhydride with benzophenone-aniline, when the β -lactam of β -anilino- α -phenoxy- $\beta\beta$ -diphenyl- α -ethylpropionic acid was obtained, colourless needles, m. p. 164° . No β -lactam could be obtained with benzylideneaniline, or even with the more reactive *p*-methoxybenzylideneaniline; these did not react with sufficient rapidity with the fugitive keten.

Methyl diphenoxymalonate was prepared from methyl dibromomalonate and sodium phenoxide in methyl alcohol solution; it has m. p. 86° . *Diphenoxymalonic acid*, m. p. 173° , forms, with

diphenylketen, *diphenylacetic-diphenoxymalonic anhydride*, decomposing at 79°. Diphenoxyketen was not isolated, but its formation was proved by obtaining its aniline derivative, *diphenoxyacetanilide*, which was also prepared from diphenoxyacetic acid; it forms white crystals, m. p. 120°. By heating the above anhydride with benzylideneaniline, β -*anilino- α -diphenoxy- β -phenylpropionic- β -lactam*, white crystals, m. p. 165°, was obtained, and with methoxybenzylideneaniline, β -*anilino- α -diphenoxy- β -anisoylpropionic- β -lactam*, colourless crystals, m. p. 143°. E. H. R.

Ketens. XLV. Attempts to Prepare an Alleneketen. H. STAUDINGER and H. SCHNEIDER (*Helv. Chim. Acta*, 1923, 6, 316—321).—Attempts to prepare a keten containing the allene structure, by heating the mixed anhydride from benzylidenemalonic acid and diphenylketen were unsuccessful; instead of the keten, $\text{Ph}\cdot\text{CH}\cdot\text{C}\cdot\text{C}\cdot\text{O}$, only diphenylketen could be obtained. No better result was obtained by heating *benzylidenemalonic-acetic anhydride*, obtained as a yellow syrup from sodium benzylidenemalonate and acetyl bromide. *Benzylidenemalonic anhydride*, $\text{C}_{10}\text{H}_6\text{O}_3$, was obtained by the action of oxalyl chloride on silver benzylidenemalonate in benzene. It forms a pale yellow, hygroscopic, amorphous powder, and is apparently highly polymerised. When heated, it decomposes without formation of any benzylideneketen. When silver benzylidenemalonate is distilled under reduced pressure, it decomposes, among the products being cinnamic acid and phenylacetylene. Attempts to apply the mixed malonic anhydride method to the preparation of *isopropylideneketen* from *isopropylidenemalonic acid* failed.

Attempts were also made to apply the same method to the preparation of ketens containing the grouping $\text{N}\cdot\text{C}\cdot\text{C}\cdot\text{O}$. Phenylhydrazinomalonic acid, $\text{NHPh}\cdot\text{N}\cdot\text{C}(\text{CO}_2\text{H})_2$, failed to react with diphenylketen and when the mixture was heated only a tar was obtained. *Diphenylhydrazinomalonic acid* was prepared by condensing mesoxalic acid with *as*-diphenylhydrazine in aqueous methyl alcohol; it forms fine needles, m. p. 164°. It decomposes in aqueous solution forming carbon dioxide, hydrocyanic acid, and diphenylamine. It does not react in the cold with diphenylketen; in the hot, complete decomposition occurs. No keten could be obtained from *isonitrosobenzylmalonic acid* by the action of diphenylketen. E. H. R.

Utilisation of *p*-Dichlorobenzene for Synthesis in the Diphenic Acid Series. EDWARD B. HUNN (*J. Amer. Chem. Soc.*, 1923, 45, 1024—1030).—*p*-Dichlorobenzene is converted successively into 2:5-dichloronitrobenzene, 4-chloro-2-nitroaniline, 4-chloro-2-nitrobenzonitrile, 4-chloro-2-nitrobenzoic acid, and 4-chloro-2-aminobenzoic acid; the latter is diazotised in dilute aqueous sulphuric acid solution and the diazotised solution gradually added at 20° to an ammoniacal solution of cuprous oxide. The product is 5:5'-*dichlorodiphenic acid*, straw-coloured plates, m. p. 297°; *anhydride*, nearly colourless needles, m. p. 206° (corr.). 2-Amino-4-chlorobenzamide, colourless, oblong plates, m. p. 181.5° (corr.), is

formed by the action of iron and acetic acid on 4-chloro-2-nitrobenzonitrile, in attempting to prepare 4-chloro-2-aminobenzonitrile. The *benzoyl* derivative of 4-chloroanthranilic acid, colourless needles, m. p. 223.5° (corr.), and the *methyl* ester, colourless needles, m. p. 68.5°, are also described. W. S. N.

The Molecular Configuration of Polynuclear Aromatic Compounds. II. 4:6:4'-Trinitrodiphenic Acid and its Resolution into Optically Active Components. GEORGE HALLATT CHRISTIE and JAMES KENNER (T., 1923, 123, 779—785).

Chemistry of Polycyclic Structures in Relation to their Homocyclic Unsaturated Isomerides. IV. The Simulation of Benzenoid Properties by the Five-carbon Intra-annular Nucleus. CHRISTOPHER KELK INGOLD, ERNEST ARTHUR SEELEY, and JOCELYN FIELD THORPE (T., 1923, 123, 853—874).

Equilibrium between Benzaldehyde and Benzoin. ERNEST ANDERSON and RALPH A. JACOBSON (*J. Amer. Chem. Soc.*, 1923, 45, 836—839).—The benzoin condensation is a reversible process; the equilibrium constant between benzaldehyde and benzoin at 79° is very nearly 0.245. The reagents are brought to equilibrium in 95% alcohol in an atmosphere of nitrogen; the benzoin is determined by precipitation by means of water. When benzaldehyde serves as starting material, equilibrium is reached in one hour, but when benzoin is used, 1.5 hours are required. The usual catalyst, sodium cyanide, is utilised. The solvent used in the most satisfactory method for preparing benzoin is 50% alcohol, from which the product is precipitated. W. S. N.

Dihydroxyphenones and Derivatives. B. H. GNAGY (*J. Amer. Chem. Soc.*, 1923, 45, 805—808).—The preparation is described (cf. Goldzweig and Kaiser, A., 1891, 447) of 2:4-dihydroxy-1-propiophenone, which reacts, in acetic acid solution, with bromine to give 3:5-dibromo-2:4-dihydroxy-1-propiophenone, white crystals, m. p. 148°, *phenylhydrazone*, rosettes of small, short, greenish-yellow needles, m. p. 173°, decomp. The action of resorcinol on butyric acid in the presence of zinc chloride leads to the formation of 2:4-dihydroxy-1-butyrophenone, *phenylhydrazone*, m. p. 191—193°, decomp., which reacts with bromine in acetic acid solution to give 3:5-dibromo-2:4-dihydroxy-1-butyrophenone, silky needles, m. p. 113°, *phenylhydrazone*, yellow, hexagonal crystals, m. p. 155°. W. S. N.

Ketens. XLII. The Preparation of Ketens from Malonic Anhydrides. H. STAUDINGER, H. SCHLUBACH, and H. SCHNEIDER (*Helv. Chim. Acta*, 1923, 6, 287—290).—It was shown some years ago (A., 1913, i, 1339) that dialkylketens could be prepared by heating the mixed anhydrides obtained by the action of diphenylketen on dialkylmalonic acid. Attempts to apply this method to the preparation of aldoketens from mono-substituted malonic acids have failed, since mixed anhydrides are not obtained by the

action of diphenylketen on mono-substituted malonic acids. The reaction failed with methyl-, ethyl-, phenyl-, benzyl-, chloro-, bromo-, and ethoxy-malonic acids as well as with malonic acid itself. In every case, only diphenylacetic anhydride was obtained. The probability is that, by the action of diphenylketen on a mono-substituted malonic acid, a ketencarboxylic acid is formed thus: $\text{RCH}(\text{CO}_2\text{H})_2 + 2\text{Ph}_2\text{C}:\text{CO} \rightarrow \text{RC}(\text{CO}_2\text{H})_2:\text{CO} + (\text{Ph}_2\text{CH}\cdot\text{CO})_2\text{O}$, the ketencarboxylic acid then forming high-molecular polymerisation products.

In the preparation of sparingly volatile ketens such as dibenzylketen by the above method, difficulty is sometimes experienced on account of the decomposition of diphenylacetic anhydride into diphenylacetic acid and diphenylketen, the latter distilling over whilst the free acid combines with the new keten. In such cases, it has been possible to extract the keten from the anhydride with a solvent. Dichloro- and diethoxy-ketens could not be obtained; they probably cannot exist, since by the method employed a keten such as ethylechloroketen, which has only a short life at -80° , can be isolated. Very unstable ketens can be recognised by combining them with Schiff's bases, with which they form well crystallised β -lactams.

Attempts to obtain mixed anhydrides of malonic acid with acetic, isobutyric, or benzoic acid were unsuccessful. With oxalic acid, a mixed anhydride was obtained which decomposed, giving a mixture of carbon monoxide and dioxide.

Acetylenedicarboxylic acid reacts slowly with diphenylketen; a crystalline mixed anhydride is not formed, but when the mixture is heated a little carbon suboxide is obtained. Acetonedicarboxylic acid does not form a mixed anhydride with diphenylketen, nor could the expected diketocyclobutane be obtained as a decomposition product of the mixture.

E. H. R.

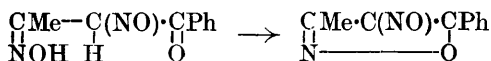
Ketens. XLIII. Alkyl- and Aryl-substituted Ketoketens. H. STAUDINGER, H. SCHNEIDER, P. SCHOTZ, and P. M. STRONG (*Helv. Chim. Acta*, 1923, 6, 291—303).—To determine the influence of substituents on the stability and colour of disubstituted ketens, a number of new ketens have been prepared by the decomposition of mixed anhydrides (cf. previous abstract). The stability of the ketens increases considerably with the weight of the alkyl groups in dialkylketens. Whilst at 25° dimethylketen polymerises to the extent of 70% in six hours, diethylketen polymerises only 28% in twenty days and dipropylketen 9% in twenty-eight days. The reactivity towards Schiff's bases decreases with increasing molecular weight, but the colour is unchanged. Dibenzylketen, on the other hand, is less stable than dimethylketen, and in a few hours changes completely into diketotetrabenzylcyclobutane. The influence of the phenyl group is remarkable, for whilst diphenylketen polymerises very slowly, it is more reactive than dimethylketen. In the side chain, the phenyl group diminishes the stability of the keten whilst increasing the reactivity of the ethylene linking. The behaviour of the substituted ketens is paralleled by that of

the corresponding carbimides, of which benzylcarbimide is the most unstable. Diallylketen is a great deal more stable than dibenzylketen, polymerising 75% in five days. The instability of the latter cannot therefore be attributed to the $\beta\gamma$ -double bond.

Diphenylacetic-methylethylmalonic anhydride, $C_{31}H_{30}O_6$, was obtained by adding diphenylketen (2 mols.) to cold methylethylmalonic acid (1 mol.) in ether, and allowing the resulting solution to crystallise. Other mixed anhydrides were prepared similarly. It melts at 82° (decomp.). *Methylethylketen* was obtained by distilling the mixed anhydride under reduced pressure and collecting the distillate at -80° ; it has b. p. -26° to $-28^\circ/12$ mm. *Diphenylacetic-diisopropylmalonic anhydride* can be crystallised from a mixture of carbon disulphide and light petroleum; it decomposes at 84° . When distilled under reduced pressure, it gives *diisopropylketen*, a yellow liquid with a suffocating odour, b. p. $30^\circ/11$ mm., the yield being 32% of theory. The yield was determined by converting the keten with aniline into *diisopropylacetanilide*, m. p. $103-104^\circ$. The polymerisation product of the keten, *diketotetrapropylcyclobutane*, forms colourless crystals, m. p. $61-62^\circ$. *Diphenylacetic-dibenzylmalonic anhydride* forms colourless crystals decomposing at 104° . *Dibenzylketen* (cf. preceding abstract) is a bright yellow, mobile liquid, b. p. $121-122^\circ/0.09$ mm. When the decomposition of the mixed anhydride takes place in presence of benzylidene-aniline, the β -lactam of β -anilino- β -phenyl- $\alpha\alpha$ -dibenzylpropionic acid, $NPh\langle\begin{smallmatrix} CHPh \\ CO \end{smallmatrix}\rangle C(CH_2Ph)_2$, is formed, white needles, m. p. 121° . *Diphenylacetic-benzylmethylethylmalonic anhydride* forms white needles, m. p. 91° . *Benzylmethylethylketen* is a yellow, mobile fluid with a suffocating odour, b. p. $45-47^\circ/0.1$ mm. *Diphenylacetic-diallylmalonic anhydride* decomposes at $95-96^\circ$. *Diallylketen* is a mobile liquid of unpleasant odour, b. p. $29-30^\circ/9$ mm., or $131^\circ/716$ mm., but the latter value is not exact, as some polymerisation occurs. At very low temperatures, it forms a colourless, crystalline mass, m. p. -123° . *Diallylacetanilide*, prepared to determine the yield of keten (80% theory) has m. p. $75-76^\circ$. *Diketotetra-allylcyclobutane* is a colourless liquid, b. p. $135^\circ/9$ mm. *Ethyl methylallylmalonate*, from ethyl allylmalonate and methyl iodide, has b. p. $112-115^\circ/17$ mm. *Methylallylmalonic acid* forms white crystals, m. p. $74-76^\circ$. *Diphenylacetic-methylallylmalonic anhydride* decomposes at $69-70^\circ$. *Methylallylketen* is a suffocating, yellow liquid, polymerising to the extent of 69% in twenty-four hours at 30° . The mixed anhydride from phenylmethylmalonic acid and diphenylketen decomposes in the cold and gives a 75% yield of phenylmethylketen. An attempt to prepare dimethyleneketene from cyclopropanedicarboxylic-diphenylacetic anhydride, white needles, m. p. 81° , was unsuccessful. E. H. R.

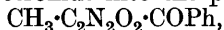
Dioximes. IV. G. PONZIO (*Gazzetta*, 1923, **53**, i, 15-19).—It has been shown previously (A., 1922, i, 1037) that the assumption that the β -oximino-group of α -benzoylmethylglyoxime may exist in the form $:CH\cdot NO$ suffices to explain the conversion of this

glyoxime into α -oximino- β - ψ -nitrole- α -keto- α -phenylbutane by the action of nitrogen tetroxide. The fact that α -benzoylmethylglyoxime loses a molecule of water and yields 4-nitroso-5-phenyl-3-methylisooxazole when treated with either acetic anhydride or anhydrous hydrochloric acid may also be explained on the same assumption :



On the other hand, the $\beta\gamma$ -dioximino- α -keto- α -phenylbutane structure is supported by the fact that the first of these reagents yields also the diacetyl compound, m. p. 113° (*loc. cit.*), whilst, with both reagents, loss of water occurs likewise in another way, giving benzoylmethylfurazan, $\text{O} < \begin{array}{l} \text{N:CMe} \\ \text{N:CBz} \end{array}$. Both these anhydrides are formed simultaneously when the α -glyoxime is heated either to the melting point or with water at 80—90°, but under such conditions the formation of the isooxazole compound is manifested only by a transitory bluish-green coloration.

β -Benzoylmethylglyoxime (m. p. 193°), which is converted by the action of nitrogen tetroxide into the peroxide,



melts without becoming green, and by acetic anhydride is converted completely into the diacetyl derivative, m. p. 68° (*loc. cit.*), no trace of nitrosoisooxazole being formed. When either heated with acetic anhydride or fused, it is transformed also into benzoylmethylfurazan, whilst the action of anhydrous hydrochloric acid yields a small proportion of 4-nitroso-5-phenyl-3-methylisooxazole in consequence of the preliminary isomerisation of part of the glyoxime into the α -form.

4-Nitroso-5-phenyl-3-methylisooxazole, $\text{C}_{10}\text{H}_8\text{O}_2\text{N}_2$ (see above), forms long, flattened, intensely blue needles, m. p. 84°; in the solid state it rapidly undergoes change to a green, and then to an almost colourless, oily substance, and when boiled with dilute sodium hydroxide solution it yields ammonia and benzoic acid.

Benzoylmethylfurazan, $\text{C}_{10}\text{H}_8\text{O}_2\text{N}_2$ (see above), crystallises in large, white prisms of slight and not unpleasant odour, m. p. 42°, b. p. about 255° (slight decomp.), and is extremely resistant towards even concentrated acids, permanganate in sulphuric acid solution, and chromic acid dissolved in acetic acid, but is decomposed by alkali hydroxide, rapidly when heated, into ammonia and benzoic acid. Its phenylhydrazone, $\text{C}_{16}\text{H}_{14}\text{ON}_4$, exists in two modifications : the labile α -form crystallises in long, golden-yellow needles, m. p. 101°; boiling dilute hydrochloric acid reconverts it into benzoylmethylfurazan, whilst 20% sodium hydroxide solution decomposes it with liberation of ammonia, the bulk of the hydrazone being transformed into the β -form by either of these reagents. The stable β -modification, which is obtained also when the α -form is heated slightly above its melting point, separates in white or pale yellow laminae, m. p. 214°, and is not sensibly altered when boiled with 20% sodium hydroxide or hydrochloric acid solution. The

p-nitrophenylhydrazone, $C_{16}H_{13}O_3N_5$, forms flattened, yellow needles, m. p. 178—182°, reddens superficially in the light, and yields a deep violet solution when suspended in sodium hydroxide solution and treated with a little alcohol. The *dinitrophenylhydrazone*, $C_{16}H_{13}O_5N_6$, obtained by the action of nitric acid (*d* 1·2) on either the α - or β phenylhydrazone or the *p*-nitrophenylhydrazone, forms orange-yellow laminae, m. p. 218°, with previous softening and reddening; when suspended in 20% sodium hydroxide solution and treated with a little alcohol, it yields a deep violet solution, which is decolorised on dilution with water. T. H. P.

Dioximes. V. G. PONZIO and A. PICCHETTO (*Gazzetta*, 1923, 53, i, 20—24).—Of the two possible dioximes of triketohydrindene, only the 1:3-isomeride, obtained by the action of nitrous acid on β -hydrindone (Heusler and Schieffer, A., 1899, i, 365) is known. The 1:2-dioxime, being analogous structurally to benzoylmethylglyoxime (A., 1922, i, 1037), should be capable of existing in two modifications. The authors find that this 1:2-form may be readily obtained by adding sodium acetate and the theoretical quantity of hydroxylamine hydrochloride to a suspension of 2-oximino-1:3-diketohydrindene in hot alcohol and maintaining the mixture for some time at 60—70°. It exists, however, in only one form, which is neither dehydrogenated nor transformed into the corresponding oximino- ψ -nitroleketo-compound by the action of nitrogen tetroxide. It gradually decomposes with evolution of nitrous fumes and, like its phenylhydrazone, crystallises with a molecule of alcohol. Thus, it exhibits certain properties of nitroso-derivatives, but it may be acetylated and benzoylated and in aqueous solution reacts with metallic nickel.

1:3-Diketohydrindene, for which improved conditions of preparation are given (cf. Wislicenus and Kötze, A., 1889, 1067), forms crystals of the tetragonal system [ZAMBONINI: $a:c=1:0\cdot984812$]; modified conditions are also given for making 2-oximino-1:3-diketohydrindene, which does not form a nickel salt, but when treated in aqueous-alcoholic solution with cobaltous acetate yields a cobaltic salt, $(C_6H_4\cdot C_2O_2\cdot C:NO)_3Co$, as a micro-crystalline, brownish-yellow powder, m. p. above 300° (decomp.). Thus, 2-oximino-1:3-diketohydrindene acts towards cobaltous salts like α -benzilmonoxime, whereas other α -oximinoketones yield cobaltous compounds.

Triketohydrindene 1:2-dioxime, $\begin{array}{c} CO-C:NOH \\ | \\ C_6H_4\cdot C:NOH \end{array}$, crystallises in white or pale straw-coloured prisms, m. p. 168° (decomp.), containing $1H_2O$, which is lost slowly at the ordinary temperature. It dissolves in solutions of alkali hydroxide or ammonia, giving reddish-yellow solutions from which it is precipitated unchanged by the action of carbon dioxide or a dilute mineral acid. With hydroxylamine hydrochloride and sodium acetate, it yields the corresponding trioxime (cf. Wislicenus and Kötze, *loc. cit.*). The *nickel* compound, $(C_6H_5O_3N_2)_2Ni$, forms microscopic, pale yellowish-brown crystals, turning brown at 180°, m. p. above 300°. The

diacetyl derivative, $C_{15}H_{10}O_5N_2$, is somewhat unstable and forms pale straw-yellow needles, m. p. 155° (decomp.). The *dibenzoyl* derivative, $C_{25}H_{14}O_5N_2$, forms microscopic needles, m. p. 174° (decomp.). The *phenylhydrazone*, $C_{15}H_{12}O_2N_4 \cdot EtOH$, crystallises in orange-red needles, m. p. $189-190^\circ$ (decomp.). T. H. P.

Dioximes. VI. G. PONZIO and L. AVOGADRO (*Gazzetta*, 1923, 53, i, 25-35).—The authors have investigated the two modifications of phenylglyoxime, m. p. 168° and 180° , regarded by Russanov (A., 1892, 321) as being the amphi- and anti-compounds, respectively, and have also obtained a second modification of aminophenylglyoxime. With such isomeric glyoximes, the prefix α is given to those which readily undergo isomerisation into the other or β -forms, the latter alone being able to form with nickel, copper, or cobalt complex salts derived from two molecules of the glyoxime by replacement of two oximinic hydrogen atoms, one from each molecule, by an atom of the bivalent metal. As might be foreseen from the results obtained with the benzoylmethylglyoximes (A., 1922, i, 1037), the two forms of phenylglyoxime behave differently towards nitrogen tetroxide, the α -form losing two atoms of hydrogen and giving the compound regarded by Scholl (A., 1891, 315) as the peroxide, $\begin{matrix} O:N:CH \\ | \\ O:N:CPh \end{matrix}$, and by Wieland

and Semper (A., 1908, i, 108) as phenylfuroxan; the β -form, on the other hand, loses three atoms of hydrogen, one of which is replaced by a nitro-group, the resultant product being phenylnitro-glyoxime peroxide. These results confirm the view that the isomerism of the two phenylglyoximes does not depend on the relative positions of the hydroxyl groups in space.

The conclusion is drawn that β -phenylglyoxime and β -benzoylmethylglyoxime, which yield complex nickel salts, are true dioximes, as they behave towards nitrogen tetroxide as if they contain two similar oximino-groups, the resulting peroxides being unaffected by ammonia. α -Phenylglyoxime, acetylmethylglyoxime, and α -benzoylmethylglyoxime, which do not form complex nickel salts, react with nitrogen tetroxide, giving rise, respectively, to the compound $C_6H_5 \cdot C_2HO_2N_2$, which with ammonia yields aminophenylglyoxime, to α -oximino- β - ψ -nitrole- γ -ketopentane, and to γ -oximino- β - ψ -nitrole- α -keto- α -phenylbutane (A., 1922, i, 627, 1037), which with ammonia yields aminomethylglyoxime. Hence the oximino-group of α -phenylglyoxime, which is united to the carbon atom carrying the hydrogen atom and originates by the action of nitrous acid on acetophenone, may, like the β -oximino-group of acetylmethyl- or benzoylmethyl-glyoxime resulting from the action of nitrous acid on acetyl- or benzoyl-acetone, assume a structure different from that of the oximino-group introduced into isonitrosoacetophenone, isonitrosoacetylacetone, or isonitroso-benzoylacetone by means of hydroxylamine.

The author's results show that Wieland and Semper (*loc. cit.*) are in error in assuming that the various modifications of one and the same dioxime give the same peroxide, even if, as follows from

the work of Korev (A., 1886, 363) and of Auwers and Meyer (A., 1889, 403, 713), α -, β -, and γ -benzildioximes give the same peroxide when dehydrogenated by means of potassium ferricyanide.

Addition of aqueous nickel acetate to an aqueous alcoholic solution of α -phenylglyoxime yields the amorphous, brownish-yellow nickel compound, probably $C_8H_6O_2N_2Ni$. With nitrogen tetroxide, the α -glyoxime gives the compound $C_8H_6O_2N_2$, m. p. 108° , which is perfectly stable in a stoppered bottle in the dark (cf. Wieland and Semper, *loc. cit.*).

In aqueous solution, β -phenylglyoxime acts on compact nickel, copper, or cobalt, slowly in the cold but rapidly at about 100° , this behaviour being characteristic of the glyoximes which Tschugaev terms *syn*-forms. The *nickel* salt, $(C_8H_7O_2N_2)_2Ni$, crystallises in dark red needles, m. p. 267° (browning); the *copper* salt, $(C_8H_7O_2N_2)_2Cu$, forms a coffee-coloured powder with green reflection, m. p. 181° (decomp.), and the *cobalt* salt, a coffee-coloured powder with red reflection. Russanov's statement that β -phenylglyoxime is transformed instantaneously into the α -form by all neutral solvents with the exception of absolute ether (*loc. cit.*) is erroneous. Nitrophenylglyoxime peroxide, obtained by the action of nitrogen tetroxide on β -phenylglyoxime in anhydrous ethereal solution, has the properties given by Wieland (A., 1903, i, 769), who found this compound among the products of the action of nitrous fumes on cinnamaldehyde.

Chlorophenylglyoxime, $NOH:CPh\cdot CCl:NOH$, prepared either by the action of hydroxylamine on chloro-oximinoacetophenone or by the action of chlorine on α - or β -phenylglyoxime, exists in only one modification, and crystallises in slender, white needles, m. p. 189 – 190° (decomp.). Its *nickel* salt, $(C_8H_6O_2N_2Cl)_2Ni$, forms slender, reddish-brown needles, m. p. 167° (decomp.), and its *diacetyl* derivative, $C_{12}H_{11}O_4N_2Cl$, slender, white needles, m. p. 82° .

β -*Aminophenylglyoxime*, $NOH:CPh\cdot C(NH_2):NOH$, obtained by boiling its α -isomeride with dilute acetic acid, and isolated as nickel salt, forms lustrous, white laminae, m. p., with rapid heating, 195° (sublim. and decomp.), and yields an intense brown coloration with ferric chloride. Its *nickel* salt, $(C_8H_8O_2N_3)_2Ni$, forms lustrous, orange-red laminae, m. p. 265 – 285° (decomp.), and the *copper* salt, $(C_8H_8O_2N_3)_2Cu$, lustrous, bronze-coloured laminae with metallic lustre, m. p., with rapid heating, 232° (decomp.). T. H. P.

The Transformation of Campholic Acid into Camphor. H. RUPE and A. SULGER (*Helv. Chim. Acta*, 1923, 6, 259–263).—The benzylidenecampholic acid of Rupe and Blechschmidt, $CO_2H\cdot C_8H_{14}\cdot CH:CHPh$ (A., 1918, i, 222), reacts with thionyl chloride to form an acid chloride, which, however, when it is distilled under reduced pressure changes with evolution of hydrogen chloride into benzylidenecamphor. The same transformation occurs spontaneously in the course of a few days when a solution of the acid chloride in thionyl chloride is kept. The chloride of benzylidenecampholic acid, however, is quite stable. The reaction in the case of benzylidenecamphoryl chloride probably takes place through

the intermediate formation of the compound $C_8H_{14} \begin{smallmatrix} <CH \cdot CHClPh \\ CO \end{smallmatrix}$, which loses hydrogen chloride forming benzylidenecamphor. In the case of benzylcampholyl chloride, this reaction is, of course, impossible. The influence of ring-closure on optical rotatory power is here very marked, the value for benzylidenecampholic acid being $[\alpha]_D^{20} + 12.60^\circ$, and for benzylidenecamphor, $[\alpha]_D^{20} + 426.55^\circ$. Camphor derivatives also show a higher rotation dispersion than those of campholic acid. The supposed ethyl ester of benzylidenecampholic acid obtained by Rupe and Blechschmidt from the chloride (*loc. cit.*) is not the ester, but benzylidenecamphor.

E. H. R.

Derivatives of Buchu-camphor. YASUHIKO ASAHINA and SATORU KWADA (*J. Pharm. Soc. Japan*, 1923, 1—9; cf. Asahina and Mituhori, A., 1922, i, 667).—The formation of buchu-camphor from menthone by the action of ferric chloride was again studied; but the yield could not be increased beyond 24%. The m. p., 113° , for the phenylurethane is confirmed (Semmler and Mackenzie, A., 1906, i, 373, gave 41°). By boiling an alcoholic solution of hydroxylamine hydrochloride, sodium carbonate, and buchu-camphor on a water-bath for five hours under reflux, the mon-oxime, plates, was obtained, m. p. 123° (Semmler and Mackenzie, *loc. cit.*, give m. p. 125° , Kondakov, A., 1901, i, 334, gives 156°); its alcoholic solution gave a green coloration with ferric chloride. When the boiling is continued for ten hours, the resulting oxime has m. p. 154 — 157° , and the analytical figures suggest that a dioxime is formed. When an alcoholic solution of buchu-camphor, hydroxylamine hydrochloride, and sodium acetate is heated at 100° in a sealed tube for ten hours, the true *dioxime*, colourless, short prisms, m. p. 192° , is formed; it gives a brownish-red coloration with ferric chloride. When oxidised with potassium permanganate in acetone solution, buchu-camphor is known to yield γ -acetyl- α -isopropylbutyric acid, but when the oxidation is conducted in 5% potassium hydroxide solution at about 5° , a *diketonic acid*, $COMe \cdot CH_2 \cdot CH_2 \cdot CHPr^s \cdot CO \cdot CO_2H$, large, square plates, m. p. 135° , is produced, which, when distilled at 190 — $195^\circ/11$ mm., or when heated with concentrated hydrochloric acid, is easily changed into the closed *ketic acid*, $CH_2 \begin{smallmatrix} <CO \text{---} CH \\ CH_2 \cdot CHPr^s \end{smallmatrix} > C \cdot CO_2H$, white plates, m. p. 104° . The *semicarbazone*, white crystals, m. p. 223° ; *phenylhydrazone*, slender, light yellow prisms, m. p. 220 — 221° ; and *oxime*, white granules, m. p. 185 — 186° , of the diketonic acid are identical with those obtained from the closed ketic acid.

K. K.

Effect of Fuller's Earth on Pinene and other Terpenes. CHARLES S. VENABLE (*J. Amer. Chem. Soc.*, 1923, 45, 728—738).—The action of fuller's earth on α -pinene and other terpenes, with and without diluents, at -20° , -5° , 25° , and 158° has been investigated.

In contrast to the conclusions of Gurvich (A., 1915, i, 933), the

reaction evidently proceeds as follows: (1) Intramolecular rearrangement to dipentene and terpinene. No camphene is formed. (2) Polymerisation to dipinene and various unidentified polyterpenes. (3) Slow decomposition of the polyterpenes at high temperatures to give paraffin hydrocarbons and *p*-cymene, but not monoterpenes. With increasing temperature of reaction, the proportion of dipinene and polyterpenes to terpenes increases.

Nopinene, dipentene, α -limonene, terpinene, camphene, sabinene, terpineol, borneol, and cineol undergo similar reactions. *p*-Cymene is quite unaffected by treatment with fuller's earth.

The maximum activity of the fuller's earth is attained when it contains 5–8% of combined moisture (burning temperature about 400°). Oxygenated diluents exert a strong inhibiting action.

Iron gel, silica gel, or activated charcoal do not promote this reaction.

W. S. N.

Pinenes. H. PARISELLE (*Ann. Chim.*, 1923, [ix], **19**, 119–135).—Previous work on α - and β -pinenes is again described (cf. A., 1921, i, 575). The preparation of nitrosochlorides of pinene resulted in confirmation of Wallach's observations on the relation of yield to rotatory power, but it is pointed out that the presence of less active β -pinene may lead to inconsistent results. The nitrosochloride formed is always inactive, and the author suggests that α -pinene consists of a mixture of active and inactive isomerides which are not capable of separation, the latter form yielding the derivative and being itself formed from the active variety. The action of dry hydrogen chloride on β -pinene yields *isobornyl* chloride, on α -pinene (from Aleppo turpentine), a crystalline hydrochloride of m. p. 124–128° and $[\alpha] +35.9^\circ$, whilst from α -pinene extracted from Bordeaux turpentine the corresponding product has m. p. 120–126° and $[\alpha] -32.5^\circ$. A method of calculating the optical activity of α -pinene based on the optical purity of β -pinene is given.

H. J. E.

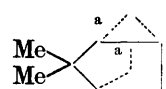
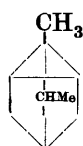
The Wagner Rearrangement. II. The Formation of Santene.

L. RUZICKA and FR. LIEBL (*Helv. Chim. Acta*, 1923, **6**, 267–281; cf. A., 1918, i, 398).—The expectation that by removal of water from α -fenchocamphorol santene would be formed has been verified. By the action of phosphorus pentachloride on fenchyl alcohol in low-boiling light petroleum, α -fenchone was obtained having $[\alpha]_D -38^\circ$ instead of -32° , as found by Wallach; its other constants were, b. p. 153–154°/720 mm.; $n_D^{25} 1.4750$, $d_4^{25} 0.870$. It was oxidised with ozone to α -fenchocamphorone, of which the semicarbazone gave two fractions from alcohol, a less soluble one having m. p. 217–218°, $[\alpha]_D -171.5^\circ$, and the more soluble one m. p. 210–211°, $[\alpha]_D -141^\circ$. The α -fenchocamphorone regenerated from the total semicarbazone had, after sublimation, m. p. 107°. Thionyl chloride with fenchyl alcohol gives *fenchyl sulphite*, $(C_{10}H_{17}O)_2SO$, colourless crystals, m. p. 72°. The α -fenchocamphorone was reduced with sodium and water to α -fenchocamphorol, and the latter heated with potassium hydrogen sulphate at 190° in a stream of carbon dioxide, when santene distilled over, b. p.

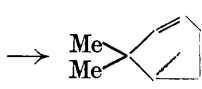
140—142°, $[\alpha]_D$ 0, n_D^{17} 1.4657, d_4^{17} 0.8720. It was identified by oxidation with ozone to 1:3-diacetylcyclopentane. A mixture of α - and β -fenchene was prepared by heating fenchyl alcohol with sodium hydrogen sulphate, and from this by the above method a mixed α - and β -fenchocamphorol was obtained. When this was heated with potassium hydrogen sulphate as above, santene was obtained having practically the same constants as that from α -fenchocamphorol. It is concluded that both α - and β -fenchene give the same santene. From santenol, by heating with potassium hydrogen sulphate, santene was also obtained.

The authors' theory of the formation of an intermediate tricyclene in the course of the Wagner rearrangement (*loc. cit.*) has been rejected by Lipp (A., 1920, i, 491) and by Meerwein and Emster (A., 1920, i, 855), who have prepared the tricyclene and found it to be quite stable under the conditions of the borneol-camphene transformation. The alternative hypotheses suggested by these authors fail, however, to account for the formation of santene, whilst the tricyclene hypothesis offers a clear picture of the mechanism of the reaction. The simplest case is the formation

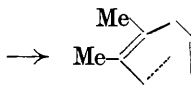
of santene from santenol, when the intermediate tricyclene is represented by I. In the formation of santene from α -fenchocamphorol, β -fenchocamphorol, and camphenilol, each of these compounds by loss of water can form the same tricyclene, represented by the space-formula II. By rupture of one of the bonds, *a*, a double-bond is formed attached to one of the bridge carbon atoms,



(II.) Tricyclene.



(III.) Unstable.



(IV.) Santene.

an unstable configuration (III) which can only be stabilised by the wandering of one of the methyl groups, giving santene (IV). It has been urged as an objection to the tricyclene hypothesis that, since the tricyclene is symmetrical, it cannot give rise to an optically active product. This objection, however, can scarcely be maintained, since in the case of the transformation of optically active linalool into active terpineol, in the course of which the active centre is changed from one carbon atom to another, on any hypothesis, there must be a symmetrical intermediate stage. It must be supposed that, in the Wagner rearrangement, formation of the tricyclene and its isomerisation take place simultaneously, and that considerations which apply to the stable tricyclene do not apply to it in the nascent state.

E. H. R.

β -Amyrin from Manilla Elemi Resin. ALEX. ROLLETT (*Monatsh.*, 1923, 43, 413—417).—Alcoholic potassium hydroxide converts dibromo- β -amyrin benzoate (A., 1921, i, 39; 1922, i, 667) into an impure potassium derivative, from which, on acidification, only a gelatinous substance is obtained. Bromination of β -amyrin in glacial acetic acid solution gives a mixture of (*a*) bromo- β -amyrin

acetate, m. p. 235—236° (solution in concentrated sulphuric acid yellow, with green fluorescence), and (b) *dibromo-β-amyrin*, m. p. 210—216° (decomp.). By oxidising β-amyrin with chromic acid, Vesterberg (A., 1892, 290) obtained β-amyrone (oxime, m. p. 262—263°). The latter substance, now called β-amyranone (oxime, m. p. 265—267°), melts at 177—179°. Potassium permanganate affords no isolable oxidation product with β-amyranone. The latter, on heating with benzoyl chloride, yields β-*amyrenol benzoate*, which melts at 181—182°, gives a yellow solution in concentrated sulphuric acid, and is converted by hot alcoholic potassium hydroxide into β-amyranone. E. E. T.

Constituents of Derris-root. I. TATSUO KARIYONE and KENJIRO ATSUMI (*J. Pharm. Soc. Japan*, 1923, 10—17).—Greshoff (A., 1891, 335) and van Sillevoldt (A., 1900, i, 109) isolated an amorphous poisonous constituent, *derrid*, from the root of *Derris elliptica*, Benth., and Wray (*Pharm. J.*, 1892, 1152) obtained the constituent *tubain*. Ishikawa (A., 1918, i, 94) isolated *tubotoxin*, $C_{18}H_{18}O_5$, white crystals, m. p. 163·5°, from the root. The authors confirm Ishikawa's results. The poisonous constituent was proved to have one carbonyl group by the formation of a *phenylhydrazone*, light yellow needles, m. p. 255°, and an *oxime*, colourless needles, m. p. 245°. When heated with sodium acetate and acetic anhydride, *tubotoxin* gives a *diacetyl* derivative, the saponification value (84·3—116·9) of which is, however, lower than the calculated value (281·8). Estimation of methoxyl by Zeisel's or by Herzig's methods indicated the presence of 1·5-methoxyl groups in *tubotoxin*. Benzoyl chloride or phthalic anhydride have no action on it. *Tubotoxin* is probably identical with *retenon* obtained by Nagai (*J. Tokyo Chem. Soc.*, 1902, 23, 744) from *Millettia taiwaniana*, Hayata, produced in Formosa. K. K.

Bixin. J. HERZIG and F. FALTIS [and, in part, BERTHA PITTMER, FRIEDRICH KLEIN, and GEORG WATZINGER] (*Annalen*, 1923, 431, 40—70; cf. A., 1917, i, 577).—Previous work on this subject, in particular the researches of Hasselt (A., 1911, i, 550; 1916, i, 495), and the facts described below, are discussed on the basis of the formula $CO_2H \cdot C_{23}H_{26} \cdot CO_2Me$ for *bixin*, where $C_{23}H_{26}$ is an unsaturated residue to which the carboxyl and carbomethoxyl groups are unsymmetrically attached.

Bixin, which cannot be esterified by means of alcoholic hydrogen chloride, absorbs eighteen atoms of hydrogen in glacial acetic acid suspension in the presence of palladium-barium sulphate, forming *hydrobixin*, a thick, almost colourless oil containing one methoxyl group, which can be esterified by means of methyl-alcoholic hydrogen chloride to *hydromethylbixin*, a thick, pale yellow oil, b. p. 280—285°/18 mm., containing two OMe groups, which is also produced when *methylbixin* absorbs eighteen atoms of hydrogen, and is hydrolysed by means of methyl-alcoholic potassium hydroxide to *hydronorbixin*, a thick oil, b. p. 220—230°/13 mm., which acts as a dibasic acid on titration; this may be reconverted into *hydromethylbixin* by means of diazomethane or 3% methyl-

alcoholic hydrogen chloride. When hydromethylbixin is hydrolysed by means of alcoholic potassium hydroxide and the product oxidised by means of potassium permanganate, six atoms of oxygen seem to be taken up; the resulting *yellow oil*, apparently $C_{25}H_{46}O_5$, contains no methoxyl group. It is readily methylated by means of 3% methyl-alcoholic hydrogen chloride to an *oil*, $C_{27}H_{50}O_5$, containing two methoxyl groups.

When hydronorbixin is heated at 320° , carbon dioxide is eliminated, but no definite product has been isolated. Nevertheless, by the action of heat on a mixture of lime and the *calcium* salt of hydronorbixin under reduced pressure, an *oil* is produced approximately of the composition $C_{23}H_{46}$; the presence of two carboxyl groups in hydronorbixin is therefore probable.

The hydrolysis of methylbixin to norbixin by means of methyl-alcoholic sodium hydroxide is demonstrated. No pure compound is obtained by the esterification of norbixin by means of concentrated methyl-alcoholic hydrogen chloride; the use of diazo-methane leads, however, to the formation of methylbixin and to a small quantity of an isomeride, β -*methylbixin*, dark violet crystals, m. p. $190-193^\circ$, which is the sole product if 3% methyl-alcoholic hydrogen chloride is used. It is also formed by the action of diazo-methane in ethereal solution on β -*bixin*, minute, bordeaux-red crystals, decomp. $211-214^\circ$, an isomeride of bixin which has been obtained during the preparation of bixin from a sample from Dutch Orleans. The existence of three isomeric monomethyl esters, bixin, β -bixin, and *isobixin* (Hasselt, *loc. cit.*), cannot be ascribed merely to the unsymmetrical position of the carboxyl groups in the norbixin molecule. It is suggested that the wandering of a double bond may underlie the change of structure which obviously must accompany the production of at least one of these isomerides.

W. S. N.

New Pirylium Salts. C. GASTALDI and G. L. PEYRETTI (*Gazzetta*, 1923, 53, i, 11-15).—Condensation of acetophenone or dyponone with propionic, butyric, and *isovaleric* anhydrides in presence of sublimed ferric chloride yields compounds analogous to that obtained under similar conditions from acetic anhydride (A., 1922, i, 573).

The *ferric chloride* compound of 4:6-diphenyl-2-ethylpyrylium chloride, $FeCl_4 \cdot O \langle \begin{smallmatrix} CEt \cdot CH \\ CPh \cdot CH \end{smallmatrix} \rangle CPh$, formed from propionic anhydride, forms long, yellowish-brown needles, m. p. 167° , and yields a pale yellow aqueous solution showing slight green fluorescence. When treated in aqueous solution with excess of ammonia, it yields 4:6-diphenyl-2-ethylpyridine, the *nitrate* of which, $C_{19}H_{18}O_3N_2$, forms slender, colourless needles, m. p. 180° (decomp.). 4:6-Diphenyl-2-ethylpyrylium *nitrate*, $C_{19}H_{17}O_4N$, crystallises in pale yellow laminae, m. p. 151° (decomp.).

The *ferric chloride* compound of 4:6-diphenyl-2-propylpyrylium chloride, $C_{20}H_{19}O \cdot FeCl_4$, formed from butyric anhydride, forms greenish-yellow plates, m. p. $197-198^\circ$, and dissolves in concen-

trated sulphuric acid with blue fluorescence. 4 : 6-Diphenyl-2-propylpyridine nitrate, $C_{20}H_{20}O_3N_2$, crystallises in colourless needles, m. p. 138° (decomp.).

The ferric chloride compound of 4 : 6-diphenyl-2-isobutylpyrylium chloride, $C_{21}H_{21}O \cdot FeCl_4$, forms yellow prisms, m. p. 165° , and gives a pale yellow, aqueous solution showing slight blue fluorescence; the nitrate, $C_{21}H_{21}O_4N$, forms yellow prisms, m. p. 156° . 4 : 6-Diphenyl-2-isobutylpyridine nitrate, $C_{21}H_{22}O_3N_2$, crystallises in colourless needles, m. p. 124° .
T. H. P.

A Synthesis of Pyrylium Salts of Anthocyanidin Type. II.
DAVID DOIG PRATT and ROBERT ROBINSON (T., 1923, 123, 745—758).

A Direct Synthesis of certain Xanthylum Derivatives.
DAVID DOIG PRATT and ROBERT ROBINSON (T., 1923, 123, 739—745).

Anhalonium Alkaloids. V. Synthesis of Anhalonidine and Pellotine. ERNST SPÄTH (*Monatsh.*, 1923, 43, 477—484).—By the action of cold, concentrated hydrochloric acid on β -5-benzyl-oxy-3 : 4-dimethoxyphenylethylamine (A., 1922, i, 852), the benzyl group is removed. Acetic anhydride converts the product into the O-N-diacetyl derivative, which, when heated in toluene solution with phosphoric oxide, gives a base which, from its mode of formation, must be either 6-acetoxy-7 : 8-dimethoxy- or 8-acetoxy-6 : 7-dimethoxy-1-methyl-3 : 4-dihydroisoquinoline, and on reduction with tin and hydrochloric acid gives a substance identical in all respects with anhalonidine. This alkaloid must therefore be either 6-hydroxy-7 : 8-dimethoxy- or 8-hydroxy-6 : 7-dimethoxy-1-methyl-1 : 2 : 3 : 4-tetrahydroisoquinoline. The former constitution accords the better with that of anhalamine, and is more probable on the grounds that the above ring-closure would be more likely to occur in the para-position to an acetoxy-group than in the similar position with respect to a methoxy-group.

By the addition of methyl iodide to the above dihydroisoquinoline derivative, and reduction of the product with tin and hydrochloric acid (the second process effecting also hydrolysis of the O-acetyl group), pellotine (i.e., N-methylanhalonidine) is obtained.

The great reactivity, with aldehydes, of the above-mentioned ethylamine derivative suggests that neither anhalonidine nor pellotine is formed in the plant as a result of enzyme action. The lability of groups attached to the asymmetric carbon atom in position 1, caused by the (probable) presence of a hydroxyl group in position 6, may explain the optical inactivity of the two natural alkaloids.
E. E. T.

Echinopsine. ERNST SPÄTH and ALFRED KOLBE (*Monatsh.*, 1923, 43, 469—475).—This alkaloid, to which Greshoff (A., 1901, i, 338) erroneously assigned the formula $C_{11}H_9ON$, is identical with 1-methyl-4-quinolone, $C_{10}H_9ON$, obtained in an impure condition

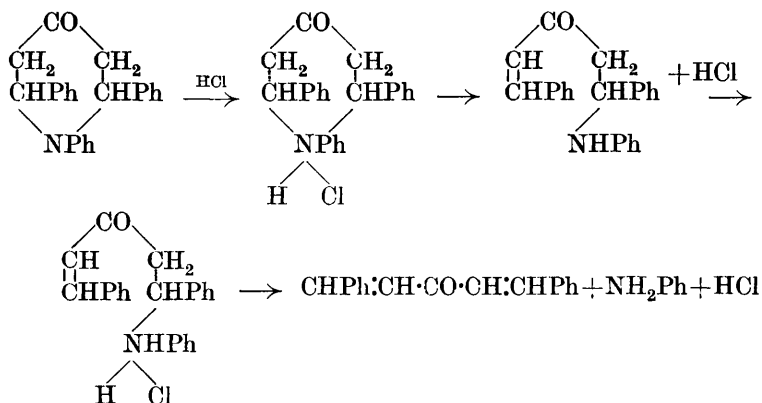
by Meyer (A., 1906, i, 604). On reduction, either with sodium and alcohol, or electrolytically, echinopsine is converted into 1-methyltetrahydroquinoline, whilst when heated with a mixture of phosphorus penta- and oxy-chlorides it is converted into 4-chloroquinoline. From the latter, quinoline is obtained by reducing with hydrogen in presence of palladium and barium sulphate. The alkaloid is readily obtained by heating 4-hydroxyquinoline with methyl iodide and sodium methoxide, and gives a *hydrochloride*, m. p. 185—186°, and a *picrate*, m. p. 223—224°. E. E. T.

Preparation of Ergotamine Salts. CHEMISCHE FABRIK VORM. SANDOZ (Brit. Pat. 170302).—Ergotamine salts are obtained in crystalline form by the action of the requisite amount of acid on the free base dissolved in an organic solvent miscible with water, such as methyl or ethyl alcohol, acetone, etc., whereby separation of the salt occurs almost immediately. The preparation of two sulphates in this way, containing 10.36% and 7.56% H_2SO_4 , respectively, is described. On recrystallisation, the former passes into the latter by loss of sulphuric acid. These and other ergotamine salts retain solvent of crystallisation very tenaciously. Salts containing a minimum amount of acid are obtained by shaking an ergotamine solution in a non-miscible organic solvent such as chloroform, with gradually increasing quantities of the acid. The precipitate is collected and recrystallised from methyl alcohol. In this way, a *hydrochloride* in the form of thin prisms containing, after drying to constant weight, 5.85% HCl, was obtained. The preparation of the tartrate in the form of compact prisms from ethyl alcohol, and of the citrate and carbonate in physiological sodium chloride solution, is also described. The ergotamine salts and their solutions are easily oxidised by air, particularly in sunlight, becoming thereby yellow or brown. Access of air should therefore be prevented during the preparation and storage of these compounds. G. F. M.

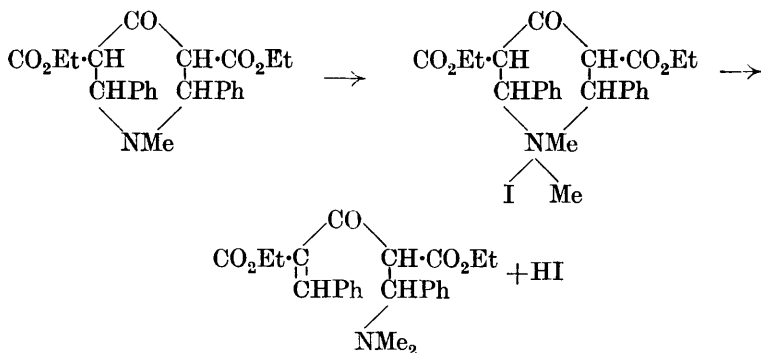
Physostigmine. I. Alkylation Products of Eseroline. GEORGE BARGER and EDGAR STEDMAN (T., 1923, 123, 758—769).

Some Pyridine Derivatives of Iridium. MARCEL DÉLÉPINE (*Ann. Chim.*, 1923, [ix], 19, 5—31).—A more detailed account of work already published (cf. A., 1922, i, 859; 1923, i, 89, 135, 243). H. J. E.

A Reaction Involving the Rupture of the Ring in Heterocyclic Compounds. I. P. PETRENKO-KRITSCHENKO, E. PUTIATA, and A. GANDELMAN (*J. Russ. Phys. Chem. Soc.*, 1916, 48, 1852—1861).—The action of hydrogen chloride and of methyl iodide on some substituted 4-piperidones is investigated. Hydrogen chloride is passed through a benzene solution of 1 : 2 : 6-triphenyl-4-piperidone. The hydrochloride thus precipitated is treated with alkali, which liberates distyryl ketone and aniline. This reaction is thus explained :



The ease with which the ring is broken in this compound is due to the close proximity of the three phenyl groups, as the corresponding *N*-methyl compound when treated in the same way regenerates the same compound. It appears also that the triphenyl derivative can be stabilised by converting the grouping $-\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2-$ into $-\text{CHR}\cdot\text{CO}\cdot\text{CHR}-$, where R is a carbethoxy-group. The action of methyl iodide on ethyl 2:6-diphenyl-1-methyl-4-piperidone-3:5-dicarboxylate is next examined. The hydriodide of this ester is prepared by the action of methyl iodide on the corresponding ester of diphenylpiperidonedicarboxylic acid, and the free 1-methyl ester, m. p. 85° , is obtained from it by the action of weak ammonia. Prolonged boiling of this substance with methyl iodide merely results in the formation of its hydriodide. The formation of this salt is explained as follows :



The hydrogen iodide thus liberated combines with unacted on 1-methyl ester to form its hydriodide. No other product was isolated from the reaction mixture. Hydrogen chloride passed through a benzene solution of this ester gives a variety of products, of which only one is identified as the stereoisomeride, m. p. 138° ,

of the original substance, m. p. 85°. The action of methyl iodide on *N*-methyltriacetonamine is to cause rupture of the ring. The latter substance is preparable by the action of methyl iodide on triacetoneamine, thus showing that the view held up to the present, that the homologues of the latter substance cannot be prepared by direct alkylation, is incorrect.

R. T.

Influence of Solvents on the Grignard Reactions. RIKO MAJIMA and MUNIO KOTAKE (*J. Chem. Soc. Japan*, 1922, **43**, 936—948; cf. this vol., i, 495).—The influence of solvents (ethyl ether and anisole) in the Grignard reaction between magnesium indole iodide and the following has been studied, with results which may be summarised as follows :

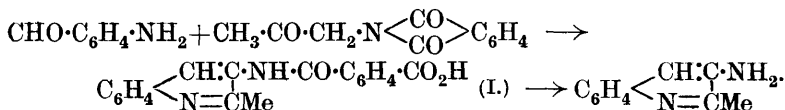
Reagent.	Reaction products.	Yields	
		In ethyl ether.	In anisole.
Formic ester . .	indole-2-aldehyde	trace	33%
Carbon dioxide . .	indole-2-carboxylic acid	8.6%	25%
Acetone . . .	2-indolyldimethylmethane	22.5%	30.4%
Benzaldehyde . .	di-2-indolylphenylmethane	20%	61.6%
Chloroformic ethyl ester . .	ethyl indole-2-carboxylate	53.5%	36.7%
Acetyl chloride . .	2-indolyl methyl ketone	93%	61%
Chloroacetyl chloride . .	2-indolyl chloromethyl ketone	45%	4.8%

From the results, the authors have drawn the conclusion that when a compound having a carbonyl group acts on magnesium indole iodide, a good yield is obtained by using anisole as a solvent; whilst if the reacting compound is an acid chloride, ethyl ether is a better solvent. β -Indolylchloromethyl ketone forms colourless, rhombic crystals, m. p. 212—214°.

K. K.

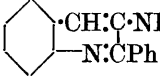
3-Amino- and 3-Hydroxy-quinolines. G. BARGELLINI and S. BERLINGOZZI (*Gazzetta*, 1923, **53**, i, 3—11).—The authors have prepared 3-hydroxy-2-phenylquinoline by the action of *o*-aminobenzaldehyde on either ω -bromoacetophenone or benzoylcarbinol, and 3-hydroxy-2-*p*-anisylquinoline from chloroacetoanisole and *o*-aminobenzaldehyde, the action of ketones containing the group $\cdot\text{CO}\cdot\text{CH}_2\text{X}$ (X=a halogen atom) on *o*-aminobenzaldehyde in presence of sodium hydroxide constituting a general method for the preparation of 3-hydroxyquinolines. Similar condensations occur if the *o*-aminobenzaldehyde is replaced by one of its derivatives or by isatin or an *o*-amino-ketone.

3-Aminoquinoline derivatives have been prepared by complicated series of reactions (Stark, A., 1907, i, 973; Mills and Watson, T., 1910, **97**, 741), but no general method is known. The authors find that 3-amino-2-methylquinoline is readily prepared by condensing *o*-aminobenzaldehyde with acetonylphthalimide in presence of sodium hydroxide and decomposing the compound formed by boiling it with 20% hydrochloric acid :



3-Amino-2-phenylquinoline may be obtained similarly from *o*-aminobenzaldehyde and phenacylphthalimide. The formation of 3-nitroquinoline from *o*-aminobenzaldehyde and methazonic acid (Badische Anilin- & Soda-Fabrik, A., 1921, i, 517) is analogous to the method described above, since methazonic acid reacts as the oxime of nitroacetaldehyde.

The compound $\text{C}_{18}\text{H}_{14}\text{O}_3\text{N}_2$ (formula I, above) forms silky, yellow needles, m. p. 220° (decomp.).

The compound  $\cdot \text{CH} \cdot \text{C} \cdot \text{NH} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$, prepared from

o-aminobenzaldehyde and phenacylphthalimide, forms white scales, m. p. $205\text{--}206^\circ$ (decomp.).

3-Amino-2-phenylquinoline, $\text{C}_{15}\text{H}_{12}\text{N}_2$, crystallises in pale yellow needles, m. p. $115\text{--}116^\circ$, and dissolves in acids, giving intensely fluorescent solutions. Its *acetyl* derivative forms colourless needles, m. p. $173\text{--}175^\circ$, and its *picrate*, yellow prisms, m. p. $194\text{--}195^\circ$.

3-Hydroxy-2-phenylquinoline, $\text{C}_{15}\text{H}_{11}\text{ON}$, prepared either by diazotisation of 3-amino-2-phenylquinoline or by the action of ω -bromoacetophenone or benzoylcarbinol on *o*-aminobenzaldehyde (cf. Koenigs and Stockhausen, A., 1902, i, 693), forms white needles, m. p. $221\text{--}222^\circ$, and yields fluorescent aqueous and alcoholic solutions, the latter giving a reddish-brown coloration with ferric chloride. The *hydrochloride* forms lustrous, yellow scales, m. p. $243\text{--}245^\circ$; the *chloroplatinate*, orange-yellow crystals, blackening above 260° ; the *picrate*, yellow prisms, m. p. $235\text{--}238^\circ$ (decomp.); the *sulphate*, yellow leaflets, turning brown at 150° and melting indistinctly at about 165° .

3-Hydroxy-2-*p*-anisylquinoline, $\text{C}_{16}\text{H}_{13}\text{O}_2\text{N}$, crystallises in white needles, m. p. $240\text{--}242^\circ$ (decomp.). The *sulphate*, yellow needles, m. p. $225\text{--}230^\circ$ (decomp.), *hydrochloride*, *chloroplatinate*, and *picrate*, m. p. $216\text{--}228^\circ$, were prepared. T. H. P.

γ -Chloropropyl Urethanes and a Synthesis of the 1 : 3-Oxazine Ring. ARTHUR W. DOX and LESTER YODER (*J. Amer. Chem. Soc.*, 1923, 45, 723–727).— γ -Chloropropyl alcohol reacts readily with carbonyl chloride in ice-cold toluene solution to give *γ -chloropropyl chloroformate*, b. p. $175\text{--}176^\circ/736$ mm., which, when heated with carbamide (2 mols.), gives *γ -chloropropyl allophanate*, white, scaly crystals, m. p. 166° . *γ -Chloropropyl carbamate*, white, pearly scales, m. p. 62° , is formed when γ -chloropropyl alcohol and carbamide nitrate (2 mols.) are heated together at $130\text{--}135^\circ$, or, in better yield (71%), when the chloroformate is slowly dropped into ice-cold 10% aqueous ammonia (2 mols.). Attempts to prepare an oxazine by the elimination of hydrogen chloride from the above carbamate were unsuccessful; the action of aqueous sodium hydroxide leads to hydrolysis, whilst with alcoholic sodium

ethoxide sodium cyanate and phenylcarbamide are produced. γ -Chloropropyl chloroformate reacts with aniline in ice-cold ethereal solution giving γ -chloropropyl phenylcarbamate, long, flat prisms, m. p. 38° , b. p. 160 — $170^\circ/5$ mm., which is also produced when chloropropyl alcohol and phenylcarbimide are gradually heated together at 150° ; the action of boiling aqueous-alcoholic sodium hydroxide on the carbanilate leads to 2-keto-3-phenyltetrahydro-1:3-oxazine, large, thick prisms, m. p. 96° , yield 84%. Chloropropyl chloroformate reacts in cold ethereal solution with *o*-toluidine to give γ -chloropropyl *o*-tolylcarbamate, small needles, m. p. 49° , b. p. 170 — $175^\circ/5$ mm., from which, by the elimination of hydrogen chloride, 2-keto-3-*o*-tolyltetrahydro-1:3-oxazine, large, flat prisms, m. p. 89° , is produced in 60% yield.

The formation of the 6-membered 1:3-oxazine ring is analogous to that of the 5-membered 1:3-oxazole ring, by the elimination of hydrogen chloride from β -halogen carbanilates (Otto, A., 1891, 1373; Johnson and Langley, A., 1910, i, 884). W. S. N.

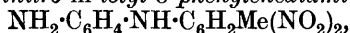
Tetrahydro-1:3:2-oxazones and Substituted γ -Aminopropanols. J. S. PIERCE and ROGER ADAMS (*J. Amer. Chem. Soc.*, 1923, 45, 790—795; cf. this vol., i, 457).— γ -Chloropropyl arylcarbamates are formed in aqueous suspension from aromatic amines and γ -chloropropyl chloroformate. γ -Chloropropyl arylcarbamates are converted by alcoholic potash (1 mol.) into tetrahydro-1:3:2-oxazones; if 4 mols. of alkali are used, γ -arylaminopropanols are produced.

The following compounds are described: γ -Chloropropyl *o*-tolylcarbamate, white needles, m. p. 46 — 46.5° , b. p. $182.5^\circ/4.5$ mm. γ -Chloropropyl phenylcarbamate, white needles, m. p. 35 — 36° , b. p. $190^\circ/3.5$ mm. γ -Chloropropyl *p*-tolylcarbamate, b. p. $188^\circ/4.5$ mm. γ -Chloropropyl *o*-chlorophenylcarbamate, b. p. $178.5^\circ/3.5$ mm. γ -Chloropropyl *p*-chlorophenylcarbamate, white needles, m. p. 53 — 53.5° , b. p. $193^\circ/5$ mm. γ -Chloropropyl *p*-anisylcarbamate, white needles, m. p. 63 — 63.5° , b. p. $198.5^\circ/4$ mm. γ -Chloropropyl *p*-carboxyphenylcarbamate, white crystals, m. p. 191 — 192.5° . γ -Chloropropyl α -naphthylcarbamate, white needles, m. p. 75.5 — 76.5° , b. p. $206.5^\circ/4$ mm. 3-Phenyltetrahydro-1:3:2-oxazone, white plates, m. p. 94 — 94.5° . 3-*o*-Tolyltetrahydro-1:3:2-oxazone, white prisms, m. p. 87 — 87.5° . 3-*p*-Tolyltetrahydro-1:3:2-oxazone, white needles, m. p. 127.5 — 128° . 3-*o*-Chlorophenyltetrahydro-1:3:2-oxazone, white cubes, m. p. 99° . 3-*p*-Chlorophenyltetrahydro-1:3:2-oxazone, white plates, m. p. 111.5 — 112° . 3-*p*-Ethoxyphenyltetrahydro-1:3:2-oxazone, white plates, m. p. 112.5 — 113° . 3-*p*-Carboxyphenyltetrahydro-1:3:2-oxazone, white plates, m. p. 231 — 232° . 3- α -Naphthyltetrahydro-1:3:2-oxazone, white needles, m. p. 149.5 — 150.5° . γ -Anilinopropyl alcohol, b. p. $180.5^\circ/20.5$ mm. or $154^\circ/5$ mm. γ -*o*-Toluidinopropyl alcohol, b. p. $164^\circ/3$ mm. γ -*p*-Toluidinopropyl alcohol, b. p. $163.5^\circ/3.5$ mm. γ -*o*-Chloroanilinopropyl alcohol, b. p. $151.5^\circ/3.5$ mm. γ -*p*-Chloroanilinopropyl alcohol, b. p. $167^\circ/3.5$ mm. γ -*p*-Phenetidinopropyl alcohol, white plates, m. p. 42 — 42.5° , b. p. $177^\circ/3.5$ mm. γ -*p*-Carboxyanilinopropyl alcohol, white

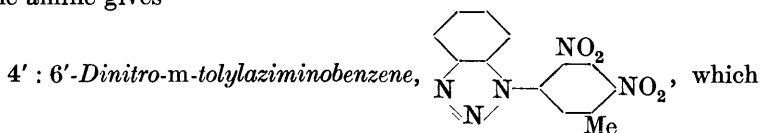
needles, m. p. 151—152°. γ - α -Naphthylaminopropyl alcohol, a yellow oil, b. p. 201.5°/3.5 mm. W. S. N.

Reactions of Thiosemicarbazones. II. Action of Esters of α -Halogenated Acids. FORSYTH JAMES WILSON and ROBERT BURNS (T., 1923, 123, 799—804).

The Action of Phenylenediamines on β - and γ -Trinitrotoluenes. MICHELE GIUA and MARIO GIUA (*Gazzetta*, 1923, 53, i, 48—52).—4' : 6'-Dinitro-*m*-tolyl-*o*-phenylenediamine,



prepared by the interaction of 2 : 4 : 5-trinitrotoluene (1 mol.) and *o*-phenylenediamine (2 mols.) in alcoholic solution, crystallises in orange-yellow needles, m. p. 195—196°, dissolves in concentrated sulphuric acid with yellow coloration, and, in alcoholic solution, gives a deep red coloration with alkalis. With benzaldehyde it yields the *benzylideneimine*, $\text{C}_{20}\text{H}_{16}\text{O}_4\text{N}_4$, which forms lustrous, red prisms, m. p. 214—215°, and gives a red coloration with concentrated sulphuric acid. The *acetyl* derivative of the amine, $\text{C}_{15}\text{H}_{14}\text{O}_5\text{N}_4$, forms pale yellow prisms, m. p. 222—223°, and, in alcoholic solution, yields a red coloration with alkali. The action of nitrous acid on the amine gives

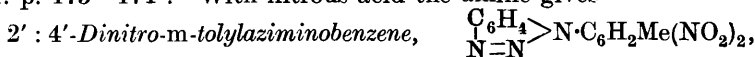


forms lustrous, white laminæ, m. p. 164—165°, and, in alcoholic solution, gives a blue coloration with excess of alkali.

4' : 6'-Dinitro-*m*-tolyl-*m*-phenylenediamine, $\text{C}_{13}\text{H}_{12}\text{O}_4\text{N}_4$, prepared from 2 : 4 : 5-trinitrotoluene and *m*-phenylenediamine, crystallises in lustrous, reddish-yellow needles, m. p. 160—161°, gives a reddish-yellow solution in concentrated sulphuric acid, and, in alcoholic solution, gives a deep red coloration with alkali. Its *acetyl* derivative forms reddish-yellow prisms, m. p. 224—225°, and gives a dark red coloration with alkali in alcoholic solution.

4' : 6'-Dinitro-*m*-tolyl-*p*-phenylenediamine, obtained from 2 : 4 : 5-trinitrotoluene (1 mol.) and *p*-phenylenediamine, crystallises in long, garnet-red needles, m. p. 174—175°, yields a red solution in concentrated sulphuric acid, and, in alcoholic solution, forms a deep red coloration with alkali. The *acetyl* derivative separates in reddish-yellow, silky needles, m. p. 222—223°.

2' : 4'-Dinitro-*m*-tolyl-*o*-phenylenediamine, prepared from 2 : 3 : 4-trinitrotoluene and *o*-phenylenediamine, crystallises in lustrous, garnet-red needles, m. p. 149—150°, dissolves in concentrated sulphuric acid to a reddish-yellow solution, and, in alcoholic solution, gives a deep red coloration with alkali; it forms a pasty, golden-yellow acetyl compound. With benzaldehyde, it yields the *benzylideneimine*, $\text{C}_{20}\text{H}_{16}\text{O}_4\text{N}_4$, which forms lustrous, red prisms, m. p. 173—174°. With nitrous acid the amine gives



which crystallises in lustrous, white prisms, m. p. 156—157°, and, in alcoholic solution, gives with alkali a violet coloration changing immediately to blue.

2' : 4'-Dinitro-*m*-tolyl-*p*-phenylenediamine, prepared from 2 : 3 : 4-trinitrotoluene and *p*-phenylenediamine, crystallises in lustrous, garnet-red needles, m. p. 174—175°. T. H. P.

Application of the Hofmann Reaction to Substituted Carbamides. GEORGE ROBERT ELLIOTT (T., 1923, 123, 804—813).

The Action of Sodamide on Pyridine, with some Observations on 2-Aminopyridine and some of its Derivatives. J. P. WIBAUT and ELISABETH DINGEMANSE (*Rec. trav. chim.*, 1923, 42, 240—250; *Proc. K. Akad. Wetensch. Amsterdam*, 1923, 25, 458—462; cf. Tschitschibabin and Zeide, A., 1915, i, 590).—The action of sodamide on pyridine results in formation of 2-aminopyridine, 4 : 4'-dipyridyl, and dipyridylamine, but 2 : 6-diaminopyridine and 4-aminopyridine were not detected. A study of the action of oxidising agents on 2-aminopyridine showed that it rapidly decolorises alkaline permanganate, has little action on alkaline chromate, and slowly reduces acid chromate solution. The oxidation products were not isolated.

2-Acetamidopyridine forms monoclinic prisms ($a : b : c = 1.4939 : 1 : 2.0719$, $\beta = 89^\circ 14' 30''$); 2-aminopyridylurethane crystallises in the monoclinic prismatic system ($a : b : c = 0.7946 : 1 : 1.3552$, $\beta = 73^\circ 21'$). H. J. E.

The Hydrolysis of the Xanthyl Derivatives of Veronal and Hypnotics of the Barbituric Acid Series, and its Importance in Toxicology. RENÉ FABRE (*J. Pharm. Chim.*, 1923, [vii], 27, 337—339).—The xanthyl derivatives of veronal and other alkyl-barbituric acids, the preparation and use of which in toxicological investigations has previously been described (A., 1922, ii, 795), are readily hydrolysed by boiling for one hour with 20% alcoholic hydrogen chloride, and the original barbituric acid is recoverable from the reaction product in almost theoretical yield by rendering alkaline, extracting insoluble matter by means of ether, acidifying the alkaline solution, and extracting once more with ether. On evaporating the rather ethereal extract, the barbituric acid is obtained in pure crystalline form. G. F. M.

The Synthesis of Iminazolyglycine [Glyoxalineaminoacetic Acid]. The Lower Homologue of Histidine. CORBET PAGE STEWART (*Biochem. J.*, 1923, 17, 130—133).—4(or 5)-Hydroxymethylglyoxaline, obtained from citric acid, was oxidised to the glyoxaline-4(or 5)-formaldehyde. The latter compound was converted by the treatment with potassium cyanide and ammonium chloride into the amino-nitrile, which was eventually hydrolysed to the amino-acid. The hydrochloride of the compound was found to be hygroscopic and decomposed when attempts were made to dry it at 100°. The picrolonate, m. p. 243° (uncorr.), was prepared in order to purify the crude product obtained by the above method. Glyoxalineaminoacetic acid forms a condensation compound with

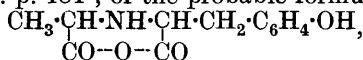
2 : 3 : 4-trinitrotoluene, $\begin{array}{c} \text{NH} \cdot \text{CH} \\ \text{CH} = \text{N} \end{array} \Rightarrow \text{C} \cdot \text{CH} \cdot \text{NH} \cdot \begin{array}{c} \text{NO}_2 \text{ Me} \\ \diagup \quad \diagdown \\ \text{NO}_2 \end{array}$, the 3-nitro-group disappearing in the condensation; it forms deep yellow crystals, decomp. 270° . S. S. Z.

Synthesis of Polypeptide Hydantoins. **Tyrosyl-Alanine Hydantoin.** DOROTHY A. HAHN, LOUISE KELLEY, and FLORENCE SCHAEFFER (*J. Amer. Chem. Soc.*, 1923, **45**, 843—857).—The alkylation of 4-*p*-anisylidenhydantoin and of 4-anisylhydantoin by means of ethyl α -bromopropionate has been investigated; the ester group enters the position 3, in contrast to the behaviour of ethyl chloroacetate, which becomes attached to nitrogen in the position 1 (cf. A., 1916, i, 504; 1917, i, 475).

The action of sodium ethoxide and ethyl α -bromopropionate on 4-*p*-anisylidenhydantoin leads to *ethyl 4-p-anisylidenhydantoin-3- α -propionate*, which exists in stereoisomeric forms, (a) large, glistening plates, m. p. 143° ; (b) long, fine, white, felted needles, m. p. 176° ; both forms of the ester are hydrolysed by means of hydrochloric acid, yielding corresponding forms of 4-*p*-anisylidenhydantoin-3- α -propionic acid, $\text{NH} \begin{array}{c} \text{CO} \cdot \text{C} \cdot \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe} \\ \text{CO} \cdot \text{N} \cdot \text{CHMe} \cdot \text{CO}_2\text{H} \end{array}$, (a) hard, white needles or plates, m. p. 245° ; (b) hard, white needles or plates, m. p. 269° . Either form of the ester, preferably the less fusible modification, is reduced by means of sodium amalgam in alcoholic solution to *ethyl 4-p-methoxybenzylhydantoin-3- α -propionate*, long, fine, white needles, or plates, m. p. 138° , which is also produced by the action of sodium ethoxide and ethyl α -bromopropionate on 4-*p*-methoxybenzylhydantoin. This ester is converted by the action of alcoholic sodium hydroxide into the *sodium salt*, crystalline, of 4-*p*-methoxybenzylhydantoin-3- α -propionic acid, hard, white prisms, m. p. 164 — 166° , which is also formed by the action of concentrated hydrochloric acid on N-carbamyl- β -*p*-methoxyphenyl- α' -iminodipropionic acid,

$\text{CO}_2\text{H} \cdot \text{CHMe} \cdot \text{N}(\text{CO} \cdot \text{NH}_2) \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$, glistening, white plates, m. p. 148 — 149° , decomp. The latter is formed as its *disodium salt*, m. p. 240° , decomp., by the action of ethyl-alcoholic sodium ethoxide (2 mols.) on ethyl 4-*p*-methoxybenzylhydantoin-3- α -propionate. 4-*p*-Hydroxybenzylhydantoin-3- α -propionic acid, rosettes of hard, compact crystals, m. p. 217° , *ethyl ester*, long, felted needles, m. p. 192° , is formed by the action of hydriodic acid and red phosphorus at 100 — 110° on either form of 4-*p*-anisylidenhydantoin-3- α -propionic acid, either form of its ethyl ester, 4-*p*-methoxybenzylhydantoin-3- α -propionic acid, or its ethyl ester. When 4-*p*-hydroxybenzylhydantoin-3- α -propionic acid is heated for four hours at 155° with concentrated hydrochloric acid, it is converted into 4-methylhydantoin-3- α -*p*-hydroxyphenylpropionic acid, $\text{NH} \begin{array}{c} \text{CO} \cdot \text{CHMe} \\ \text{CO} \cdot \text{N} \cdot \text{CH}(\text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OH}) \cdot \text{CO}_2\text{H} \end{array}$, m. p. 221° , by an intramolecular rearrangement, probably involving the addition and subsequent elimination of the elements of water. The action

of concentrated hydriodic acid and red phosphorus at 180° on 4-*p*-hydroxybenzylhydantoin-3- α -propionic acid leads to a crystalline substance, m. p. 184°, of the probable formula,

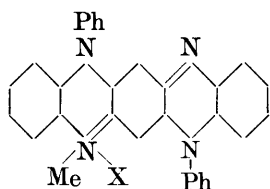


and ammonia; the production of ammonia in this experiment, and the interconversions described, are clear proof that the propionic residue enters in the position 3 during the original alkylations.

W. S. N.

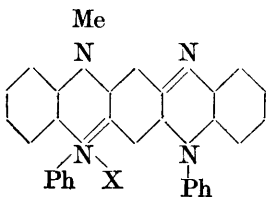
Fluorindinium Salts. F. KEHRMANN and PETER LEUZINGER (*Helv. Chim. Acta*, 1923, 6, 239—248).—By the action of methyl sulphate on diphenylphenofluorindine bases (cf. A., 1896, i, 512), basic dyes are formed, which are stable to alkalis and have the

properties of ammonium salts. A number of such compounds have been prepared and characterised as fluorindinium salts. It was found that, by heating hydroxyaposafranone (annexed formula) with *o*-aminodiphenylamine or its hydrochloride, using benzoic acid as solvent, only the green *iso*-diphenylphenofluorindine was formed, unaccompanied by the red diphenylphenofluorindine. The constitution of



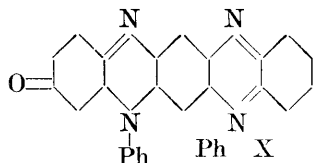
diphenylmethylphenofluorindinium mono-acid salts is expressed by the accompanying formula, where X is the acid radicle. *Diphenylmethylphenofluorindinium perchlorate*, $\text{C}_{31}\text{H}_{23}\text{O}_4\text{N}_4\text{Cl}$, crystallises in bronze needles, and the *di-perchlorate* forms bright, brassy needles. Both are practically insoluble in water, but soluble in boiling 80—90% alcohol. The colour in concentrated sulphuric acid is greenish-blue with a strong red fluorescence, not changing on dilution, but becoming pure blue when the free acid is neutralised. Cold alkali hydroxide does not change the colour of the alcoholic solution, but on warming the colour becomes reddish-violet with a fiery red fluorescence, through hydrolysis of the methyl group. Aqueous solutions of phenofluorindinium salts have an intensely bitter taste, whilst salts of diphenylphenofluorindine are tasteless. Ethyl sulphate reacts more slowly than methyl sulphate with diphenylphenofluorindine in nitrobenzene solution. *Diphenylethylphenofluorindinium diperchlorate* resembles the lower methyl homologue; the reactions are similar but decomposition of the ammonium base by alkali is considerably slower.

The constitution of salts of *isodiphenylmethylphenofluorindinium* may be expressed by the annexed formula, although alternatives are possible. *isoDiphenylmethyl(ethyl)phenofluorindinium mono- and di-perchlorates* resemble closely the isomeride described above. When the bases are warmed with alkali in alcoholic solution, an olive-green colour quickly develops, but this green is not due to formation of



isodiphenylphenofluorindine, since it slowly changes to a reddish-violet with a strong red fluorescence. The nature of these changes has not yet been determined.

When *isodiphenylphenofluorindine* is oxidised with chromic acid, the reaction cannot be stopped at the di-phenazonium stage, but proceeds to the formation of a fluorindinone, corresponding closely with the oxidation of phenylphenazonium salts to *aposafranone* by



air. *isoDiphenylphenofluorindinone perchlorate*, annexed formula, $C_{30}H_{19}O_5N_4Cl$, forms small, green needles with a brassy reflex, dissolving in 80% alcohol with a permanganate-red colour, unaltered by ammonia or carbonate, but changing to orange-yellow with sodium hydroxide.

In concentrated sulphuric acid it has a yellowish-green colour, becoming violet-red on dilution. When reduced in alcohol with stannous chloride, it becomes intensely bluish-green, probably due to the formation of a *hydroxyisodiphenylphenofluorindine* salt. This is reoxidised by ferric chloride. The nitrate forms fairly large brassy crystals, and the *chloroplatinate*, $(C_{30}H_{19}ON_4)_2PtCl_6$, a heavy, greenish-grey, metallic, microcrystalline powder. E. H. R.

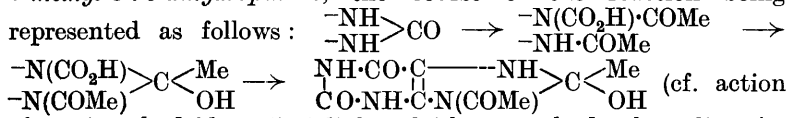
Solubility of Uric Acid in Water. HEINRICH BILTZ and LISBET HERRMANN (*Annalen*, 1923, 431, 104—111).—It is shown that the supersaturation which occurs (cf. A., 1921, i, 606, 609; also Schade and Boden, A., 1913, i, 403) when a warm aqueous solution of uric acid is allowed to cool to room temperature in contact with solid uric acid is probably the cause of the high values for the solubility found by Bensch (*Annalen*, 1845, 54, 190) and Behrend and Roosen (*Annalen*, 1889, 251, 250). A true equilibrium is, however, slowly reached when a cooled supersaturated solution is shaken, or, more rapidly, when solution is effected by shaking the solid acid with water at the room temperature; the values for the solubility found in this way agree with the figures of His and Paul (A., 1901, i, 131; cf. Kohler, A., 1911, i, 690). The observation of His and Paul, that the solubility increases with the time of shaking, has not been confirmed, but it is agreed that saturation is quickly attained.

In these experiments, solution is effected in vessels of Jena glass, the concentrations being determined by evaporation of the filtered liquid in a platinum dish. After weighing, the basin and contents are brought to a red heat, cooled, and re-weighed, to determine the soluble matter present in the solution, derived from the glass.

Incidentally, the stability of uric acid and of 3 : 9-dimethyluric acid to water is demonstrated by means of measurements of hydrogen-ion concentration. W. S. N.

Action of Acetic Anhydride on Uric Acid. HEINRICH BILTZ and WALTER SCHMIDT (*Annalen*, 1923, 431, 70—104).—During the preparation of 8-methylxanthine by the action of acetic anhydride on uric acid (A., 1902, i, 125), Boehringer & Söhne isolated an intermediate product (A., 1902, i, 504) which they described as

2 : 4-dioxy-5 : 6-diacetamidopyrimidine; this could undoubtedly give 8-methylxanthine by elimination of acetic acid. Since, however, only one acetyl group can be eliminated by hydrolysis, it is now suggested that this intermediate product, the preparation of which is described, is to be formulated as 9-*acetyl*-2 : 6 : 8-*trioxy*-8-*methyl*-8 : 9-*dihydropurine*, the course of the reaction being represented as follows :



of acetic anhydride on 5 : 5-diphenyl-4-ketotetrahydroglyoxaline, A., 1922, i, 871). If ring formation occurs before the elimination of the carboxyl group, the process is comparable with the formation of carbinols from orthodiamines (Fischer, A., 1901, i, 413; 1902, i, 188). It is shown that the formula also agrees with the other properties of the substance.

Hydrolysis by means of aqueous sodium hydroxide or of fuming hydriodic acid leads to 2 : 6 : 8-*trioxy*-8-*methyl*-8 : 9-*dihydropurine*, which forms tabular prisms, decomp. above 300°, and yields an amorphous *silver* salt, a *perchlorate*, decomp. 163—164°, a *sulphate*, *hydrochloride*, and *nitrate*, and also a *potassium* salt, ciliate needles, which reacts with benzoyl chloride, giving a *benzoyl* derivative (? benzoate), very small leaflets of high melting point. Trioxymethylidihydropurine gives alloxan when oxidised by means of chlorine water. Trioxymethylidihydropurine, or its acetyl derivative, when heated with acetic anhydride loses water, or acetic acid, with formation of 8-methylxanthine, identical with Boehringer & Söhne's product, after the latter has been purified (details given) through the potassium salt; the *perchlorate*, colourless, tabular crystals, decomp. 292—294°, *hydriodide*, large, tabular crystals, *sulphate*, long, slender, four-sided prisms, *mononitrate*, small crystals, and the *dinitrate*, slender needles, are described. The reduction of trioxy-methylidihydropurine by means of hydriodic acid, or, as a side-reaction, the hydrolysis of the acetyl derivative by the same reagent, leads to 8-*methyl*-8 : 9-*dihydroxanthine*, small, colourless, transparent leaflets of high melting point, *hydriodide*, small, glistening six-sided tablets, decomp. indefinitely.

The methylation of trioxymethylidihydropurine by means of methyl sulphate leads to 2 : 6 : 8-*trioxy*-3 : 8-*dimethyl*-8 : 9-*dihydropurine*, long, slender needles, decomp. 305—306°, in which the second methyl group is attached to nitrogen, since no methoxyl is removable by means of hydriodic acid. That the methyl group is in position 1 or 3 is shown by the production, when oxidised with chlorine water, of a product which gives methylvioluric acid monohydrate on treatment with hydroxylamine acetate. The structure of the above dimethyl compound is finally proved by the production, by the action of acetic anhydride and a little pyridine, of 3 : 8-*dimethylxanthine* (A., 1902, i, 125), the constitution of which is now fixed beyond doubt by its synthesis from acetic anhydride and a sample of 3-methyluric acid (A., 1919, i, 292, 293) absolutely free from 9-methyluric acid.

2 : 4-Dioxy-5 : 6-diaminopyrimidine (Traube, A., 1900, i, 389), the preparation of which is described, gives a *sodium salt*, small, faintly yellowish-brown leaflets, which with hydrochloric acid gives a *hydrochloride*, pale yellow crystals, decomp. 253—255°; a *nitrate* has also been prepared. The action of acetic anhydride and a little pyridine on the above sodium salt leads to 2 : 6 : 8-*trioxy-1 : 9-diacetyl-8-methyl-8 : 9-dihydropurine*, small, brown prisms of high melting point, probably identical with the product described by Boehringer & Söhne (*loc. cit.*) as triacetyldiaminouracil; the *monohydrate* of a *sodium salt* of the same compound, slender needles, decomp. 258—260°, is also formed. The latter gives the 9-acetyl derivative on partial hydrolysis by means of sodium hydroxide; both the diacetyl compound and the sodium salt give trioxymethyl-dihydropurine on prolonged alkaline hydrolysis. W. S. N.

Reactions of Diazonium Salts with Cupric Compounds. I.
A. CONTARDI (*Ann. Chim. Appl.*, 1923, 7, 13—28).—Previous work on the transformations of diazo-compounds, especially those effected with the help of cupric salts, is discussed, and a table is given showing, for forty different amino-derivatives, the compounds obtained when the corresponding diazo-salts are treated with cupric chloride (or bromide) or sodium or cupric nitrite, and also those obtained when the diazophenols are treated with cupric chloride or bromide. Considerations of these results leads to the following generalisations: (1) In monohalogenated and mononitroanilines replacement of the amino-group by a nitro-group proceeds regularly and, usually, with almost theoretical yields; exceptions are *m*-nitro-aniline, which gives a poor yield of *m*-dinitrobenzene, and certain compounds of analogous structure. (2) The amino-group in a monohalogenated nitroaniline or in a dinitroaniline may be replaced by a nitro-group by passing through the diazo-compound only when the new nitro-group enters in such a position that its elimination and replacement by an amino-group by heating with alcoholic ammonia is possible; Fry's theory, according to which the eliminability of nitro-groups depends on their polarity, is discussed. (3) Halogen atoms introduced into the benzene nucleus exert comparatively little influence on these transformations, which, however, they may render impossible if they occupy the 2-, 4-, or 6-position with respect to the amino-group; in other cases, however, they facilitate the changes or render them practicable to some degree. (4) It has not yet been found possible to introduce a new nitro-group into trinitro-substituted amines by diazotisation. (5) During the substitution of the amino-group by the nitro-group, certain aromatic amines, especially those containing no strongly electro-negative substituent elements or groups in the nucleus, are converted into the corresponding mononitrophenols. T. H. P.

Liquid Crystals of Anisylidene-*p*-aminoazotoluene. P. GAUBERT (*Compt. rend.*, 1923, 176, 907—909).—Polemical. The author maintains the accuracy of his observations on the isotropic forms of anisylidene-*p*-aminoazotoluene, which have been disputed by Friedel (this vol., ii, 223). G. F. M.

Existence of an Unidentified Sulphur Grouping in the Protein Molecule. I. On the Denaturation of Proteins. LESLIE J. HARRIS (*Proc. Roy. Soc.*, 1923, [B], 94, 426—441).—It has been found that, whereas crystalline egg-albumin does not give the sodium nitroprusside reaction, a strongly positive reaction is given with the denatured protein. It is suggested that the denaturation of proteins involves the setting free of a reactive group, probably sulphhydrol. It is considered probable that in heat coagulation of proteins a chemical change into metaprotein first takes place, followed by a physical change into the coagulated protein.

W. O. K.

Existence of an Unidentified Sulphur Grouping in the Protein Molecule. II. On the Estimation of Cystine in certain Proteins. LESLIE J. HARRIS (*Proc. Roy. Soc.*, 1923, [B], 94, 441—450).—Cystine is estimated by hydrolysis of the protein and isolation of the cystine under standard conditions. The actual amount found is estimated multiplied by 100/39·53, this factor being based on the amount of cystine isolated after hydrolysis, from gelatin to which a definite amount of pure cystine had been added. Whereas, in serum-albumin, the cystine accounts for no less than 89% of the total sulphur content, in ovalbumin 86% of the sulphur still remains to be accounted for. W. O. K.

The Action of Sodium Chloride on Collargol. A. F. GERASIMOV (*J. Russ. Phys. Chem. Soc.*, 1916, 48, 1848—1851).—It is shown that if a collargol solution is coagulated by acetic acid, and a sodium chloride solution slowly added, the coagulated silver at first redissolves and then, as the concentration of sodium chloride increases, is reprecipitated. This phenomenon is explained by the adsorption law, according to which adsorption is a function of ionic concentration. It is assumed that at low concentrations, chloridion is more adsorbed than natrion, whilst at higher concentrations the reverse is the case. Thus, in the former case, a preponderating quantity of negatively charged chloridions is adsorbed by the discharged particles of silver, which thus acquire a negative charge, and once again go into solution. When, however, the concentration of sodium chloride rises beyond a certain point, more natrions are adsorbed on the particles than chloridions, and their negative charge is again neutralised, causing them to be reprecipitated.

R. T.

Autoclave Hydrolysis of Proteins with Carbon Dioxide and Oxalic Acid. V. S. SADIKOV (*Biochem. Z.*, 1923, 136, 238—240).—Egg-albumin and goose feathers were hydrolysed by aqueous solutions of carbon dioxide under pressure in an autoclave at 160—185°. The biuret reaction was negative. Gelatin and casein under similar conditions with oxalic acid gave products soluble in alcohol which do not give the biuret or ninhydrin reaction. The results are preliminary.

H. K.

Products of the Catalytic Fission of Proteins. V. S. SADIKOV and N. D. ZELINSKY (*Biochem. Z.*, 1923, 136, 241—249).—This

paper is a description of results obtained for which the experimental details and methods of separation are promised later. Six kg. of goose feathers were hydrolysed in an autoclave at 180° with 1% hydrochloric acid for six hours. The product does not give the biuret reaction. It was extracted successively with ether, ethyl acetate, chloroform, and amyl alcohol, which accounted for 50% of the material. The ethereal extract contained crystalline anhydrides, a number of which have been identified, and a syrupy mixture of anhydrides. The ethyl acetate contained crystalline and syrupy anhydrides and free amino-acids. The chloroform extract contained syrupy and crystalline anhydrides. The amyl-alcoholic extract contained anhydrides and free amino-acids. The aqueous liquor left after extraction with solvents contains simple and complex amino-acids and also nitrogen-free acids. H. K.

Determination of the Rate of Digestion of Albumin. A. FRIEDERICH (*Chem. Ztg.*, 1923, **47**, 265—266).—The increase of concentration of soluble albumin taking place during the process of digestion with pepsin is measured by means of Löwe's interferometer (*ibid.*, 1921, **45**, 405, 1025), which admits of a high degree of accuracy. 2.5 Grams of the substance under examination are placed in a 250 c.c. flask together with 150—200 c.c. of water and 10 c.c. of dilute hydrochloric acid. The mixture is incubated at 37° and repeatedly shaken until the interferometer readings of two samples filtered off at intervals of one hour are the same, showing that all soluble albumin has gone into solution. 0.5 Gram of pepsin is then added and the volume in the flask made up to the mark with water at 37°. The contents are shaken and 1 c.c. is filtered off and its interferometer reading taken as the zero reading of the solution. The contents of the flask are incubated at 37° and small samples withdrawn and filtered every hour and their interferometer readings taken until these readings remain constant. A larger quantity of the solution is then filtered and the soluble albumin in the clear filtrate estimated by a micro-Kjeldahl method. This gives the total digestible albumin present, and enables the interferometer readings to be transposed into terms of percentage of albumin digested. The method gives consistent results. The data from two specimen analyses and curves showing the rate of digestion in each case are given. One sample was completely digested in two hours, whilst the other required twenty-seven hours. The percentages of digestible albumin present were 82.6 and 67.6, respectively. Other methods only showed a trifling difference between these two samples. H. C. R.

Conphaseolin. A New Globulin from the Navy Bean, *Phaseolus vulgaris*. HENRY C. WATERMAN, CARL O. JOHNS, and D. BREESE JONES [with S. PHILLIPS] (*J. Biol. Chem.*, 1923, **55**, 93—104).—In addition to the globulins phaseolin and phaselin isolated by Osborne (A., 1896, i, 454; 1897, i, 207), the navy bean contains a third globulin, *conphaseolin*. This has been isolated by fractional precipitation of a sodium chloride extract of the bean with ammonium sulphate. Conphaseolin resembles the α -globulins

obtained from other beans of the genus *Phaseolus* (cf. for example, A., 1922, i, 1101), and is distinguished from phaseolin and phaselin by its high sulphur content. Analysis by Van Slyke's method gave the following values for basic amino-acids: Cystine 1·18%, arginine 6·87%, histidine 0·85%, lysine 10·69%. Phaseolin has been similarly analysed, with the following results (cf. A., 1920, i, 401): cystine 1·16%, arginine 6·36%, histidine 2·36%, lysine 9·42%. E. S.

Chlorinated Proteins. E. SALKOWSKI (*Biochem. Z.*, 1923, 136, 169—189).—Albumose and casein have been chlorinated. Chlorocasein on hydrolysis yields the same products as casein with fewer reducing substances. It is very resistant to pepsin and trypsin, and shows little tendency to putrefy. H. K.

The Optical Properties of Leguminates of the Alkali Metals. M. A. RAKUZIN and G. F. PEKARSKAJA (*J. Russ. Phys. Chem. Soc.*, 1916, 48, 1888—1889).—Various optically active alkali metal leguminates have been prepared, and their optical rotations measured: the ammonium salt has $[\alpha]_D -67\cdot33^\circ$, the lithium salt, $[\alpha]_D -38\cdot86^\circ$, the sodium salt, $[\alpha]_D -39\cdot31^\circ$, and the potassium salt, $[\alpha]_D -39\cdot62^\circ$. The low values obtained for the last three salts are undoubtedly due to racemisation, but a gradual increase in the optical rotation is observable with increasing atomic weight of the metal. R. T.

Crystals of Hæmoglogin of Rodents, particularly of the Hamster (German Marmot). OTTO KRUMMACHER (*Z. Biol.*, 1923, 77, 175—180).—Crystals of hæmoglobin prepared from the blood of a hamster have been found to belong to the monoclinic system. Those obtained from most other mammals are rhombic, except those from the squirrel, which are hexagonal. Those from the pigeon are quadratic. W. O. K.

The Effect of Carbon Dioxide and Acetic Acid on the Osmotic Pressure of Hæmoglobin. HELENE CONNET WILSON (*Biochem. J.*, 1923, 17, 59—71).—The osmotic pressure of solutions of purified hæmoglobin is three or four times as great when dialysed against acetic acid or water saturated with carbon dioxide (both about P_H 4) as against water alone. The author is of the opinion that this phenomenon is due to the ionisation of some salt of hæmoglobin such as the one which ionises into protein-ions, or into protein- and acetate-, or protein- and bicarbonate-ions. S. S. Z.

Preparation and Estimation of Guanylic Acid: the Solubility of Sodium Guanylate in Salt Solutions and Water. R. FEULGEN and H. ROSSENBECK (*Z. physiol. Chem.*, 1923, 125, 284—288).—The solubility of sodium guanylate in solutions of sodium acetate and of sodium chloride has been determined, with reference to the isolation of guanylic acid as the sodium salt by Feulgen's method, which depends on the relative insolubility of that acid in sodium acetate solution (A., 1921, i, 136). W. O. K.

Keratin. III. A. HEIDUSCHKA and E. KOMM (*Z. physiol. Chem.*, 1923, 126, 130—142; cf. this vol., i, 69).—By the use of

the iron method of Siegfried, a peptone has been isolated from the products of the partial hydrolysis of horn (cf. *loc. cit.*), having the empirical formula $C_{11}H_{20}O_5N_3$ and $[\alpha]_D^{20} -15.5^\circ$ approx.

W. O. K.

A New Synthesis of *r*-Tryptophan. RIKO MAJIMA and MUNIO KOTAKE (*J. Chem. Soc. Japan*, 1922, 43, 926—936).—*r*-Tryptophan has been synthesised from indole. Alessandri (A., 1915, i, 988) failed to obtain β -indolealdehyde, $C_8H_6N \cdot CHO$, from magnesium indole halide and formic ester using ether as a solvent, whilst the authors have succeeded in obtaining the aldehyde by the same method using anisole as a solvent, the yield being 40%. When phenetole was used instead of anisole, the yield decreased to about 23%, and when ethyl ether, amyl ether, or dimethylaniline were used, the aldehyde was not obtained. Using ethoxymethyleneaniline instead of formic ester, the aldehyde was also obtained, but the yield was less and the product was impure. β -Indolehydantoin, $C_8H_6N \cdot CH \cdot C_3H_2O_2N_2$, is formed by heating β -indolealdehyde and hydantoin with anhydrous sodium acetate and acetic anhydride at 106 — 108° during thirty minutes; the product was boiled with alcohol and filtered after cooling and the residue dissolved into *N*-sodium hydroxide solution, precipitated by acidifying the solution with acetic acid, and crystallised from glacial acetic acid, the yield being 46.6%. β -Indolehydantoin is reduced by sodium amalgam in sodium hydroxide solution to ω -hydantoylskatole, $C_8H_6N \cdot CH_2 \cdot C_3H_3O_2N_2$ (yield 68%), which is then decomposed into *r*-tryptophan, $C_8H_6N \cdot CH_2 \cdot CH(NH_2) \cdot CO_2H$, by heating with saturated baryta water at 108° for six hours, the yield being 53%. The product forms long, hexagonal plates with silky lustre, and decomposes at 283 — 285° . As a by-product, an unknown compound, $C_{12}H_{13}O_3N_3$, crystallising in plates, m. p. 207° (decomp.), is obtained.

K. K.

Apparatus for Preparing Dry Powders of Dissolved or Suspended Thermolabile Substances. DAG SALOMONSON and H. VON EULER (*Arkiv Kem. Min. Geol.*, 1922, 8, No. 24, 1—3).—The loss of activity of enzyme solutions by alcohol precipitation may be diminished by concentrating at low temperatures and pressures before precipitating. Dry preparations of enzymes are readily obtained by using a modified form of Krause's apparatus (D.R.-P. 297388 of 1918). The solution or suspension to be evaporated is blown by means of carbon dioxide from a capillary jet surrounded by a slightly wider one through which the same gas is blown, warm carbon dioxide (70°) being blown through a third jet enclosing the other two. The jets pass into a large glass cylinder, the other end of which is covered with silk. The dry material collects in the cylinder. Air may be used for evaporating yeast solutions by this method, but for enzymes carbon dioxide is essential, to prevent oxidation.

E. E. T.

Nomenclature of Proteases. CARL OPPENHEIMER (*Biochem. Z.*, 1923, 136, 140—141).—The proteases can be provisionally

classified as follows. A. *True proteases* which break down protein to the peptide stage. These include *pepsinases*, characterised by an optimum in acid solution, *tryptases* with an optimum zone near neutrality. B. *Peptidases* or *creptases* which only split peptides or peptones. H. K.

Saccharase. H. VON EULER and KARL JOSEPHSON (*Arkiv Kem. Min. Geol.*, 1922, 8, No. 23, 1—9).—The amino-nitrogen present in saccharase has been estimated by Van Slyke's methods (A., 1916, ii, 61). About two-thirds of the total nitrogen present is apparently in ring-combination. The following figures are given for the complete analysis of saccharase: ash 1—4, phosphorus 1—2, hexoses 60—20, pentoses under 5, total nitrogen 5—8, amino-nitrogen 2, easily-eliminable nitrogen about 1 per cent. These figures do not seem to be at variance with the suggestion that saccharase contains nucleic acid groupings (cf. A., 1922, i, 959), although the absence of positive tests for pentoses makes it improbable that Levene's type of nucleotide groupings is present. It is thought that combination between saccharase and sucrose is more likely to be due to partial valency addition than to adsorption.

The irreversible inactivation of saccharase by iodine (cf. A., 1922, i, 1076) has been further studied. It is now found that saccharase, cinnamic acid, benzaldehyde, and alanine behave similarly in not combining with or adsorbing iodine in dilute aqueous solutions. Bromine, under similar conditions, is taken up by saccharase, 1 g. of which combines with or adsorbs 0.48 g. of bromine. Cinnamic acid combines with 1 molecular proportion of bromine in like circumstances, alanine reacts with bromine in amounts depending on time, whilst benzaldehyde scarcely reacts at all. The authors therefore refrain from discussing the presence of definite groupings in the saccharase molecule. E. E. T.

Inactivation of Saccharase by *p*-Phenylenediamine, *p*-Toluidine, and Formaldehyde. H. VON EULER and KARL MYRBÄCK (*Z. physiol. Chem.*, 1923, 125, 297—314).—*p*-Phenylenediamine and *p*-toluidine inhibit the action of saccharase (invertase), the former being the more effective if they are applied in molecular proportions. The action of *p*-phenylenediamine decreases with increase in the concentration of the substrate and is minimal at a P_H of about 3.5. Similar effects are obtained with *p*-toluidine, the exact effect of the hydrogen-ion concentration depending on the amount of the inhibitor added. Preliminary incubation of enzyme and inhibitor before addition of sugar appears to have little effect, whereas the inhibiting effect of formaldehyde is increased by such incubation. Diphenylphosphoric acid also inhibits the action of invertase, an effect which decreases with increasing acidity. W. O. K.

Purification of Yeast-saccharase. KARL JOSEPHSON (*Arkiv Kem. Min. Geol.*, 1922, 8, No. 26, 1—21).—An examination of the methods used by Willstatter and Racke (A., 1922, i, 598) for the

preparation of saccharase. It is found that bottom-yeast is better for this purpose than top-yeast, presumably because it is freer from yeast-gum. Purification is effected by the following series of processes: autolysis in presence of 10% of toluene and 1% of ethyl acetate; filtration; precipitation with alcohol; dissolution in water and adsorption on aluminium hydroxide, using as small a volume as possible; elution, using potassium dihydrogen phosphate and sucrose solution; and dialysis through collodion membranes (Euler and Svanberg, A., 1920, i, 689). Kaolin then removes yeast-gum, by adsorption, as stated by Willstätter and Racke, and affords very active saccharase. A second adsorption on aluminium hydroxide, followed by elution, gives a still more active product, whereas a second kaolin adsorption effects no improvement. Adsorption on cupric hydroxide apparently causes complete loss of activity, whilst sugar-charcoal adsorbs neither saccharase nor the accompanying substances. For further work, see Euler and Josephson (this vol., i, 402).
E. E. T.

Poisoning of Starch Amylase; Starch Liquefaction. III. URBAN OLSSON (*Z. physiol. Chem.*, 1923, 126, 29—99).—A comparison of the effect of copper sulphate, iodine, and aniline on the liquefaction of starch and on the production of sugar from it by malt diastase shows that the decrease in activity in the first two cases is quantitatively parallel, whilst in the case of aniline the liquefactive power is practically unaffected, although the sugar-producing power is decreased up to 21%. The method previously described (A., 1922, ii, 401) is adapted to quantitative measurement of the liquefactive power. It is found that the amount of sugar corresponds with a unimolecular reaction, whilst the liquefactive power is proportional to the amount of enzyme.

The effect of silver nitrate on maltase is proportional to the amount of the salt present, except with comparatively large amounts, when the decrease in activity lessens in proportion to the amount of silver nitrate present.
W. O. K.

The Reversibility of the Ferment Action of α -*D*-Mannosidase. H. HÉRISSEY (*Compt. rend.*, 1923, 176, 779—782).—The action of α -*D*-mannosidase is reversible, and according to the composition of the medium in which it is working it can bring about either the hydrolysis of a *D*-mannoside to mannose, or the synthesis of the mannoside from mannose. In a medium consisting of 10% methyl alcohol and about 1% of either mannose or α -*D*-methylmannoside, an identical position of equilibrium is eventually reached in each case which corresponds with 46—47% of the methylmannoside.

G. F. M.

Urease. I. The Chemical Changes Involved in the Zymolysis of Urea. WILLIAM ROBERT FEARON (*Biochem. J.*, 1923, 17, 84—93).—Cyanic acid has been isolated as the silver salt from solutions of urea undergoing decomposition by urease. It is suggested that urease acts as a dissociating enzyme which decomposes the neutral urea molecule into ammonia and cyanic

acid; the latter is further decomposed by the solvent into ammonia and carbon dioxide. The cyanic acid attains a maximum concentration in the urea-urease system and is being produced as fast as it is hydrolysed. The decomposition of urea through the medium of the enzyme proceeds similarly to the normal decomposition of urea by acids, alkalis, and heat. S. S. Z.

Vitamins. H. VON EULER and ALLAN BERNTON (*Arkiv Kem. Min. Geol.*, 1922, 8, No. 21, 1—9).—Continuing previous work (A., 1908, ii, 724), the authors have isolated from carrots a *phosphatide*, $C_{46}H_{88}O_{13}N$ (or N_2)P, and a *sterol*, $C_{25}H_{44}O$, m. p. 142° . The latter substance causes no appreciable increase in the fermentation of dextrose by bottom-yeast (freed from co-enzyme by previous washing and drying) in presence of sodium phosphate at p_H 4.5. The fermentation of dextrose by a similar yeast is unaffected by sodium pyruvate in presence of sodium phosphate at p_H 5 (cf. Neuberg, A., 1915, i, 1045). E. E. T.

Additive Reactions of Phosphorus Halides. VII. Addition of Alkyloxy- and Aryloxy-chlorophosphines to Carbonyl Compounds. J. B. CONANT, V. H. WALLINGFORD, and S. S. GANDHEKER (*J. Amer. Chem. Soc.*, 1923, 45, 762—768).—A continuation of previous work (A., 1918, i, 74; 1920, i, 454; 1921, i, 69; 1923, i, 69, 186) dealing with the 1:2 and 1:4 addition of phosphorus trichloride and its aryl derivatives.

Benzaldehyde condenses at the ordinary temperature, in the presence of acetic acid, with phenoxydichlorophosphine, methoxydichlorophosphine, and ethoxydichlorophosphine, forming, respectively, the *phenyl*, *methyl*, and *ethyl* esters of α -hydroxybenzylphosphinic acid, $OH \cdot CHPh \cdot PO(OH) \cdot OR$, as oils; the constitution of these esters is proved by the production of α -hydroxybenzylphosphinic acid on hydrolysis by means of 15% aqueous hydrochloric acid, the free acid being readily identified as its aniline salt.

Phenoxydichlorophosphine condenses with phenyl styryl ketone in the presence of acetic acid, or, better, acetic anhydride, with formation of phenyl β -benzoyl- α -phenylethylphosphinate.

In the presence of acetic acid, diphenoxychlorophosphine undergoes the following condensations: with benzaldehyde, to form *diphenyl α -hydroxybenzylphosphinate*, m. p. 146° , identified by hydrolysis to the acid; with acetone, to form *diphenyl α -hydroxyisopropylphosphinate*, m. p. 113 — 114° , *acetate*, m. p. 72 — 72.5° ; with methyl ethyl ketone, to form *diphenyl α -hydroxyisobutylphosphinate*, m. p. 128.5° ; with acetophenone, to form *diphenyl α -hydroxy- α -methylbenzylphosphinate*, m. p. 143.5° . *Diphenyl α -hydroxy- β -chloroisopropylphosphinate*, white cubes, m. p. 119° , is formed from chloroacetone and diphenoxychlorophosphine in the presence of benzoic acid, but those substances do not condense in the presence of acetic acid.

The diphenoxychlorophosphine used in these experiments is prepared by heating phosphorus trichloride (0.5 mol.) with triphenylphosphite (1 mol.) for six hours at 150° ; the yield is 90% of theory. W. S. N.

Organic Arsenic Derivatives. HEINRICH WIELAND (*Annalen*, 1923, 431, 30—40).—[With A. KULENKAMPEFF.]—The direct introduction of arsenic into the benzene nucleus (cf. Michaelis and Rabinerson, A., 1892, 1321) is accomplished by the addition of aluminium chloride (2·5 mols.) to a boiling solution of arsenic trichloride (1 mol.) in a large excess of benzene. Since aromatic arsenic derivatives are decomposed by aluminium chloride, 30—40% of the total arsenic present is converted into the free element; the remainder appears as phenylarsine dichloride (5 parts), diphenylarsine chloride (1 part), and triphenylarsine (14 parts). [With W. MADELUNG.]—Triphenylarsine is also obtained in 60% yield by the gradual addition of diphenylarsinic acid (26 g.) to warm phenylhydrazine (11 g.); the suggested mechanism of this reaction is indicated by the following equations: (1) $\text{AsPh}_2\text{O}\cdot\text{OH} + \text{NH}_2\cdot\text{NHPh} = \text{AsPh}_2\cdot\text{OH} + \text{C}_6\text{H}_6 + \text{N}_2 + \text{H}_2\text{O}$. (2) $\text{AsPh}_2\cdot\text{OH} + \text{NH}_2\cdot\text{NHPh} = \text{AsPh}_2\cdot\text{NH}\cdot\text{NHPh} + \text{H}_2\text{O}$. (3) $\text{AsPh}_2\cdot\text{NH}\cdot\text{NHPh} + \text{AsPh}_2\text{O}\cdot\text{OH} = \text{AsPh}_2\cdot\text{N}\cdot\text{NPh} + \text{AsPh}_2\cdot\text{OH} + \text{H}_2\text{O}$. (4) $\text{AsPh}_2\cdot\text{N}\cdot\text{NPh} = \text{Ph}_3\text{As} + \text{N}_2$. If phenylarsinic acid is used, the reaction proceeds less readily, whilst arsenic acid is merely reduced to arsenious acid.

[With A. BLOEMER.]—When acetylene is led into a cooled mixture of aluminium chloride and arsenic trichloride, addition of the latter at the triple bond of the acetylene occurs (cf. A., 1922, i, 1033), with formation of *β-chlorovinylarsine dichloride*, a colourless oil, b. p. 77—78°/12 mm., which reacts with a second molecule of acetylene to give *di-β-chlorovinylarsine chloride*, a heavy, colourless oil, b. p. 113°/11 mm., previously described by Dafert (*Monatsh.*, 1919, 40, 313) as a molecular compound. This secondary arsine chloride combines with a further molecule of acetylene, forming *tri-β-chlorovinylarsine*, a colourless oil, b. p. 138°/12 mm., m. p. 13°. All three compounds appear in the product. The tertiary arsine is apparently not attacked by dilute hydrogen peroxide, but the secondary and primary arsine chlorides are readily oxidised to *di-β-chlorovinylarsinic acid*, long, glistening prisms, m. p. 122°, and *β-chlorovinylarsinic acid*, long, glistening plates, m. p. 129°, respectively, both of which are decomposed by concentrated alkali hydroxide into acetylene, hydrogen chloride, and arsenic acid.

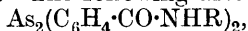
[With H. WESCHE.]—*Cacodyl carbide*, a golden-yellow oil, b. p. 84·5°/14 mm., has been prepared by the gradual addition of cacodyl chloride to a suspension of magnesium acetylene bromide in boiling ether; the substance is highly unsaturated, explodes in contact with nitric acid, and is reconverted by alkali into acetylene, with elimination of the arsine radicle.

W. S. N.

Arsenated Benzanilide and its Derivatives. W. LEE LEWIS and C. S. HAMILTON (*J. Amer. Chem. Soc.*, 1923, 45, 757—762).—The arsenated benzanilides are prepared by the action of *p*-dichloroarsinebenzoyl chloride (1 mol.) on aromatic amines in benzene solution. The impure product, which still contains chlorine united to the arsenic, is isolated as the arsenic acid after oxidation in glacial acetic acid solution by means of 3% hydrogen peroxide solution. The addition of sodium halide to the acetic acid solution gives the

corresponding dihalide, whilst the arsino-derivatives are best prepared by reduction by means of phosphorous acid or hypophosphorous acid in hot concentrated alcoholic solution.

The following arsino-compounds, $\text{AsO}_3\text{H}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NHR}$, form colourless crystals of high melting point: *p*-Arsinobenzanilide, *p*-arsinobenzanthranilide, *p*-arsinobenzo-*p*-anisidide, *p*-arsinobenzo-*p*-phenetidine, and *p*-arsinobenz-*o*-anisidide. *p*-Arsinobenzoyl-arsanilide, $\text{AsO}_3\text{H}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{AsO}_3\text{H}_2$, is formed by the oxidation, by means of alkaline hydrogen peroxide, of *hydrated p*-arsinosobenzoylarsanilide, $\text{As}(\text{OH})_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{AsO}_3\text{H}_2$, produced by the condensation of arsanilic acid with *p*-dichloroarsinebenzoyl chloride. The following arseno-compounds,



are yellow, insoluble, and of high melting point. *p*-Arsenobenzanilide, *p*-arsenobenzanthranilide, *p*-arsenobenzo-*p*-anisidide, *p*-arsenobenzo-*p*-phenetidine, *p*-arsenobenzo-*p*-xylylide, *p*-arsenobenzo- α -naphthylidide. The following halogen derivatives are described: *p*-di-iodoarsinebenzo-*p*-anisidide, yellow needles, m. p. 209—210°, *p*-di-iodoarsinebenzo-*p*-phenetidine, yellow needles, m. p. 227—228°; *p*-di-iodoarsinebenzethylanilide, canary-yellow needles, m. p. 115—116°, *p*-di-iodoarsinebenz-*o*-anisidide, m. p. 148—149°, *p*-dibromoarsinebenz-*o*-anisidide, slightly yellow crystals, m. p. 167—168°, *p*-dichloroarsinebenz-*o*-anisidide, slightly yellow crystals, m. p. 164—165°, *p*-dichloroarsinebenzethylanilide, colourless cubes, m. p. 147—148°.

Gluconic acid condenses rapidly with *p*-arsanilic acid in hot methyl-alcoholic solution to form *gluconyl-p*-arsanilic acid, $\text{OH} \cdot \text{CH}_2 \cdot [\text{CH} \cdot \text{OH}]_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{AsO}_3\text{H}_2$, and more slowly in cold methyl-alcoholic solution with 3:4-diaminophenylarsinic acid to form 3:4-di(*gluconylamino*)phenylarsinic acid, yield 70%; both these acids are readily hydrolysed by means of dilute alkali.

W. S. N.

Arsination of *o*-Cresol and *m*-Cresol. WALTER G. CHRISTIANSEN (*J. Amer. Chem. Soc.*, 1923, **45**, 800—804).—In the arsination of *o*-cresol the formation of tar is much greater, the yield less, and the isolation of the products more difficult than in the case of phenol (Jacobs and Heideberger, A., 1919, i, 604); the arsination of *m*-cresol proceeds with less formation of tar.

The action of arsenic acid on *o*-cresol at 155—160° leads to 6-hydroxy-*m*-tolylarsinic acid, 6:6'-dihydroxydi-*m*-tolylarsinic acid, 2-hydroxy-*m*-tolylarsinic acid, m. p. 198—200°, and 2:6'-dihydroxydi-*m*-tolylarsinic acid, m. p. 208—210°; the last two acids give a purple coloration with ferric chloride.

The action of arsenic acid on *m*-cresol at 140—146° leads to 5-hydroxy-*o*-tolylarsinic acid, 3-hydroxy-*o*-tolylarsinic or 3-hydroxy-*p*-tolylarsinic acid, m. p. 165—167°, giving a red coloration with ferric chloride. Secondary arsenic acids are also produced, which are not, however, completely separable, although a partial separation is effected by fractional decomposition of the calcium salts.

W. S. N.

Preparation of *p*-Tolyl Mercury Compounds. FRANK C. WHITMORE, FRANCES H. HAMILTON, and NEAL THURMAN (*J. Amer. Chem. Soc.*, 1923, 45, 1066—1068).—The preparation of sodium toluene-*p*-sulphinat from toluene-*p*-sulphonyl chloride and zinc dust in aqueous suspension is described in an improved form, the yield being 80—90%. Sodium toluene-*p*-sulphinat and mercuric chloride react in boiling aqueous solution to give mercury *p*-tolyl chloride, yield 58%, which is converted into mercury di-*p*-tolyl by means of sodium iodide in boiling alcoholic solution, yield 80% (cf. Kharasch and Chalkley, A., 1921, i, 377). W. S. N.

Reactions of Organic Mercury Compounds with Halides.
I. Mercury Di-*p*-tolyl and Sulphonyl Halides. FRANK C. WHITMORE and NEAL THURMAN (*J. Amer. Chem. Soc.*, 1923, 45, 1068—1071; cf. preceding abstract).—Toluene-*p*-sulphonyl iodide reacts with mercury di-*p*-tolyl, in boiling carbon tetrachloride solution, to give di-*p*-tolylsulphone, mercuric iodide, and tolyl-mercuric iodide; toluene-*p*-sulphonyl chloride does not react under the same conditions, but this chloride or benzenesulphonyl chloride reacts with mercury di-*p*-tolyl at higher temperatures in toluene or xylene solution, giving, however, only traces of definite organic products. No mercury phenyl chloride is obtained by the action of benzenesulphonyl chloride on mercury di-*p*-tolyl. W. S. N.

Physiological Chemistry.

The Anticatalytic Action of Hydrocyanic Acid. OTTO WARBURG (*Biochem. Z.*, 1923, **136**, 266—277).—In opposition to Wieland's theory of cell respiration, but in support of the author's theory that cell respiration is catalysed by a surface effect of the heavy metals contained in living cells, experiments are detailed. Hydrocyanic acid in minute amounts inhibits the oxidation of leucine and oxalic acid by blood charcoal, but if the charcoal be heated with concentrated hydrochloric acid to diminish its content of iron, it still oxidises leucine and oxalic acid, but hydrocyanic acid has less inhibiting action. Hydrocyanic acid inhibits by attachment to the heavy metals and prevents the activation of oxygen.

H. K.

Observations on the Effect of High Altitude on the Physiological Processes of the Human Body, Carried Out in the Peruvian Andes. JOSEPH BARCROFT and OTHERS (*Phil. Trans.*, 1923, [B], 211, 351—480).—The chief result obtained by the expedition is that the lungs do not secrete oxygen. The pressure of oxygen in the blood was so nearly the same as that in the alveolar air that the passage of the gas through the pulmonary epithelium can only be attributed to diffusion. The increased concentration of corpuscles at high altitudes is not merely to transport a certain quantity of

*l**

oxygen; it also brings about an extra degree of buffering of the blood, allowing of a more alkaline corpuscle at a given carbon dioxide pressure of 25 mm., a higher dissociation curve, and therefore a corpuscle which is more acquisitive of oxygen in the lung.

G. B.

The Respiratory Exchange, Blood-reaction, and Level of Phosphoric Acid in the Blood During Mental Work. HUGO WILHELM KNIPPING (*Z. Biol.*, 1922, **77**, 165—174).—Mental work is accompanied by only small increases in heat production. Nevertheless, on the commencement of such work, there is an immediate rise in the respiratory quotient which then rapidly decreases to a value below that found at rest. From analyses of the phosphoric acid content of the blood before and during mental activity, it is concluded that this effect is due to the entrance of free phosphoric acid into the blood with the consequent liberation of carbon dioxide.

E. S.

The Immediate Effect of Heavy Exercise (Stair-running) on some Phases of Circulation and Respiration in Normal Individuals. I. Oxygen and Carbon Dioxide Content of Blood Drawn from the Cubital Vein Before and After Exercise. CHRISTEN LUNDGAARD and EGGERT MÖLLER (*J. Biol. Chem.*, 1923, **55**, 315—321).—Heavy exercise, in which the muscles of the arm were not used, produced, in sixteen out of seventeen cases investigated, a marked decrease in the oxygen content of blood taken from the cubital vein. In one case, no change was observed. Variations in carbon dioxide were small and irregular. Possible explanations are discussed.

E. S.

The Inorganic Phosphorus Content of the Blood of Normal Children. GRACE HAY ANDERSON (*Biochem. J.*, 1923, **17**, 43—48).—The inorganic phosphorus content of the whole blood of twenty-four normal children between three months and thirteen years ranges from 4—6.6 mg. per 100 c.c. The average came to 4.9 mg. It is advisable to use whole blood for the estimation of phosphorus, as a considerable error may be obtained if serum is used which has been in contact with clot for some time. Twenty-four hours of fasting and a recent ingestion of a diet rich in phosphorus made no difference to the inorganic phosphorus content of the blood. The Bell-Doisy method for the estimation of phosphorus which was employed was found to have a range of experimental error of not more than plus or minus 10%.

S. S. Z.

The Calcium Content of the Blood during Pregnancy. SIBYL TAITE WIDDOWS (*Biochem. J.*, 1923, **17**, 34—40).—The calcium metabolism during pregnancy is so well balanced that the blood maintains a constant value in spite of varying demands made on it by the foetus during this period. Even in the later stages of pregnancy, when these demands are high, no diminution in the calcium content of the blood is observed.

S. S. Z.

Carbohydrate Metabolism. I. Some Comparisons of Blood-sugar Concentrations in Venous Blood and in Finger Blood. II. An Interpretation of the Blood-sugar Phenomena following the Ingestion of Dextrose. G. L. FOSTER (*J. Biol. Chem.*, 1923, 55, 291—301, 303—314).—I. Preliminary experiments indicated that the sugar concentration of arterial blood is identical with that of blood drawn from the finger tip. Hence the latter was used in place of arterial blood for the purpose of comparing the concentrations of sugar in venous and arterial blood during periods of active sugar absorption. The results show that, in the fasting condition, the concentrations are identical. After ingestion of dextrose or starch, the initial rise in concentration is much greater in finger than in venous blood; the subsequent hypoglycæmia is, moreover, much less marked in the case of finger blood. Ingestion of lævulose is followed by a slight rise in the sugar concentration of both finger and venous blood, that in the latter being sometimes practically absent; apparently lævulose is much more completely absorbed by the liver than dextrose. No marked hypoglycæmia was observed in the case of lævulose. Galactose causes a much higher level of hyperglycæmia than dextrose, the values for venous and finger blood being similar. This agrees with the fact that galactose is a poor glycogen former. Contrary to the results of Cammidge, Forsyth, and Howard (A., 1922, i, 81), the ingestion of a non-carbohydrate (agar-agar) meal produced no change in blood-sugar. II. Experiments are reported which support the conclusion of McLean and de Wesselow (*Quart. J. Med.*, 1921, 14, 103) that glycogen formation is stimulated by a rise in blood sugar, thus preventing excessive hyperglycæmia after the ingestion of dextrose. Further, the subsequent hypoglycæmia is due to over-activity of the glycogen-forming mechanism. E. S.

Blood Gas Analysis. XIII. Influence of α -Rays on Hæmoglobin and Blood-corpuscles. H. STRAUB and KL. GOLLWITZER-MEIER (*Biochem. Z.*, 1923, 136, 128—139).—The action of positively charged α -rays and of radium-*F* on hæmoglobin and suspensions of corpuscles in isotonic sodium chloride solution is to effect a change in the form of the curves obtained by plotting the carbon dioxide in combination against the tension. The results are held to support the authors' views on the existence of an electrical double layer at the boundary surface of corpuscles, α -rays neutralising the negative charge. H. K.

An Uneven Ionic Exchange between Corpuscles and Phosphate Buffer Mixtures of Increasing Hydrogen-ion Concentration. CHRISTIAN KROETZ (*Biochem. Z.*, 1923, 136, 250—265).—When washed corpuscles were added to phosphate mixtures of known p_H and then centrifuged after fifteen minutes, the p_H redetermined colorimetrically was always more alkaline, and although the original phosphate mixtures made up were of increasing p_H , the redetermined values after treatment with corpuscles, although higher, showed a tendency to retain a constant

value. An analogy is drawn with the parallel results of the carbon dioxide combination curve of hæmoglobin of Straub and Meier.

H. K.

Inorganic Phosphorus of the Serum and Plasma of Ninety-one Normal Adults as Determined by the Bell and Doisy Method. EDWARD TOLSTOI (*J. Biol. Chem.*, 1923, 55, 157—160).—The values found lie between 2.5 and 3.3 mg. of phosphorus per 100 c.c. Practically identical values were obtained for plasma and serum, provided the latter was not left for too great a time in contact with the clot.

E. S.

The Increase of Calcium-ions in Human Serum after Intravenous Injection of Calcium Salts. ERNST SIEBURG and ADOLF KESSLER (*Arch. exp. Path. Pharm.*, 1923, 96, 180—192).—After the injection of aqueous solutions of various calcium salts (chloride, formate, propionate, lactate) in amounts sufficient to double the calcium content of the blood, the concentration of calcium-ions (as distinct from total calcium) in the serum returned to the normal within half an hour. The effect of calcium hypophosphite was of shorter duration, probably owing to its rapid oxidation to phosphate. Admixture of the salts with gum arabic or agar-agar increased the time by about 25%; gelatin, however, had no such effect. Separate experiments on rabbits indicate that the condition of lipæmia has no influence on the rate of disappearance of injected calcium-ions.

E. S.

Comparative Content of Plasma and of Serum in Lipoids. (MME) PAULETTE JUNG and RENÉ WOLFF (*Bull. Soc. Chim. biol.*, 1923, 5, 137—147).—The blood lipoids appear to pass into the serum on coagulation, as the content of the serum in them is greater than that of the plasma. This difference is less, and in fact sometimes does not exist, in blood taken from fasting animals, and in those not fasting the difference varies, to some extent depending on the food which is being digested.

W. O. K.

Mode of Action of Formaldehyde with the Colloids of the Organism. II. H. KÜRTEN (*Biochem. Z.*, 1923, 135, 536—545).—Further experiments in support of the view that formaldehyde alters the state of serum proteins by a reversal of the state of swelling. The viscosity of the globulin and albumin fractions of sera were determined and compared with the value after heating at 60° for two hours. These values were then compared with the viscosities obtained after treatment with dilute formaldehyde solution. In each case the heated serum showed a greater reactivity to formaldehyde than the unheated.

H. K.

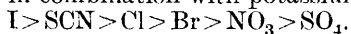
So-called Anti-enzymes. EMIL ABDERHALDEN and ERNST WERTHEIMER (*Fermentforsch.*, 1922, 6, 286—301).—The authors have made experiments with rabbits to ascertain if intravenous injection of an enzyme solution results in the appearance in the blood-serum of a substance with anti-enzymic properties, the enzymes employed being: polypeptidase from yeast maceration

juice and from pancreas, diastase from liver, lipase from pancreas, and saccharase obtained from yeast by Euler's method. In all cases were negative results obtained (cf. Knaffl-Lenz, A., 1922, i, 694). Even highly active saccharase preparations are incapable of undergoing dialysis.

T. H. P.

Hæmolytic Experiments with Salts of the Alkalies and Alkaline-earths under Normal and Pathological Conditions.

KURT BECKMANN (*Biochem. Z.*, 1923, 135, 317—328).—Contrary to Hamburger's results, but in agreement with Höber's, the degree of hæmolysis of blood-corpuscles is not the same for isotonic solutions. Over the range of hæmolysis from 0 to 100%, the kations combined with chloridion produce hæmolysis in the following order of effectiveness: $K > Rb > Li > Na > Cs$; $Ca > Ba > Sr, Mg$, and for the anions in combination with potassium



Under pathological conditions, the same sequence of ions holds good with slight variations.

H. K.

Does Injection of Peptone to Prevent Clotting Interfere with the Gaseous Metabolism?

G. KELEMEN (*Biochem. Z.*, 1923, 136, 154—158).—In experiments on a dog which received an intravenous injection of a 5% solution of Witte peptone to prevent blood-clotting, the oxygen consumption was considerably reduced and in all cases the respiratory coefficient increased. The conclusion is drawn that peptone cannot be used in experiments on the gaseous metabolism.

H. K.

Chemical Kinetics of the Digestion of Carbohydrates in the Duodenum of Mammals.

CARL BÖHNE (*Fermentforsch.*, 1922, 6, 200—229).—The principal co-enzymes of the diastase of the pancreas in the animal organism are phosphates, carbonates, and sodium chloride. In presence of potassium dihydrogen phosphate, 2% amylose solution having p_H 4.6—5 is digested by the enzyme in one hundred minutes, whilst with disodium hydrogen phosphate and p_H 8.4—9.1, twelve hours are required. The activity of the two phosphate-diastases increases as the hydrogen-ion concentration approaches the neutral point. When a mixture of the two phosphates is present and the value of p_H is 5.9—6.9, the digestion occupies eighty minutes. In presence of sodium hydrogen carbonate and with p_H 8.3, digestion is complete in twelve hours, but the intensity of the action varies with the concentration of the salt; if the latter is partly saturated with carbon dioxide, so that p_H becomes 6.7, the time of digestion is reduced to eighty minutes.

These results, depending mainly on the concentration of the hydrogen-ions, undergo marked alteration if small proportions of sodium chloride are added to the digestion mixture. If the latter has an alkaline reaction, sodium chloride activates the digestion to such an extent that the duration may be shortened from twelve hours to sixty to seventy minutes. Similar accelerating effects are produced by sodium chloride when the digestion liquid has

an acid reaction due to the presence of a mixture of either potassium dihydrogen phosphate and disodium hydrogen phosphate or sodium hydrogen carbonate and carbon dioxide. No explanation is advanced of the observation that, with either of these mixtures as co-enzyme, the optimum reaction for pancreatic diastase is displaced by sodium chloride towards the neutral point.

Thus the anions of the diastase-salt complexes, Cl' , HCO_3' , $\text{H}_2\text{PO}_4'$, and HPO_4'' , effect conversion of an inactive, resting enzyme into the active state, the course of the digestive process being governed mainly by the hydrogen-ion concentration and, to a less extent, by the concentration of the added salt.

The physiological consequences of these results are discussed.

T. H. P.

Carbohydrate Metabolism in Avitaminosis. II. Glycogen.

J. A. COLLAZO (*Biochem. Z.*, 1923, 136, 20—25).—Deficiency of vitamins-A, -B, and -C leads to a hyperglycæmic state in doves, fowls, guinea-pigs, and dogs, in which there is also a disappearance of glycogen from the various depôts. Under parallel conditions, fasting animals with slight hyperglycæmia show a higher liver, heart, and muscle content of glycogen.

H. K.

Carbohydrate Metabolism in Avitaminosis. III. Influence of Dextrose Administration.

J. A. COLLAZO (*Biochem. Z.*, 1923, 136, 26—37).—The author has examined the effect on the blood-sugar of the oral, rectal, intraperitoneal, intravenous, and subcutaneous administration of dextrose in large and small quantities to normal or fasting dogs or to dogs suffering from avitaminosis. Large doses (80 g.) in avitaminosis produce a more pronounced and protracted hyperglycæmia than in fasting or normal animals, whilst small doses (5 to 10 g.) produce in all cases a slight hyperglycæmia followed by a return to the normal level in normal and fasting dogs, but showing a transient hypoglycæmia in avitaminosis.

H. K.

Carbohydrate Metabolism in Avitaminosis. IV.

J. A. COLLAZO (*Biochem. Z.*, 1923, 136, 278—290).—Administration of carbohydrates to animals in a state of avitaminosis produces toxic symptoms. Dextrose, lævulose, and galactose are highly toxic, sucrose, lactose, and maltose less toxic, and starch least of all. If vitamins (yeast) be given at the first manifestations of toxic symptoms, these symptoms vanish and the hyperglycæmic condition of the blood subsides. Five g. of yeast were always found sufficient to counteract 10 g. of dextrose. It is concluded that vitamins are essential to the cells for the metabolism of carbohydrates.

H. K.

The Action of Thyroxin and of Very Small Amounts of Iodine [Potassium Iodide] on the Metabolism.

FRITZ HILDEBRANDT (*Arch. expt. Path. Pharm.*, 1923, 96, 292—304).—The identity of the physiological effects (increased oxygen consumption and decrease in body-weight) produced by injections of thyroxin and by the administration of thyroid gland by the mouth, observed

by Kendall, has been confirmed for rats. The effect of a thyroid-gland diet on rats is decreased by injection of small amounts of potassium iodide and increased by larger amounts. That the result in the former case is not due to an inhibition of the function of the thyroid gland has been shown by experiments on thyroid-ectomised animals. E. S.

Proteolytic Enzymes of the Lymph Glands. S. G. HEDIN (*Z. physiol. Chem.*, 1923, 125, 289—296).—When lymph glands are treated with dilute acid and subsequently extracted with a solution of casein, two enzymes are obtained, one with an optimum reaction of p_H 5.5, and an erepsin, with the optimum reaction p_H 8. If the glands are further extracted with a solution of sodium chloride, another proteolytic enzyme is obtained, optimum p_H 9—10.

W. O. K.

Oil of the Liver of *Squalus acanthias* from Moroccan Waters. SERGIO BERLINGOZZI and MARIA TOMASINI (*Ann. Chim. Appl.*, 1923, 7, 29—33).—This oil, expressed from the liver of the young fish, closely resembles cod-liver oil in its physical and chemical constants, and is readily converted into a solid fat by hydrogenation [cf. *J.S.C.I.*, 1923, May]. T. H. P.

Pancreatic Enzymes. III. Pancreas Amylase. RICHARD WILLSTÄTTER, ERNST WALDSCHMIDT-LEITZ, and ALBERT R. F. HESSE (*Z. physiol. Chem.*, 1923, 126, 143—168; cf. this vol., i, 403).—The action of amylase in the glycerol extract of dried pancreas is influenced by the presence of salts and by the hydrogen-ion concentration. The production of sugar from starch follows approximately a unimolecular reaction, and is proportional to the amount of enzyme present. On the basis of these findings, a method is devised for the estimation of amylase, the result being expressed in amylase units, an amylase unit being that amount for which, under given conditions, the constant of unimolecular reaction is 0.01. The amylase value of a preparation is the number of amylase units in 1 cg.

To isolate amylase from the crude extract of pancreas, the lipase is adsorbed on aluminium hydroxide, and then the trypsin is adsorbed by kaolin from a solution made slightly acid with acetic acid. The amylase is further purified by adsorption from 50% alcohol. The adsorbability of amylase decreases with increasing purity. An amylase preparation with an amylase value of at least 1205 has been obtained. The purified material showed no protein reactions, but still gave Molisch's reaction. W. O. K.

Polypeptide-cleaving Enzyme System in Pancreas Press-juice. Action of Vegetable Mucus on Enzyme Extracts of the Pancreas. A. FODOR (*Fermentforsch.*, 1922, 6, 269—285; cf. A., 1920, i, 464; 1921, i, 701).—By the method used to separate phosphorus-containing proteins in the sol-forming condition from yeast extracts, it is possible to obtain from pressed or maceration juice of the pancreas a phosphorus-containing protein approaching closely in composition those of yeast, but showing greater variations

in nitrogen and phosphorus content; thus purer products are obtainable from yeast juices than from animal cells and tissues.

The condition of the colloids in the pancreatic maceration juice has been investigated ultramicroscopically and experiments have been made on the influence exerted by carrageen extract on the polypeptidolytic activity of the juice. The results obtained indicate that the protein is the principal carrier of the enzyme action, but that the lipoids of the pancreas cells favour the suspensibility and the distribution of the enzyme colloids over large surfaces in virtue of their power of retarding aggregation and molecular agglomeration. The possibility of a connexion between enzymic activity and phosphorus content is discussed. T. H. P.

Tethelin: a Growth-controlling Substance obtainable from the Anterior Lobe of the Pituitary Body. THORBURN BRAILSFORD ROBERTSON (*Biochem. J.*, 1923, **17**, 77—82).—Polemical. The author asserts that Drummond and Cannan's repetition of his work (A., 1922, i, 491) was vitiated by a faulty method of preparation of tethelin and by not adopting the statistical method of comparing the growth of animals receiving this dietary principle with that of normal animals. S. S. Z.

Muscle Respiration and Sarcoplasma. GUSTAV EMBDEN and HERMANN LANGE (*Z. physiol. Chem.*, 1923, **125**, 258—283).—The skeletal muscles of frogs, if immersed in isotonic sucrose solution after being in Ringer's solution, show marked increase in oxygen consumption and increased liberation of phosphoric acid. These increases are accompanied by marked swelling of the sarcoplasma, and are greatest at a certain optimum swelling. W. O. K.

The Selective Absorption of Potassium by Animal Cells.
III. The Effect of Hydrogen-ion Concentration on the Retention of Potassium. RALPH E. STANTON (*J. Gen. Physiol.*, 1923, **5**, 461—468).—By perfusing frog's muscles with potassium-free Ringer solution of P_H from 6.0 to 8.0, it is shown that within this range the hydrogen-ion concentration has little or no effect on the retention of potassium. W. O. K.

Cholesterol Content of Various Muscles of Rabbits. GUSTAV EMBDEN and HEINZ LAWACZECK (*Z. physiol. Chem.*, 1923, **125**, 199—209).—The cholesterol content of various muscles in rabbits has been determined by heating the muscle with a 25% solution of potassium hydroxide, extracting with ether, evaporating the ethereal extract, and using an aliquot part of the chloroform extract for colorimetric estimation (heating with acetic anhydride and sulphuric acid). The white musculus biceps femorio contains about 0.04—0.06% of cholesterol, the red musculus semitendinosus, and the diaphragm 0.07—0.10%, whilst the heart contains 0.12—0.16%. W. O. K.

The Cholesterol Content of Various Muscles. HEINZ LAWACZECK (*Z. physiol. Chem.*, 1923, **125**, 210—219).—The cholesterol content of the muscles of various animals has been

investigated. It is concluded that in general there is a very strong parallelism between cholesterol content and resistance to fatigue.

W. O. K.

Chemical Differences between Skeletal Muscles of the Calf and the Ox. KAZUO HORTA (*Z. physiol. Chem.*, 1923, **125**, 220—228).—Analyses have been made of the nitrogen, cholesterol, and phosphoric acid contents of the biceps of the calf and the ox. There is more cholesterol, and correspondingly more “rest”-phosphoric acid, in the muscle of the calf than of the ox.

W. O. K.

The Interconversion of Creatine and Creatinine. IV. Origin of Creatinine in the Organism. AMANDUS HAHN and GEORG MEYER (*Z. Biol.*, 1923, **78**, 91—118; cf. this vol., ii, 195).—Quantitative experiments on the serum, blood, liver, and kidney of the ox and on the liver of the pig and dog show that during sterile autolysis at 38° there is no destruction either of creatine or of creatinine and no interconversion of these substances. Where occasionally an increased creatinine content was observed, it was shown to be due to the development of acidity, for, by the use of buffer mixtures of the same acidity and added creatine, a transformation into creatinine followed. Ferments for the interconversion of creatine and creatinine or their destruction are non-existent. Similar relations hold for creatinine and creatine in urine. When creatine is taken by mouth in solution by man, there is no increased creatinine output in the urine. Subcutaneous injections of creatine in the rabbit do not cause an increased creatinine excretion, and the whole of the creatine is excreted in twenty-four hours. The origin of creatinine in man is ascribed to transformation of the creatine of muscle brought about by the reaction of the tissue.

H. K.

Pigment in Horse Hair. KARL TUTSCHKU (*Biochem. Z.*, 1923, **135**, 585—586).—The hair of various coloured horses after washing with water was covered with a mixture of 75% alcohol and ether (9 : 1) for ten weeks. The solvent acquired a yellowish-green colour and gave the colour reactions for lipochrome with sulphuric acid and with nitric acid. The crystals obtained on removal of the solvent gave the Liebermann cholesterol reaction. If the hair is first of all treated with potassium hydroxide and filtered, the filtrate is free from lipochrome, but the insoluble matter when extracted with the alcohol-ether mixture gives the lipochrome reaction.

H. K.

Structural Colour in Feathers. I. CLYDE W. MASON (*J. Physical Chem.*, 1923, **27**, 201—251).—The colours of feathers have been investigated. It is shown that the non-iridescent blue of feathers is due to the scattering of blue light by very fine pores in the walls of the outer layer of cells of the barbs of the feathers. This is the blue described by Tyndall, which is commonly observed in turbid media. No blue pigments, and no other structural causes of blue colour, have been observed in non-iridescent feathers.

Green feathers are essentially the same as blue feathers, except that the blue cells are overlaid by a transparent, yellow layer.

J. F. S.

Substances Extracted from *Eledone moschata*. I. D. ACKERMANN, F. HOLTZ, and F. KUTSCHER (*Z. Biol.*, 1923, 77, 241—244).—Adenine and arginine have been isolated from the mussel, *Eledone moschata*.

W. O. K.

Chemical Composition of Coral from the Tyrrhenum. N. PASSERINI (*Gazzetta*, 1923, 53, i, 35—40).—The percentage composition of bright red coral (*d* 2.640) gathered in the Tyrrhenian Sea about 10 kilometres south of Leghorn and air-dried, is found to be: water, 0.600; organic matter, 2.545; calcium carbonate, 85.495; magnesium carbonate, 9.102; calcium sulphate, 1.230; other mineral constituents and loss, 1.028; manganese and iron, scarcely detectable traces. These results are compared with those of other investigators.

T. H. P.

The Sterol Content of Cow's Milk. FRANCIS WILLIAM FOX and JOHN ADDYMAN GARDNER (*Biochem. J.*, 1921, 17, 94—102).—Cholesterol is present in milk in the free state and in the form of esters. These compounds are found to be present in proportions of 0.351 g. to 100 g. of milk-fat—a figure which is in close agreement with those obtained by other workers. The output of cholesterol appears to follow approximately the output of fat. Although most of the cholesterol (free and ester) is present dissolved in the milk fat, some of it is also present in another form in the milk. The fraction which is precipitated from the unsaponifiable fraction of milk by digitonin consists entirely of cholesterol. The remaining portion of the unsaponifiable fraction consists of oils which are in part at least stable esters capable of withstanding saponification by alkali. The chemical behaviour of these oils is described.

S. S. Z.

The Rate of Decline of Milk Secretion with the Advance of the Period of Lactation. SAMUEL BRODY, ARTHUR C. RAGSDALE, and CHARLES W. TURNER (*J. Gen. Physiol.*, 1923, 5, 441—444).—The average daily production of milk varies with the month of lactation, and is found to be given by the formula $M_t = M_0 e^{-kt}$, where M_0 and k vary with the breed of cows. This is the formula of a unimolecular chemical reaction, and the result is considered to confirm the view that milk secretion is limited by a chemical reaction.

W. O. K.

Influence of the Acid and Base Content of the Food on the Composition of the Urine of Growing Dogs. JONAS BORAK (*Biochem. Z.*, 1923, 135, 480—492).—From consecutive experiments on a single dog or parallel experiments on two dogs of a litter, it was found that feeding with foodstuffs of an acid character such as rye meal, rye bread, or tripe resulted in a greater increase of weight than feeding with foodstuffs of a basic character such as milk, potatoes, carrots, and soja beans. The difference is

attributed to retention of water by the dogs fed on an acid diet, as nitrogen estimations on the food and urine showed a greater nitrogen excretion on an acidic diet than on a basic one, although the volume of urine in the former case was less than in the latter.

H. K.

Influence of the Composition of Food on the Calcium Output. B. SJOLLEMA (*Proc. K. Akad. Wetensch. Amsterdam*, 1923, 25, 395—398).—The variation of the amount of calcium and phosphorus in the faeces of a rabbit fed on various foods to which various amounts (3—12%) of non-digestible ballast have been added (such as oat straw or sawdust which had been boiled with acid and alkali) has been determined. The experiments show that an increase of the amount of non-digestible matter in the food causes a greater loss of calcium via the intestinal canal. All the calcium present in the faeces is not necessarily derived directly from the food, a large portion of it may be supplied by the organism, from which it is concluded that calcium plays a rôle in the production of faeces. In view of this, it follows that only under certain conditions can an examination of the faeces show whether calcium occurs in an available form in the food or in any part of it. In animals which are yielding much milk, feeding with much ballast increases the danger of a negative calcium balance.

J. F. S.

The Selective Action of the Kidney as Regards the Excretion of Inorganic Salts. W. DENIS (*J. Biol. Chem.*, 1923, 55, 171—181).—Analyses of the blood of dogs following the administration by the intestine or intravenously of magnesium sulphate, sodium sulphate, magnesium chloride, sodium chloride, and sodium phosphate indicate that the kidney exercises a selective retention for the sulphate-ion.

E. S.

Rate of Excretion of Urea. V. The Effect of Changes in Concentration of Urea in the Blood on the Rate of Excretion of Urea. T. ADDIS and D. R. DRURY (*J. Biol. Chem.*, 1923, 55, 105—111; cf. A., 1916, i, 352, 864; 1917, i, 367).—Under special conditions, the chief of which is abstention from food, the rate of excretion of urea is directly proportional to its concentration in the blood (cf. also Austin, Stillman, and Van Slyke, A., 1921, i, 383).

E. S.

Rate of Excretion of Urea. VI. The Effect of Very High Blood Urea Concentrations on the Rate of Excretion of Urea. D. R. DRURY (*J. Biol. Chem.*, 1923, 55, 113—118).—Experiments on rabbits indicate that the relation between the rate of excretion of urea and its concentration in the blood (preceding abstract) holds even when the latter is increased by injection to more than 700 mg. per 100 c.c.

E. S.

Constituents of the Urine Known as "Oxyproteic Acid." E. FREUND and ANNA SITTENBERGER-KRAFT (*Biochem. Z.*, 1923, 136, 145—153).—The preparation of oxyproteic acid from the

urine of carcinomatous patients is described and depends on the removal of foreign substances by alkaline copper sulphate and precipitation of the required acid by mercuric acetate. The amorphous barium salt precipitated by alcohol corresponds with an acid, $C_{10}H_{22}O_{10}N_2$. It had no characteristic protein reactions, but is possibly a derivative of carbamide, which it yields on hydrolysis.

H. K.

Hydrogen-ion Concentration of the Blood in Carcinoma.

I. From the Colorimetric Estimation of the Blood Dialysate.

WILLIAM H. CHAMBERS (*J. Biol. Chem.*, 1923, **55**, 229—255).—Estimations were made of the hydrogen-ion concentration of the dialysates from the venous blood of normal subjects and of patients suffering from carcinoma and other diseases. The method employed was similar to that of Dale and Evans (*A.*, 1921, i, 142); loss of carbon dioxide was prevented by carrying out the various stages under a layer of oil. The following are the average P_H values found at 20°: normal subjects 7.31, carcinoma cases 7.45, pathological cases other than carcinoma 7.36. The dialysates from the carcinoma patients were thus distinctly more alkaline than the others; the individual values show, further, that, in general, the alkalinity increased with the size of the tumour.

E. S.

Hydrogen-ion Concentration of the Blood in Carcinoma.

II. From the Carbon Dioxide-Bicarbonate Ratio.

WILLIAM H. CHAMBERS and R. E. KLEINSCHMIDT (*J. Biol. Chem.*, 1923, **55**, 257—290).—When calculated from the carbon dioxide-bicarbonate ratio, the hydrogen-ion concentration of the venous blood of carcinoma patients was found not to differ from that of normal subjects. The following are the average P_H values found at 38°: normal subjects 7.29, carcinoma cases 7.34, pathological cases other than carcinoma 7.33. The value found for normal blood at 38° thus agrees with that obtained from the dialysate at 20° (preceding abstract); at 38°, however, the latter would have a greater P_H value than the former. This greater alkalinity of the dialysate is explained by the authors on the basis of Donnan's theory of membrane equilibria. The same theory indicates that the still greater alkalinity of the dialysates from the blood of carcinoma patients is due to an increase of non-diffusible anions in the plasma.

E. S.

Zinc in Cancerous Tissues. Physicopathology of Zinc, and, Particularly, its Significance in Tumours.

PAUL CRISTOL (*Bull. Soc. Chim. biol.*, 1923, **5**, 23—40).—Estimations have been made of the zinc present in the liver, spleen, and blood in a case of leucæmia, and in a large number of tumour tissues. The zinc content appears to vary with the activity of the tumour.

W. O. K.

Behaviour of Cholesterol in Pigeon-Beri-beri. HEINZ LAWACZECK (*Z. physiol. Chem.*, 1923, **125**, 229—247).—There is an increase of cholesterol in the skeletal muscles of pigeons suffering from avian beri-beri.

W. O. K.

Influence of Cholesterol on the Consumption of Oxygen by Lecithin. HERMANN LANGE and HEINZ LAWACZECK (*Z. physiol. Chem.*, 1923, 125, 248—257).—Ciaccio has shown that there is a diminution of lecithin, whilst Lawaczek (preceding abstract) shows there is an increase of cholesterol, in skeletal muscles in avian beri-beri. The antagonistic action of cholesterol and lecithin on intercellular respiration deduced from this is confirmed in the present research. The addition of cholesterol to an emulsion of lecithin containing ferric chloride influences the consumption of oxygen by the lecithin, a maximum being attained when a certain proportion of cholesterol to lecithin is present.

W. O. K.

Change in the Nature of the Blood-sugar of Diabetics caused by Insulin. W. DEVEREUX FORREST, W. SMITH, and L. B. WINTER (*J. Physiol.*, 1923, 57, 224—233).—The two last-named authors have recently shown (*J. Physiol.*, 1922, 57, 100) that the normal blood-sugar in man and in animals has a lower rotatory power than would be given by the α - β -equilibrium form of glucose as deduced from the copper reduction value. The sugar gives an osazone with the same crystalline form and melting point as that of glucosazone. The instability of the sugar is shown by its transient rotatory power, the curve of the polarimeter readings reaching the copper reduction value in three or four days in acid solution. The sugar at first decolorises potassium permanganate more rapidly than a solution of α - β -glucose in similar concentration. This distinction no longer obtains when the polarimeter reading corresponds with that of α - β -glucose. These facts, in conjunction with the work of Hewitt and Pryde (*A.*, 1920, i, 508, 648) on sugar solutions introduced into the intestine, suggest that normal blood-sugar is γ -glucose. In diabetes, it is shown that this sugar is not present in amounts capable of detection by the method employed. The polarimeter reading in this disease is initially greater than the copper reduction value, suggesting that, besides α - β -glucose, disaccharides or other substances with a higher polarimeter : copper reduction ratio are present in the blood of diabetic persons. It is suggested that α - β -glucose cannot be directly stored or utilised, but that an enzyme is responsible for the conversion of α - β -glucose into γ -glucose; the absence of this enzyme is suggested as the direct cause of diabetes mellitus.

In the present communication, the above observations are confirmed in seven cases. The greatest change in the rotation observed, due to the administration of insulin, was 0.15° , the smallest about 0.01° (cf. also *Annual Reports*, 1923, 19, 195).

G. B

An Enzyme Responsible for Alteration of the Rotatory Powers of Glucose and Fructose. Some Evidence for the Existence of Polysaccharides in the Blood of Diabetics. The Lowering of the Blood-sugar by an Extract of Yeast. L. B. WINTER and W. SMITH (*Proc. Physiol. Soc.*, 1922, 1923; *J. Physiol.*, 1923, 57, xiii, xxxi, xl).—I. The enzyme appears to be present in the liver. Glucose and fructose solutions incubated

with very small amounts of insulin and liver extract have their rotations altered in a downward and upward direction, respectively. The insulin preparations are thermostable in this respect, and always contained phosphates; addition of phosphates accelerates the change in rotation. Boiled liver extracts are inactive.

II. Further evidence is obtained of the occurrence of polysaccharides (cf. preceding abstract).

III. A solid preparation of yeast has been obtained, which, like insulin, definitely lowers the blood-sugar on injection into rabbits. Rats, when it is injected, die in convulsions similar to those caused by insulin.

G. B.

Influence of the Nutritional Condition of the Animal on the Hypoglycaemia Produced by Insulin. N. A. McCORMICK, J. J. R. MACLEOD, E. C. NOBLE, and K. O'BRIEN (*J. Physiol.*, 1923, 57, 234—252; cf. *Annual Reports*, 1923, 19, 196).—The amount of glycogen in the animal has a distinct influence on the dose of insulin required to produce a given lowering of the blood-sugar, or to produce convulsions. Hence it is impossible to make a precise physiological assay of insulin by determining the percentage of blood-sugar at varying periods after the injection. An approximate assay can best be made by determining the blood-sugar ninety minutes, and three hours, after the injection in animals which have had no food for twenty-four hours.

G. B.

Ammonia Content of the Blood in Nephritis. DOROTHY STUART RUSSELL (*Biochem. J.*, 1923, 17, 72—76).—Estimations of blood-ammonia in a series of cases of advanced renal disease showed values under 0.1 mg.%. These values are of the same order as those found in the blood of normal patients. The author suggests that this observation lends support to Nash and Benedict's hypothesis that the ammonia formation in the body takes place in the kidneys.

S. S. Z.

The Inorganic Constituents of the Blood-serum in Nephritis. W. DENIS and S. HOBSON (*J. Biol. Chem.*, 1923, 55, 183—190).—The sera of twenty-two patients suffering from nephritis and cardiorenal disease have been analysed for non-protein nitrogen, creatinine, uric acid, and inorganic constituents. No marked regularity in the results has been observed. In many cases, a high value was obtained for the sulphate-ion, which appears to be excreted with more difficulty than any other inorganic radicle normally present in the blood.

E. S.

Analysis of Bone Ash in Cases of War Osteopathy. WILHELM LOLL (*Biochem. Z.*, 1923, 135, 493—503).—An analysis has been made of the bones of four severe cases of war osteopathy. Normal human bones contain CaO, 51.8—52.1%, MgO, 0.78—0.85%, and P₂O₅, 38.8%. In war osteopathy, the ribs and pelvis contain CaO, 56.8—76.8%, MgO, 0.74—0.8%, and P₂O₅, 16.2—37.3%. The composition of the tibia was nearly normal.

H. K.

Experimental Tetany. I. Distribution of Calcium in the Plasma and Cells. II. Variation in Colloidal and Ionic Calcium. E. W. H. CRUICKSHANK (*Biochem. J.*, 1923, 17, 13—29).—An immediate state of alkalosis which is not necessarily marked follows parathyroidectomy and with the onset of severe tetany it passes rapidly into a condition of acidosis. There is an immediate relief of the condition in dogs on withdrawing 70—100 c.c. of blood, which suggests a toxic causative factor. In tetany there was observed a loss of calcium amounting to 37.2% for whole blood, 54.4% for the cells, and 35.2% for the plasma. The diffusible calcium in sera of parathyroid tetanic animals amounted to 94% of the total calcium, whilst in the serum of normal animals the diffusible calcium was only 60—70% of the total calcium. The author concludes that the calcium deficiency and the great loss of colloidal calcium are due to a rapid protein disintegration. S. S. Z.

The Physiological Action of Amino-acid Esters. MINORU ARAI (*Biochem. Z.*, 1923, 136, 203—212).—The physiological actions of histidine methyl ester, tyrosine ethyl ester, *dl*-phenylalanine ethyl ester, *l*-leucine ethyl ester, *l*-cystine ethyl ester, and glycine ethyl ester have been examined. In general, the action is weak. On the blood-pressure, they may have a pressor or depressor effect, depending on the animal used, and on the isolated uterus they have a stimulating action. The actions are similar to those of the corresponding amines. H. K.

Hydrolysis of Amides in the Animal Body. The Comparative Stability of Surface Active Homologues in Relation to the Mechanism of Enzyme Action. CYRUS H. FISKE (*J. Biol. Chem.*, 1923, 55, 191—220).—Acetamide, propionamide, *n*-butyramide, and *n*-valeramide were injected subcutaneously into cats and the amount of unchanged amide excreted in the urine estimated in each case. The results indicate that the rate of hydrolysis of amides in the animal organism increases with the length of the carbon chain, the order of stability *in vivo* thus being the reverse of that shown *in vitro*. Attention is directed to other reactions (hydrolysis of esters, oxidative processes) in which a similar relation holds. Since the tendency to adsorption of homologous compounds increases with the length of the carbon chain, it is suggested that the greater reactivity in the body of the higher homologues is due to the greater ease with which they are adsorbed by enzymes. E. S.

The Relation between the Chemical Constitution of Proteinogenous Amines and their Effect on Body Temperature and Blood Pressure. M. CLOETTA and F. WÜNSCHE (*Arch. exp. Path. Pharm.*, 1923, 96, 307—329).—The following new substances have been obtained: *ethyl carbethoxyglutamate*; *carb-ethoxyglutamodiamide*, m. p. 179° (corr.); *pyroglutaminoamide*, glistening scales, m. p. 103° (corr.); *diacetyltyrosine ethyl ester*, fine white needles, m. p. 86° (corr.); *dicarbethoxytyrosine*, m. p. 97° (corr.); *diacetyltyramine*, m. p. 103° (corr.); *carbethoxytyramine*, m. p. 80—81° (corr.); *nitrotyramine*, a yellow powder, m. p. 210°

(corr.); *aminotyramine*, long, white crystals, m. p. 225° (decomp.); *p-hydroxyphenylethylcarbamide*, glistening, white scales, m. p. 122° (corr.). The effect of these and other substances on body temperature and blood pressure has been investigated. W. O. K.

Influence of Aliphatic Narcotics on the Swelling of Cell Colloids. M. KOCHMANN (*Biochem. Z.*, 1923, 136, 49—65).—The action of the first five normal chain aliphatic alcohols, of chloral hydrate, urethane, chloroform, and ether on the swelling of finely powdered fibrin and on the gastrocnemius muscle of the frog has been examined in relation to narcosis. The order in which the narcotics inhibit the swelling of fibrin particles is approximately the same as the order of their narcotic activity towards the electrically stimulated gastrocnemius muscle. The results support the theory of narcosis that narcotics change the permeability of the cells by removal of water. H. K.

Chemistry of Vegetable Physiology and Agriculture.

The Botulinus Toxin. KONRAD SCHÜBEL (*Arch. expt. Path. Pharm.*, 1923, 96, 193—259).—When cultivated in a bouillon medium, *Bacillus botulinus* gives rise to gaseous products, amongst which carbon dioxide, hydrogen sulphide, and hydrogen have been identified. At the same time, the medium becomes distinctly acid owing to the production of *n*-butyric acid and small quantities of other organic acids. In addition to these products, butyl alcohol, isobutyl alcohol, ammonia, and trimethylamine have been isolated; qualitative tests indicating the presence of small quantities of an aldehyde have also been obtained. From the quantitative results, the author concludes that the dextrose contained in the medium is decomposed mainly into butyl alcohol and butyric acid, according to the equation $2\text{C}_6\text{H}_{12}\text{O}_6 = \text{C}_4\text{H}_8\text{O}_2 + \text{C}_4\text{H}_{10}\text{O} + 4\text{CO}_2 + 2\text{H}_2 + \text{H}_2\text{O}$.

The botulinus toxin may be partly separated from colloidal material by ultra-filtration. It is insoluble in alcohol, acetone, chloroform, or ether, is readily destroyed by boiling its solution for a few moments, but is stable to air and light. Alkalis destroy it more readily than hydrochloric acid; concentrations of 0.91% of the latter are necessary for destructive effects to become apparent. The toxin is precipitated from solution by salts of the heavy metals, by certain protein and alkaloid precipitants, and by saturation with ammonium sulphate. It is adsorbed by animal charcoal and by certain inorganic colloids; its behaviour in this respect suggests that it possesses a negative charge. It dialyses readily through parchment and collodion membranes, its toxic properties being thereby apparently increased. Pepsin and trypsin are without action on it.

The pharmacological action of the toxin has also been investigated.

E. S.

The Formation of Dextrorotatory β -Furyl-lactic Acid by *Bacillus proteus*. TAKAOKI SASAKI and ICHIRO OTSUKO (*Biochem. Z.*, 1923, **135**, 504—505; cf. A., 1922, i, 302).—d- β -Furyl-lactic acid is formed in small yield by the action of *Bacillus proteus* on dl- β -furylalanine. It has m. p. 95—96° and $[\alpha]_D^{25} + 27.36^\circ$ in water.
H. K.

Formation of Mercaptan from l-Cystine by Bacteria. MASATOSHI KONDO (*Biochem. Z.*, 1923, **136**, 198—202).—*Proteus vulgaris* produces mercaptan from l-cystine in presence of lactose, dextrose, sucrose, glycerol, and histidine, but *Bacillus coli* is variable in its action. Both, however, produce hydrogen sulphide from l-cystine, and also probably ethyl sulphide.
H. K.

Culture of *Bacillus pyocyaneus* on Definite Chemical Media. A. LIOT (*Ann. Inst. Pasteur*, 1923, **37**, 234—274).—*Bacillus pyocyaneus*, which produces normally a blue pigment in the medium on which it is grown, will grow on agar if a suitable source of nitrogen is added. Various substances, such as ammonium salts of monobasic and dibasic fatty acids, amides, amino-acids, and alcohols and sugars, along with inorganic ammonium salts, have been investigated as to their efficiency in producing growth and pigment.
W. O. K.

The Bactericidal Action of Tellurium Derivatives of certain Aliphatic β -Diketones. GILBERT THOMAS MORGAN, EVELYN ASHLEY COOPER, and ARNOLD WIGHAM BURTT (*Biochem. J.*, 1923, **17**, 30—33).—A series of tellurium derivatives of aliphatic β -diketones has been tried with the purpose of ascertaining the influence of chemical constitution on the germicidal power of these compounds, and also their specific action on different micro-organisms. It is found that the bactericidal action increases considerably as the homologous series is ascended, until with a third substitution of the methyl group a limit is reached beyond which there may even be a diminution in the germicidal action.

The bactericidal action of the compounds is determined by the chemical structure of the β -diketone, position isomerism being a determining factor. Experiments with various organisms have disclosed that the above compounds exert a selective action on the coliform organisms. Cocci are more resistant to them. S. S. Z.

Stimulation of Alcoholic Fermentation by Chemically Defined Substances. T. SODA (*Biochem. Z.*, 1923, **135**, 610—620).—Cell-free fermentation of dextrose is accelerated by trimethylamine oxide, allyl alcohol, cinnamyl alcohol, α -crotonic acid, $\alpha\alpha$ -diketopimelic acid, benzoylacetone, and α -methylhexanone.
H. K.

Enzymes. II. A. VON EULER and KARL MYRBÄCK (*Arkiv Kem. Min. Geol.*, 1922, **8**, No. 22, 1—31).—A study, in the first place, of the autofermentation (as distinct from autolysis) of fresh bottom-yeast. Autofermentation is accelerated by toluene, but retarded if ethyl acetate is also added, more particularly in

presence of dextrose. Chloroform also inhibits the process. With dried yeast, autofermentation is inhibited by mixtures of toluene and ethyl acetate, either in presence or in absence of dextrose. The latter substance, in presence of phosphate (p_H 5), retards the process, as also does sodium chloride. The inhibiting effect of toluene is more marked in presence of yeast-gum, which is itself unaffected.

The fermentation of dextrose by dried yeast, in presence of phosphate, is practically unaffected by the addition of lactose, which is not appreciably fermented. Lactose or toluene, or mixtures of these two substances, inhibit the autofermentation of dried yeast. Complete hydrolysis of dried yeast, before and after autofermentation, shows a loss of dextrose constituents corresponding with the carbon dioxide produced.

The second section of the paper deals with the purification and adsorption of saccharase along the lines laid down by Willstätter and Racke (A., 1921, i, 823). The results of the latter authors are confirmed in connexion with autolysis, acetone and alcohol precipitation, adsorption by aluminium hydroxide and kaolin, etc. Kieselguhr does not adsorb saccharase.

In the third section of the paper, it is shown that the inactivating effect on saccharase solutions of *p*-phenylenediamine and formaldehyde depends on the hydrogen-ion concentration (cf. Rona and Bloch, A., 1922, i, 65).
E. E. T.

Alcoholic Fermentation by Means of Yeast-cells under Various Conditions. V. Formation of Glycerol when the Intermediate Acetaldehyde is Retained by Animal Charcoal.

EMIL ABDERHALDEN and SUSI GLAUBACH (*Fermentforsch.*, 1922, 6, 143—148).—Neuberg's observation that acetaldehyde forms an intermediate stage in the degradation of dextrose to alcohol and carbon dioxide by means of the enzymic complex, zymase, is now supplemented by the discovery that the fixation of acetaldehyde from a fermenting or fermented solution by means of animal charcoal (A., 1922, i, 92) is accompanied by increase in the amount of glycerol formed. The extent of such increase is augmented when the quantity of charcoal present is increased.
T. H. P.

Alcoholic Fermentation by Means of Yeast-cells under Various Conditions. VI.

EMIL ABDERHALDEN (*Fermentforsch.*, 1922, 6, 149—161).—The influence of various substances on alcoholic fermentation (cf. Neuberg and Sandberg, A., 1922, i, 408) is as follows. Yeast maceration juice dialysate: first dialysate accelerating, second dialysate, retarding; tyrosine, at first retarding, later accelerating; di-iodotyrosine, at first accelerating, later retarding; dihydroxyphenylalanine, accelerating in small, retarding in large, doses; cystine in large doses, greatly accelerating at first and retarding later, but in smaller doses, accelerating; cysteine at first retarding but afterwards considerably accelerating; tryptophan, histidine, and, especially, arginine, accelerating; caffeine, at first accelerating, later retarding, the reverse being the case with allantoin; xanthine, or *dl*-adrenaline, greatly accelerating; diethyl-

amine, retarding; cholesterol, or homovanillin, at first retarding, later accelerating; vanillin, choline, acetylcholine, retarding.

T. H. P.

Alcoholic Fermentation by Means of Yeast-cells under Various Conditions. VII. Influence of Animal Charcoal and other Substances on the Time-course of Alcoholic Fermentation. EMIL ABDERHALDEN (*Fermentforsch.*, 1922, 6, 162—171).—Animal charcoal accelerates alcoholic fermentation of sugar solution to a more marked extent than either dipotassium hydrogen phosphate or sodium lævulosediphosphate, the acceleration being still further increased by use of the charcoal and one of these phosphates together. The very great retardation of the fermentation produced by toluene almost entirely disappears if animal charcoal also is present; adsorption of the toluene by the charcoal appears to be the cause of this protective action of the charcoal. The effect of toluene on fermentation by dried yeast is far less marked than when fresh yeast is used.

The initial stimulation of fermentation by dried yeast sometimes caused by toluene is confirmed, but not explained. Especially in presence of animal charcoal, toluene produces a very marked acceleration of the rate at which carbon dioxide is liberated from pyruvic acid by dried yeast.

T. H. P.

Alcoholic Fermentation by Means of Yeast-cells under Various Conditions. VIII. Formation of Glycerol when the Intermediate Acetaldehyde is Retained by Animal Charcoal. EMIL ABDERHALDEN and WALTER STIX (*Fermentforsch.*, 1922, 6, 345—347).—The proportion of glycerol formed during the fermentation of dextrose by yeast may be considerably increased by increase of the amount of animal charcoal present and by expelling the air from the fermentation vessel by means of carbon dioxide (cf. Abderhalden and Glaubach, preceding page).

T. H. P.

Adsorption of Acetaldehyde and Pyruvic Acid, Separately and Together, by Animal Charcoal and Other Adsorbents. EMIL ABDERHALDEN and HIDEKI SUZUKI (*Fermentforsch.*, 1922, 6, 137—142).—The amount of acetaldehyde or pyruvic acid adsorbed from aqueous solutions by a certain weight of animal charcoal under definite conditions increases with, but less rapidly than, the concentration of the solution. That the action represents a true reversible adsorption is shown by the results of equilibrium experiments. It appears, but it is not yet certain, that part of the adsorbed acetaldehyde undergoes change at the surface of the charcoal. When both acetaldehyde and pyruvic acid are present in solution, the amount of each adsorbed by the charcoal is diminished (cf. Abderhalden, A., 1922, i, 92; Grab, A., 1922, i, 306; Abderhalden and Glaubach, preceding page).

T. H. P.

Formation of Citric Acid in Cultures of *Aspergillus niger* and *Penicillium glaucum* on Sugar. WL. BUTKEWITSCH (*Biochem. Z.*, 1923, 136, 224—237).—When *Aspergillus niger* and

Citromyces glaber were grown on media containing sucrose in presence of calcium carbonate, citric and oxalic acids accumulate much more rapidly in the case of the former than the latter. This also happens if there be available a plentiful source of nitrogen. Evidence is adduced to show that a soluble calcium salt is formed in these solutions, but the acid has not yet been isolated. *Penicillium glaucum* is also able to produce small quantities of citric and oxalic acids in culture media of sucrose and calcium carbonate. H. K.

The Carbamide Content of Fungi. NICOLAUS N. IVANOV (*Biochem. Z.*, 1923, 136, 1—8).—The carbamide content of fungi varies not only from genus to genus, but also among the species of a genus, *Lycoperdon echinatum*, containing 1.26% and *L. gemmatum*, 10.7%, of carbamide on the dried material. The genera *Psalliota* and *Pholiota* also show similar variations. The carbamide content increases to a maximum at the beginning of ripening, but then falls off to nothing when fully ripe. H. K.

Formation of Carbamide in Fungi. NICOLAUS N. IVANOV (*Biochem. Z.*, 1923, 136, 9—19).—During ripening, fungi treated with ammonia compounds can convert ammonia into carbamide. This takes place even if the mycelium be detached. The carbamide functions, it is thought, as a nitrogenous reserve substance. H. K.

Comparative Studies on Respiration. XXIV. The Effects of Chloroform on the Respiration of Dead and of Living Tissue. GEORGE B. RAY (*J. Gen. Physiol.*, 1923, 5, 469—477).—The rate of production of carbon dioxide by living and by dead *Ulva*, a green marine alga, in the presence of chloroform, has been investigated, and the influence of ferric sulphate and hydrogen peroxide determined. W. O. K.

The Biological Action of Röntgen Rays. III. EUGEN PETRY (*Biochem. Z.*, 1923, 135, 353—383).—Seed embryos submitted to the action of a number of oxidising agents are not thereby rendered more or less sensitive to Röntgen radiation. The only oxidising agent which confers greater sensitiveness is hydrogen peroxide. H. K.

Chemical Constituents of Green Plants. XXIV. Citric Acid. HARTWIG FRANZEN and FRITZ HELWERT (*Biochem. Z.*, 1923, 135, 384—415).—From a critical survey of the available literature on the occurrence of citric acid in plants, the authors conclude that the generally accepted view that citric acid is widely distributed is erroneous, as in many cases the identification is insufficient. H. K.

Chemical Constituents of Green Plants. XXVI. Tartaric Acid. HARTWIG FRANZEN and FRITZ HELWERT (*Biochem. Z.*, 1923, 136, 291—305).—A critical survey of the literature on the recorded occurrence of tartaric acid in eighty-two plants leads to the conclusion that tartaric acid only occurs with certainty in five,

Vitis vinifera (berries), *Tamarindus indica* (fruit), *Beta vulgaris* (unripe beet), *Acer saccharinum* (juice), and *Pyrus aucuparia* (berries). It also, probably, occurs in *Quercus pedunculata*. H. K.

The Formation of Vitamin-A in Plant-tissues. II. KATHARINE HOPE COWARD (*Biochem. J.*, 1923, **17**, 134—144; cf. A., 1921, i, 837).—Light is necessary for the formation of vitamin-A in plant-tissues. Ultra-violet rays of the spectrum are not essential, and the formation of the vitamin can take place under the influence of electric light in the absence of sunlight. The process of vitamin-A synthesis can be carried on in the absence of carbon dioxide and of oxygen in the surrounding atmosphere, and is independent of the presence of chlorophyll in the plant. The presence of chloroform in the atmosphere, however, prevents the formation of the vitamin. Almost complete absence of calcium salts from the nutrient solution of a water culture of *Tradescantia* does not prevent the synthesis of vitamin-A in the leaves of the plant. S. S. Z.

The Association of Vitamin-A with Lipochromes of Plant Tissues. KATHARINE HOPE COWARD (*Biochem. J.*, 1923, **17**, 145—156).—Some lipochrome (generally carotene) is always associated with the vitamin in plant-tissues and consequently the presence of carotene, particularly carotene exposed to sunlight, suggests the presence of vitamin-A also. S. S. Z.

Hydrocyanic Acid in Burmah Beans (*Phaseolus lunatus*). J. CHARLTON (*Agric. Res. Inst. Pusa Bull.*, **140**, 7 pp.).—The amount of hydrocyanic acid liberated by enzyme action in Burmah beans increases with the age of the bean. The elaboration of enzymes in the beans therefore probably continues after the normal ripening process is complete. H. C. R.

Influence of Sulphur Dioxide on the Respiration of Phanerogams. JULIUS STOKLASA [with J. ŠEBOR, V. ZDOB-NICKÝ, and V. NEKOLA] (*Biochem. Z.*, 1923, **136**, 306—326).—As a result of comparative experiments on young pines, it is found that small quantities of sulphur dioxide cause a diminution of the carbon dioxide output. The larger the content of sulphur dioxide, the less the respiratory activity. The pine needles show at the same time a bleaching of the chloroplasts. H. K.

The Mobilisation of Mineral Substances and of Nitrogen in the Bark and Wood in Spring Growth. AUGUST RIPPEL (*Biochem. Z.*, 1923, **135**, 518—531).—During sprouting of shoots of *Sambucus nigra*, the potassium, phosphorus, and nitrogen are strongly mobilised, the magnesium and sodium to a lesser extent, and calcium, sulphur, and chlorine scarcely at all. The potassium content of the wood increased by 28% after sprouting. H. K.

Walnut Oil. KAZUO MATSUMOTO and YOSHISUKE UYEDA (*J. Chem. Ind. Japan*, 1922, **25**, 1438—1440).—The fruit of the walnut (*Juglans Sieboldiana*) produced in the Prefecture of Ishikawa

gave 26.54% of kernel, from which 59.58% of oil was obtained by pressure. The oil is light yellow in colour and without odour, and shows the properties of a drying oil: d_{15}^{20} 0.9332, n_D^{20} 1.4800, acid value 0.68, Hehner value 92.3, saponification value 191.1, Reichert-Meißl value 0.62, and iodine value (Hübl) 150.8. K. K.

Amino-acids of Feeding Stuffs. II. Amino-acids of Linseed Meal, Wheat Bran, Soja Beans, and Red Clover Hay.

T. S. HAMILTON, N. UYEL, J. B. BAKER, and H. S. GRINDLEY (*J. Amer. Chem. Soc.*, 1923, **45**, 815—819; cf. A., 1922, ii, 92).—The amino-acid contents are tabulated of linseed meal, wheat bran, soja beans, and red clover hay, and of other foodstuffs already investigated, as estimated by the modified Van Slyke method previously described. [Cf. *J.S.C.I.*, 1923, 418A.] W. S. N.

The Potassium-Nitrogen Ratio of Red Clover as Influenced by Potassium Fertilisers.

PAUL EMERSON and JOHN BARTON (*J. Amer. Soc. Agron.*, 1922, **14**, 182—192).—The solubility of soil potassium, as indicated by absorption by the plant, is increased by applications of manure, acid phosphate, or combinations of both. The ability of red clover to take up potassium varies with the kind of compound supplied; for instance, the potassium of kainite is more easily absorbed than that of potassium chloride or sulphate. Calcium carbonate, when applied to an acid soil, appears not to affect the solubility of native soil potassium, but may possibly over-stimulate nitrate production. The potassium: nitrogen ratio is widened slightly by applications of lime, but narrowed by applications of manure or acid phosphate, or both, in the presence of lime. CHEMICAL ABSTRACTS.

Disappearance of Nitrates from Soil under Timothy Grass.

J. A. BIZZELL (*J. Amer. Soc. Agron.*, 1922, **14**, 320—326).—The addition of sodium nitrate to timothy grass sod in early spring is followed by a rapid disappearance of the nitrate from the 20 cm. of surface soil; this disappearance is due only in part to the absorption of nitrogen by the growing crop. Leaching or denitrification apparently did not remove the nitrogen from the soil. Various organisms of the soil evidently transformed the nitrate into ammonia or into some form of organic combination. CHEMICAL ABSTRACTS.

Hydrogen-ion Concentration of the Soil and its Significance to the Vegetation, especially to the Natural Distribution of Plants.

CARSTEN OLSEN (*Compt. rend. Trav. Carlsberg*, 1923, **15**, 1—166).—The object was to ascertain to what extent the natural flora of soils is affected by the hydrogen-ion concentration, and whether the effect is direct or caused by secondary changes. Botanical analyses of natural vegetation were compared with the reaction of the soils on which it grew. Individual species were found only to occur on soils having a definite range of p_H values. Within this range is a narrower one in which the species appeared with the greatest average frequency. The number of

species and their frequency of occurrence is greatest on nearly neutral soils. Increased p_H value corresponds with a decrease in the number of species and their density. In water culture solutions, acid-soil plants grow best in media of p_H 4; whilst plants characteristic of neutral and alkaline soils are favoured by nutrient solutions with p_H 6—7. Typical acid-loving plants show poor growth and became chlorotic when grown in culture solutions which are only faintly acid. The theory that the apparent toxicity of acid soils (Hartwell and Pember, *Soil Sci.*, 1914, 6, 259) is due to soluble aluminium salts is not confirmed. Alkaline-soil plants were not injured by small amounts of aluminium salts. The acid-soil plants are not characterised by the power of utilising ammonium salts. Both acid- and alkaline-soil plants are nourished equally well by ammonium salts and by nitrates. Acid-soils cannot be differentiated from normal ones on account of their lack of nutrients. The flora of a rich acid-soil bear no resemblance to those of a poor alkaline soil. It is concluded that the hydrogen-ion concentration of a soil directly, and to a considerable extent, affects the nature of the vegetation growing upon it.

A. G. P.

Influence of Hydrogen-ion Concentration on the Adsorption of Plant Food by Soil Colloids. E. B. STARKEY and NEIL E. GORDON (*Soil Sci.*, 1922, 14, 449—457).—The adsorption by silica and ferric hydroxide gels of various plant nutrients was determined. The adsorption of kations was generally greater with increasing p_H values. Anions were adsorbed in the following order: phosphate, sulphate, nitrate. Acidity increased the adsorption of phosphate but the adsorption of sulphates and nitrates was scarcely affected by the reaction of the medium. Ferric hydroxide gel was a considerably more active absorbent than silica gel. Near the neutral point, slight changes in p_H values caused relatively large changes in the adsorption of potassium-ions.

A. G. P.

Factors Affecting the Soil Reaction. I. Soil-Water Ratio. ROBERT M. SALTER and M. FRANCIS MORGAN (*J. Physical Chem.*, 1923, 27, 117—140).—The hydrogen-ion concentration of nine acid soils has been determined at soil-water ratios from 1 : 1 to 1 : 3125 by the hydrogen electrode method. The velocity of hydrolysis of sucrose by five of the same soils of soil-water ratio between 1 : 0.0894 and 1 : 625 has also been determined. Both methods of determination show that the hydrogen-ion concentration varies systematically with the soil-water ratio, the highest hydrogen-ion concentration occurring at high soil-water ratios, with a progressive decrease as the dilution is increased. In general, the changes in hydrogen-ion concentration at varying soil-water ratios agree with the distribution of hydrogen-ions between soil and solution, which could be expected if controlled by an adsorption mechanism. A slight tendency is noted with all soils to deviate from the theoretical adsorption values over a restricted range of dilution. With two of the nine soils examined, this deviation was sufficient to prevent the determination of a theoretical equation which would describe

the variation in hydrogen-ion concentrations observed. On the basis of the results obtained, it appears that the reaction of a soil is dependent mainly on the total dissociated acid present and to a lesser extent on the adsorptive capacity of the soil for hydrogen-ions and the soil-water ratio. It is urged that the soil-water ratio should be stated in all results on hydrogen-ion measurements of soils and that one of the ratios, 1 : 5, 1 : 25, or 1 : 125, should be chosen as a standard.

J. F. S.

Relations Between the Active Acidity and Lime Requirement of Soils. EDGAR T. WHERRY (*J. Wash. Acad. Sci.*, 1923, 13, 97—102).—A correlation coefficient is employed to express the relationship between soil acidity and lime requirement, based on the equation lime requirement = $C \times (\text{Specific acidity} - 1)$. (For "Specific acidity" see Wherry, *ibid.*, 1920, 9, 305.) Values of C are calculated from published data, and are shown to vary to so great an extent with soil type and treatment that no calculations of lime requirement from it seem practicable. The coefficient C is believed to be a measure of the adsorptive power of soils for the hydrogen-ion, and may be used as a basis for a rough classification of soils.

A. G. P.

Catalytic Action of Soils. SHIGERU OSUGI (*Ber. Ohara Inst. landw. Forsch.*, 1922, 2, 197—218).—The power of soils to decompose hydrogen peroxide would appear to be associated with humus, ferric compounds, and manganese compounds, although no relationship between catalytic power and the soil content of these substances was found. Soil catalysis was increased by coagulating agents and decreased by peptisation.

The reaction of the soil may influence its catalytic power directly, and also as a result of its effect on the physical state of the soil particles. The effect of bacteria on soil catalysis is small, and that of enzymes larger, but the organic and inorganic soil constituent are the most important factors.

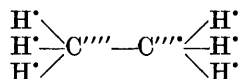
A. G. P.

Adsorption of Plant Food by Colloidal Silica. R. C. WILEY and NEIL E. GORDON (*Soil Sci.*, 1922, 14, 441—447).—The adsorption of various plant foods was determined by shaking with silica hydrosol and hydrogel. Negative adsorptions may be due either to the water being more strongly adsorbed than the dissolved salts, or to the fact that the water of hydration does not all act as a homogeneous solvent, or to lower concentrations existing in the finer capillaries. In general, metals are negatively adsorbed by both gel and sol. Nitrates and sulphates are negatively adsorbed to a slight degree. The phosphate radicle is positively adsorbed by the gel, and negatively by the sol. In the former case, more phosphate was adsorbed than the radicle with which it was associated, and, moreover, was extremely difficult to wash out.

A. G. P.

Organic Chemistry.

The Foundations of an Electronic Theory of Organic Chemistry. A. M. BERKENHEIM (*J. Russ. Phys. Chem. Soc.*, 1917, 49, [ii], 1—181).—A theoretical paper in which an attempt is made to apply J. J. Thomson's and Stark's views of the structure of the atom to explain the reactions of carbon compounds. It is suggested that the neutral carbon atom acquires positive or negative polarity according to whether it parts with one or more electrons on becoming connected with other atoms or, conversely, acquires one or more electrons in the process; this polarity of the carbon atom then determines its reactions. Ethane is represented as



and acetylene as $\text{H} \cdot \text{C}''' - \text{C}''' \text{H} \cdot$; a large number of organic reactions is discussed and shown to support the theory.

G. A. R. K.

Low Temperature Tar. II. FRANZ SCHÜTZ, WILHELM BUSCHMANN, and HEINRICH WISSEBACH (*Ber.*, 1923, 56, [B], 869—874; cf. this vol., i, 195).—The communication deals mainly with the components of the light oils which boil below 75°.

The isolation of the paraffin hydrocarbons is effected by treatment of the various fractions with concentrated sulphuric acid and examination of the unabsorbed and non-polymerised portions. The fraction, b. p. up to 10°, contains *n*-butane (4%), that of b. p. 15—35° contains methylbutane, b. p. 17—18° (2.4%), and *n*-pentane (5.1%). Methylpentane, b. p. 62—63° (18%), and *n*-hexane (24%) are, respectively, present in the fractions of b. p. 63° and 68—72°, whereas *n*-heptane (21%) and *n*-octane (1%) are found in those of b. p. 98—102° and 120—130°. The isolation of the paraffins from the fractions of higher boiling point is particularly difficult, since the aromatic hydrocarbons largely predominate. Heptane is possibly present in the benzene fraction, b. p. 77—78.5°.

The identification of the unsaturated hydrocarbons is effected by preliminary fractional distillation within very narrow limits, followed by treatment of the individual fractions with bromine and isolation of the bromides. Ethylene, propylene, Δ^{α} -butylene, Δ^{β} -butylene, and Δ^{α} -pentene are thus shown to be present. *cyclo*-Pentadiene is shown to occur to the extent of 5—7% in the fraction, b. p. 40°, and is identified by conversion into dimethylfulvene, b. p. 154—155°.

The first runnings of the light oil contain acetaldehyde in addition to acetone, whilst methyl ethyl ketone and acetonitrile are present

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in the benzene fraction. Methyl mercaptan and dimethyl sulphide are also found in the first runnings. The fraction, b. p. 20–40°, contains carbon disulphide in very small amount. H. W.

Lignite Low Temperature Tar. E. FROMM and H. ECKARD (*Ber.*, 1923, 56, [B], 948–953).—The low temperature tars obtained in rotary furnaces from two geologically similar lignites, termed, respectively, “Louise” and “Grefrath,” obtained from the neighbourhood of Cologne have been investigated; they exhibit peculiar differences, which are possibly due to differences in botanical origin.

The neutral components of the “Louise” tar which are volatile with steam, have boiling points 140–240°, and the densities of the individual fractions increase regularly from 0.835 to 0.895. They appear to be mixtures of unsaturated hydrocarbons and oxygenated substances. The similarly obtained components of the “Grefrath” tar have b. p. 115–240°, d 0.819–0.897, and give a portion, b. p. 115–160°, d 0.823–0.832, which contains an ether and a terpene-like compound, $C_{10}H_{18}$ or $C_{11}H_{20}$, b. p. 185°, d 0.8659.

The neutral components of the “Louise” tar which are not volatile with steam consist of a mixture of paraffins which is separated by fractional distillation and subsequent crystallisation into the following individuals, which are assumed to belong to the normal series: $C_{23}H_{48}$, m. p. 46°; $C_{24}H_{50}$, m. p. 52°; $C_{26}H_{54}$, m. p. 57.5°; $C_{28}H_{58}$, m. p. 62°; $C_{32}H_{66}$, m. p. 69.6°; $C_{34}H_{70}$, m. p. 73°. The occurrence of the first member is remarkable, since only hydrocarbons with an even number of carbon atoms have been isolated previously from tars.

The basic portions of the “Louise” tar which are volatile with steam contain a yellowish-brown oil from which a benzoyl derivative, m. p. 36°, could be obtained in small amount, and pyridine which is identified as its additive product with mercuric chloride, m. p. 194°. The presence of pyridine in the similarly isolated fraction of the “Grefrath” tar could not be detected; by treatment of it with aqueous oxalic acid it was, however, found possible to isolate an oxalate, m. p. 177–178°, which is possibly derived from methylpyridine.

The acidic components which are volatile with steam contain only traces of carboxylic acids. The phenols are subdivided by fractional distillation under diminished pressure and analysed as their phenylurethanes. *m*-Cresol is the only substance of this class which could be identified with certainty; it is present in the “Grefrath” tar. Several phenols, $C_8H_9\cdot OH$, and a phenol, $C_9H_{11}\cdot OH$, are also present, the phenylurethanes of which are not apparently identical with any known compounds of this class.

H. W.

β -Methyl- Δ^8 -pentene. H. VAN RISSEGHEM (*Bull. Soc. chim. Belg.*, 1923, 32, 144–150).—The hydrocarbon was prepared by condensation of acetic and butyric acids to methyl propyl ketone (pentane- γ -one), which, on treatment with magnesium methyl

iodide, yielded a hexanol; this was then dehydrated by means of toluene-*p*-sulphonic acid. A second method, dehydration of δ -methylbutyl alcohol, was also used. β -Methyl- Δ^2 -pentene so obtained forms an additive product with bromine, and yields propaldehyde, acetone, and propionic acid on oxidation. It has b. p. $66.7-67.1^\circ/760$ mm., m. p. -134.75° ; d_4^{20} 0.7051, d_4^{15} 0.69145, $n_{D_a}^{15}$ 1.4003, $n_{H_\beta}^{15}$ 1.4093, $n_{H_\gamma}^{15}$ 1.4144, n_D^{15} 1.4028. The bromo-derivative has b. p. $69.5-70.5^\circ/14$ mm., m. p. -54.49° ; d_4^{20} 1.6024, d_4^{15} 1.5825, $n_{D_a}^{15}$ 1.50294, $n_{H_\beta}^{15}$ 1.51473, $n_{H_\gamma}^{15}$ 1.52144, n_D^{15} 1.506225. The action of chlorine on the hydrocarbon results in the formation of an additive product together with a more halogenated chloro-substitution compound and a derivative resulting from the fixation of one molecule of hydrogen chloride on the double bond.

H. J. E.

Action of Bromine on Hydrocarbons. B. K. MERESHKOWSKY (*Annalen*, 1923, **431**, 113—132).—It is shown from the author's experiments and previous work on this subject that specific catalysts not only influence the rate and initial direction of halogenation, but also determine the simultaneous production of different end-products, if the reaction is allowed to continue; the production of polyhalogenated isomerides may therefore be selectively catalysed. The catalysts used are shown to form the following series, in the order of decreasing production of the more symmetrical isomeride: (1) pure bromine without a catalyst, (2) metallic iron, (3) metallic aluminium or aluminium tribromide, (4) ferric bromide. The substitution rules of Markovnikov, Städel, and V. Meyer are combined and extended as follows. (1) If the number of carbon atoms in the hydrocarbon is n , then, either with or without a catalyst at temperatures below 100° , $n-1$ halogen atoms will become successively attached to carbon atoms on which substitution has not yet occurred. (2) If $n-1$ atoms of the hydrocarbon already carry a halogen atom, a further halogen atom will enter partly on the remaining halogen-free carbon atom, and partly on that one of the other carbon atoms which carries the greatest number of hydrogen atoms. (3) Further substitution generally occurs on the carbon atom bearing the greatest number of hydrogen atoms. (4) Substitution always occurs in several directions, depending on the catalyst.

The action of pure bromine on propylene in the absence of a catalyst gives propylene bromide, 90%, and $\alpha\beta\gamma$ -tribromopropane, about 4%. In the presence of metallic iron, $\alpha\beta\gamma$ -tribromopropane and $\alpha\alpha\beta$ -tribromopropane are formed in the proportion of 40 : 17; with ferric bromide or aluminium, the same compounds are produced in the ratio 8 : 33, and with aluminium bromide in the ratio 1 : 1. In the presence of aluminium a product of higher boiling point, $130-150^\circ/20$ mm., is also formed. The action of bromine on isobutylene in the absence of a catalyst at $45-50^\circ$ leads mainly to the formation of dibromoisobutane, 45%, and of $\alpha\beta\gamma$ -tribromoisobutane, m. p. -32° , b. p. $222-225^\circ/75$ mm. (Pogorshelsky, A., 1905, i, 315), 44%, together with smaller amounts of tetra-

bromo-, pentabromo-, and hexabromo-derivatives. In the presence of metallic iron, the above is the only tribromo-derivative produced, but the use of ferric bromide leads to the formation of $\alpha\alpha\beta$ -tribromoisobutane and $\alpha\beta\gamma$ -tribromoisobutane in the ratio 31:11; the former gives $\alpha\alpha$ -dibromoisobutylene, $\text{CMe}_2\cdot\text{CBr}_2$, the latter α -bromo- γ -acetoxy- β -methylpropylene, $\text{CHBr}\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{OAc}$, on treatment with potassium acetate. The same tribromo-derivatives are formed in the ratio 3:5 in the presence of aluminium or aluminium tribromide. Two tetrabromo-derivatives are found in the fractions of higher boiling point. (1) $\alpha\alpha\beta\gamma$ -Tetrabromoisobutane, b. p. $134\text{--}136^\circ/14\text{ mm.}$, $d_4^{20} 2.45445$, which is converted by heating with potassium acetate into $\alpha\alpha$ -dibromo- γ -acetoxy- β -methylpropylene, $\text{CBr}_2\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{OAc}$, b. p. $114^\circ/16\text{ mm.}$, $d_4^{20} 1.75070$, which gives $\alpha\alpha$ -dibromopropenylcarbinol, $\text{OH}\cdot\text{CH}_2\cdot\text{CMe}\cdot\text{CBr}_2$, on hydrolysis. (2) $\alpha\beta\gamma\delta$ -Tetrabromoisobutane, m. p. 25° , b. p. $150\text{--}151^\circ/14\text{ mm.}$, $d_4^{20} 2.55953$, the constitution of which is certain, since other possible tetrabromo-derivatives could not be produced from $\alpha\beta\gamma$ -tribromoisobutane; moreover, the action of potassium acetate and acetic acid gives the bromo-ester, $\text{CHBr}\cdot\text{C}(\text{CH}_2\cdot\text{OAc})_2$, b. p. $136^\circ/14\text{ mm.}$, $d_4^{20} 1.45335$, from which the glycol, $\text{CHBr}\cdot\text{C}(\text{CH}_2\cdot\text{OH})_2$, m. p. -80° , b. p. $158^\circ/16\text{ mm.}$, $d_4^{20} 1.69582$, is produced by hydrolysis. Hexabromoisobutane, m. p. 93° , occurs in small amounts in the residue left after the more volatile halides have been distilled in steam. The constitution of $\alpha\alpha\beta\gamma$ -tetrabromoisobutane is established by its formation by the addition of bromine in ethereal solution to the unsaturated dibromo-derivative, $\text{CHBr}\cdot\text{C}\cdot\text{Me}\cdot\text{CH}_2\text{Br}$ (A., 1914, i, 508).
W. S. N.

Mechanism of the Reactions of Alkyl Halides. ADOLF FRANKE and RUDOLF DWORZAK (*Monatsh.*, 1923, 43, 661—671).—The possibility of the intermediate formation of unsaturated compounds during the conversion of bromo- into hydroxy-derivatives, etc. (cf. A., 1914, i, 7), has suggested to the authors to study similar displacements of halogen attached to an asymmetric carbon atom, when, if an optically active derivative is obtained, no intermediate unsaturated compound can have been formed. Active secondary butyl bromide and iodide give an active *mercaptan* on treatment with alcoholic potassium hydrosulphide. The product is converted for purposes of identification, etc., into the *mercury* derivative, which is shown to be $\text{C}_4\text{H}_9\cdot\text{S}\cdot\text{HgCl}$, not $(\text{C}_4\text{H}_9)_2\text{Hg}$, the formula given to the corresponding inactive product by Reymann (A., 1875, 141). This author recorded a m. p. 189° , but the present authors obtain no evidence of melting at much higher temperatures.

Potassium hydrosulphide converts $\alpha\gamma$ -dibromo- $\beta\beta$ -dimethylpropane into the corresponding *dithiol*, which with mercuric chloride gives the *compound*, $\text{CMe}_2(\text{CH}_2\cdot\text{S}\cdot\text{HgCl})_2$.

When optically active *sec.*butyl iodide is heated with aqueous sodium carbonate until it is converted into the alcohol, the latter is inactive. The bromide, on similar treatment, gives a slightly active alcohol.
E. E. T.

The Labile Nature of the Halogen Atom in Organic Compounds. IX. The Electrical Conductivities and the Reduction of Derivatives of Nitroform. THOMAS HENDERSON, EDMUND LANGLEY HIRST, and ALEXANDER KILLEN MACBETH (T., 1923, 123, 1130—1137).

$\alpha\beta$ -Dinitroethane and the Action of Silver Nitrite on Ethylene Iodide. ALEXEI V. IPATOV (*J. Russ. Phys. Chem. Soc.*, 1917, 49, 297—303).— $\alpha\beta$ -Di-iodoethane is treated with silver nitrite by Demjanov's method and the mixture of $\alpha\beta$ -dinitroethane and nitroethyl nitrite thus obtained fractionally distilled. Three fractions are obtained, the first of which, b. p. $70-72^{\circ}/5$ mm., is mainly unchanged $\alpha\beta$ -di-iodoethane, the second, b. p. $70-78^{\circ}/5$ mm., is a mixture of the latter with nitroethyl nitrite and dinitroethane, whilst the third, b. p. $81-106^{\circ}/5$ mm., is mainly the latter. The $\alpha\beta$ -dinitroethane thus obtained, b. p. $94-95^{\circ}/5$ mm., d_4^{20} 1.4597, n_D^{20} 1.4488, forms a *tetrabromo*-derivative, $C_2O_4N_2Br_4$, yellow needles, m. p. $46-47^{\circ}$, and gives on reduction ethylenediamine, the hydrochloride of which sublimes without melting at 208° . R. T.

The Examination and Dehydration of Methyl Alcohol by Means of Magnesium. NIELS BJERRUM and LÁSZLÓ ZECHMEISTER (*Ber.*, 1923, 56, [B], 894—899).—Clean magnesium reacts vigorously with absolute methyl alcohol at the atmospheric temperature giving magnesium methoxide and hydrogen. The rate at which the latter is evolved is greatly dependent on the water content of the alcohol, which is also indicated by the appearance of the mixture, since magnesium hydroxide is precipitated if water is present. The reaction is given a quantitative form by measuring the time necessary for the evolution of 5, 10, or 20 c.c. of hydrogen under standard conditions and reference to a table which is fully given in the original.

Magnesium is also very suitable for the preparation of anhydrous methyl alcohol. About 10 g. of the clean metal are placed in about a litre of methyl alcohol contained in a distillation apparatus. The reaction speedily becomes so vigorous that the alcohol is brought to its boiling point. When the metal has dissolved, the solution is kept gently boiling during several hours, after which the methyl alcohol is distilled, the first portion of the distillate being rejected. A single treatment usually suffices. It is advantageous to carry out the distillation in a current of dry air. The utility of magnesium is restricted to specimens of methyl alcohol which do not contain more than 0.5—1% of water, but it has the advantage over calcium that it does not introduce ammonia into the alcohol.

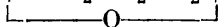
Magnesium methoxide, $Mg(OMe)_2 \cdot 3MeOH$, crystallises in rhombic plates. At 18° it dissolves in methyl alcohol to the extent of 0.9 mol. per litre. H. W.

Addition of Hydrogen to Acetylene Derivatives. IX. Addition of Hydrogen to Acetylenic γ -Alcohols. J. S. ZALKIND and (MLLE) M. A. VILENKINA (*J. Russ. Phys. Chem. Soc.*, 1917, 49, 130—148).—It was observed (A., 1914, ii, 257) that if $\beta\epsilon$ -dimethyl- $\Delta\gamma$ -hexinene- $\beta\epsilon$ -diol is reduced by the Sabatier method, using as

catalyst colloidal palladium, only two atoms of hydrogen per molecule are added on, whilst using platinum black as the catalyst, four atoms of hydrogen are absorbed, and a saturated alcohol results. The reduction of this substance is now repeated, using, not Paal's colloidal palladium, which is made up with sodium protalbuminate, as in the previous experiments, but Skita's colloidal palladium, for which gum arabic is used. The latter form of catalyst is found to be less active than the former when added in small quantity; when larger quantities are present they are equally active, and the character of the reaction is the same for both, namely, rapid reduction to an ethylenic linking, after which further reduction goes on, but very slowly, k being more than twenty times greater for the first stage than for the second. The $\beta\epsilon$ -dimethyl- Δ^7 -hexene- $\beta\epsilon$ -diol obtained at the end of the first stage has been shown (this vol., i, 434) to exist in two stereoisomeric forms melting at $69-69.5^\circ$ and $76.5-77^\circ$, respectively, the quantity of the latter isomeride increasing with the speed of the reaction, and the same is found to hold when Skita's colloidal palladium is used. Paal's colloidal platinum is next taken as the catalyst, and, in this case, no tendency exists for the process to cease with the formation of an ethylenic compound, but addition goes on regularly to saturation. The catalytic action of platinum is therefore essentially the same, whether it be used in its colloidal form or as platinum black. The velocity of the process of the reduction of acetylenic to ethylenic linkings is approximately equal, in this case, to that of the reduction of ethylenic to saturated compound. The rate of reduction of the two stereoisomerides of the ethylenic alcohol is slightly greater for the higher melting isomeride, for which k is 0.0083, than for the other isomeride, for which k is 0.0058.

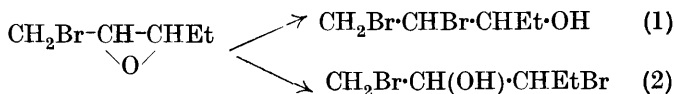
R. T.

The Action of Sulphuric Acid on the Higher Diprimary Glycols. ADOLF FRANKE and OTTO LIEBERMANN (*Monatsh.*, 1923, 43, 589—599; cf. A., 1915, i, 490; this vol., i, 10).—In a previous paper, Franke and Lieben showed that the higher diprimary glycols, containing an even number of carbon atoms, on treatment with sulphuric acid give $\alpha\epsilon$ -oxides; the present investigation was to determine whether the same rule held (1) for glycols containing an odd-numbered carbon chain and (2) for glycols with very long chains. It was found that the rule appeared to hold good in both cases. (1) Azelaic acid was esterified and the ethyl ester reduced by the Bouveault-Blanc process with sodium and dry amyl alcohol, to nonamethylene glycol, $\text{OH}\cdot\text{CH}_2\cdot[\text{CH}_2]_7\cdot\text{CH}_2\cdot\text{OH}$ (b. p. $169^\circ/14\text{ mm.}$). (The amyl alcohol was dried completely by careful fractionation, as treatment with metallic sodium was found to be inadequate.) The glycol was then treated with sulphuric acid by the Franke-Lieben method and a new oxide, $\text{C}_9\text{H}_{18}\text{O}$, boiling at $175-177^\circ$, obtained, which yielded on oxidation with permanganate n -valeric acid and succinic acid as anticipated, together with traces of acetic and oxalic acids. The oxide is therefore $\alpha\epsilon$ -oxidononane, $\text{CH}_3\cdot[\text{CH}_2]_3\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2$.



(2) Potassium ethyl sebacate, $\text{CO}_2\text{Et}\cdot[\text{CH}_2]_8\cdot\text{CO}_2\text{K}$, was electrolysed by the method of Brown and Walker (A., 1891, ii, 1192) to give *n*-hexadecanedicarboxylic ethyl ester, $\text{CO}_2\text{Et}\cdot[\text{CH}_2]_{16}\cdot\text{CO}_2\text{Et}$ (as a by-product was obtained an acid, b. p. 248—249°, which was identified as Δ^7 -nonenoic acid, $\text{CH}_3\cdot\text{CH}\cdot[\text{CH}_2]_6\cdot\text{CO}_2\text{H}$, giving an ester boiling at 226—228° [Brown and Walker gave about 250° for the ester, which is incorrect]). The *n*-hexadecanedicarboxylic ester was reduced by sodium and amyl alcohol to the new *glycol*, $\text{OH}\cdot\text{CH}_2\cdot[\text{CH}_2]_{16}\cdot\text{CH}_2\cdot\text{OH}$, which forms white crystals, m. p. 92°, b. p. 238°/13 mm., and on gentle oxidation with permanganate gives the known acid, $\text{C}_{18}\text{H}_{34}\text{O}_4$, m. p. 118°. On treatment with sulphuric acid, a new *oxide* was obtained as a semi-solid, yellow mass, in amount insufficient to purify for analysis; it is probably α -*oxido-octadecane*, $\text{CH}_3\cdot[\text{CH}_2]_{12}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2$, since on oxidation with dilute permanganate it yields an acid the silver salt of which, when analysed, gave figures approximating to those required for the salt of myristic acid, $\text{CH}_3\cdot[\text{CH}_2]_{12}\cdot\text{CO}_2\text{H}$. F. A. M.

Action of Organomagnesium Compounds on the Epibromohydrin of Ethylglycerol. RAYMOND DELABY (*Compt. rend.*, 1923, 176, 1153—1156).—The action of organic magnesium halides on the epibromohydrin of ethyl glycerol is but little comparable with that on glycerol epibromohydrin, as in the case of both alkyl and aryl magnesium bromides the main reaction consists in the addition of the elements of hydrogen bromide to the epibromohydrin, and only traces of an aryl derivative are formed. The addition of hydrogen bromide might occur in either of the two following ways:



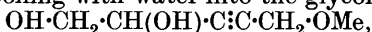
The compound (1) has already been obtained by the addition of bromine to ethylvinylcarbinol (this vol., i, 289) and in the present case it is exclusively the compound (2), $\alpha\gamma$ -*dibromopentane- β -ol*, b. p. 119—119.5°/23 mm., which is formed. The two compounds were differentiated by the preparation of the picrates of the corresponding tetramethyldiaminopentanol, by oxidation to the corresponding ketones, and conversion of the latter into semicarbazones. The $\alpha\gamma$ -*dibromopentane- β -one*, b. p. 85—100°/19 mm., reacted with 1 mol. of semicarbazide, giving a ketotriazine by elimination of one of the bromine atoms with a H of the NH_2 -group. The substance melts at 115—117°. On the other hand, the $\alpha\beta$ -*dibromopentane- γ -one* reacts with 2 mols. and gives a semicarbazone-ketotriazine, m. p. 229—230°. G. F. M.

Some Derivatives of the Glycerol,

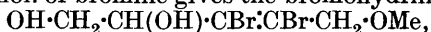


ROBERT LESPIEAU (*Compt. rend.*, 1923, 176, 1068—1070).—The *oxide* of the *methyl ether* of this glycerol having the constitution

$\begin{array}{c} \text{CH}_2 \\ | \\ \text{O} \end{array} \text{---} \text{CH} \cdot \text{C} \cdot \text{C} \cdot \text{CH}_2 \cdot \text{OMe}$ was obtained by the action of chloroacetaldehyde on a mixture of magnesium ethyl bromide and methyl propargyl ether. The product was decomposed with acidified water, extracted with ether, and treated with potassium hydroxide, whereby polymerisation products of the aldehyde were resinified and the chlorohydrin was converted into the oxide. It has b. p. $75-76^\circ/15$ mm., d^{26}_D 1.024, n_D 1.4573. By treatment with hydrogen chloride, it is converted into the *chlorohydrin*, $\text{CH}_2\text{Cl} \cdot \text{CH}(\text{OH}) \cdot \text{C} \cdot \text{C} \cdot \text{CH}_2 \cdot \text{OMe}$, b. p. $117.5-118.5^\circ/12$ mm., d^{21}_D 1.1717, n_D 1.4866. Sodium methoxide converts it into the *ether*, $\text{OMe} \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{C} \cdot \text{C} \cdot \text{CH}_2 \cdot \text{OMe}$, a liquid, b. p. $119-120^\circ/12$ mm., d^{23}_D 1.0508, n_D 1.4608. The ethylene oxide is converted on boiling with water into the glycol ether,



a thick liquid, b. p. $155-156^\circ/12$ mm., d^{22}_D 1.1274, n_D 1.481. Addition of 1 mol. of bromine gives the bromohydrin,



a solid melting at $51-52^\circ$, b. p. $192^\circ/11$ mm. Treatment of this compound with hydrogen bromide at 100° causes demethylation, but the product was not isolated in a pure condition. G. F. M.

The Preparation of Ethers from Primary Alcohols. JEAN POPELIER (*Bull. Soc. chim. Belg.*, 1923, 32, 179—194).—A study of the conditions necessary for the etherification of some primary alcohols in order to obtain a high yield of the corresponding ethers showed that this may be effected by means of a study of the binary mixtures of alcohol and water and the ternary mixtures of alcohol, ether, and water. From a knowledge of the boiling points of these mixtures and the composition of the vapour phase in each case, the preparation of the ethers may be effected with yields of about 90% by simple distillation of the alcohols with sulphuric acid. In general, the process is discontinuous, as adjustments in the composition of the mixture undergoing distillation must be made from time to time. The most suitable proportion of acid varies considerably, according to the alcohol used. Details are given of the application of the method to propyl, butyl, *isobutyl*, amyl, and *isoamyl* alcohols. Formation of unsaturated hydrocarbons may be obviated by working at a sufficiently low temperature.

H. J. E.

The $\alpha\alpha'$ -Dichlorodialkyl Sulphides. FREDERICK GEORGE MANN and (SIR) WILLIAM JACKSON POPE (*T.*, 1923, 123, 1172—1178).

Crystal Structure of Basic Glucinum Acetate. (SIR) W. H. BRAGG (*Nature*, 1923, 111, 532).—X-Ray analysis shows that the molecule of basic glucinum acetate, $\text{Gl}_4\text{O}(\text{C}_2\text{H}_3\text{O}_2)_6$, is a perfect tetrahedron, the oxygen atom being at the centre, the glucinum atoms lying on lines from the centre to the corners, and each $\text{C}_2\text{H}_3\text{O}_2$ -group being associated in a symmetrical manner with the edges of the tetrahedron. The crystal structure is that of diamond, a molecule replacing each atom of carbon.

A. A. E.

The Addition of Hydrogen to Acetylenic Acids. DAVID EMBRY WILLIAMS and THOMAS CAMPBELL JAMES (*Aberystwyth Studies*, 1922, 4, 197—207).—By reduction of phenylpropionic acid with hydrogen in presence of colloidal platinum, Paal and Hartmann obtained *allocinnamic* acid (A., 1909, i, 926) showing that *cis* addition had taken place. Experiments on the same lines with tetrolic acid have given similar results, 63% of the theoretical yield of *allo*-crotonic and only 4% of ordinary crotonic acid being obtained. Reduction of acetylenedicarboxylic acid in the same manner, in the form of its normal potassium salt, gave, however, fumaric acid without any trace of maleic acid. The addition thus takes place in the *trans* position, and supports the views of Michael (A., 1918, i, 249) on the relation between the energy content of such systems and their stereochemical activity. When acetylenedicarboxylic acid is reduced with hydrogen and colloidal platinum in presence of less than two equivalents of alkali, the fumaric acid is further reduced to succinic acid almost as quickly as it is formed.

E. H. R.

The Constitution of Elæomargaric [Elæostearic] Acid. A. VERCRUYSE (*Bull. Soc. chim. Belg.*, 1923, 32, 151—156; cf. Kametaka, T., 1903, 83, 1042; Majima, A., 1909, i, 204).—It has been shown that elæostearic acid, $C_{18}H_{32}O_2$, contains two ethylenic linkings (Fokin, A., 1907, i, 10), and the author has effected oxidation with concentrated permanganate solution, obtaining valeric and azelaic acids, these two products accounting for fourteen of the carbon atoms in the chain. Further oxidation experiments with subsequent weighing of the carbon dioxide evolved showed that the remaining carbon was completely oxidised. Ozonisation of the acid confirmed this result, the products being 75% of the theoretical yield of azelaic acid, 50% of that of valeric acid, and a small quantity of succinic acid. The formula of elæostearic acid is therefore $CH_3 \cdot [CH_2]_3 \cdot CH : CH \cdot [CH_2]_2 \cdot CH : CH \cdot [CH_2]_7 \cdot CO_2H$.

H. J. E.

The Labile Nature of the Halogen Atom in Organic Compounds. VIII. The Action of Hydrazine on the Halogen Derivatives of Acetoacetic and Benzoylacetic Esters and of Benzoylacetone. ALEXANDER KILLEN MACBETH (T., 1923, 123, 1122—1130).

Chlorine Derivatives of Pyruvic Acid. EFIM FILIMINOVITSCH KLIMENKO (*J. Russ. Phys. Chem. Soc.*, 1917, 49, 290—293).—In view of the statement made by Seissl (A., 1889, 489), that the ester obtained by Klimenko (*Ber.*, 1870, 3, 465) from the product of the reaction between phosphorus pentachloride and pyruvic acid is not ethyl dichloropropionate but a mixture of the ethyl esters of monochloro- and dichloro-pyruvic acids, the latter acid is synthesised by the chlorination of pyruvic acid. *Ethyl dichloropyruvate* boils at 160—190°, whereas the ethyl dichloropropionate previously obtained is a crystalline solid, m. p. 115°. Seissl's views must therefore be considered to be incorrect.

R. T.

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The Conversion of Malonic Acid into *d*-Malic Acid. ALEX. MCKENZIE and HAROLD JAMES PLENDERLEITH (T., 1923, 123, 1090—1096).

Ring-chain Tautomerism. V. The Effect of the *gem*-Dipropyl Grouping on the Carbon Tetrahedral Angle. LESLIE BAINS and JOCELYN FIELD THORPE (T., 1923, 123, 1206—1214).

Physical Properties of Maleic, Fumaric, and Malic Acids. JOHN MORRIS WEISS and CHARLES R. DOWNS (*J. Amer. Chem. Soc.*, 1923, 45, 1003—1008).—Maleic anhydride has m. p. 52.6°; *i*-malic acid, m. p. 128.5—129°; maleic acid, m. p. 130—135°; fumaric acid, m. p. 284°; the solubility of these compounds in various common solvents has been determined and compared with previously recorded values. It is also shown that *i*-malic acid is less hygroscopic than citric and tartaric acids. The specific gravity of solutions of *i*-malic and maleic acids of various concentrations is shown graphically. W. S. N.

Chromium Malate and Chromomalic Acid. J. BARLOT and PANAITOPOL (*Bull. Soc. chim.*, 1923, [iv], 33, 306—311).—Chromium malate was obtained in less than 10% yield by dissolving chromium hydroxide in an aqueous solution of malic acid by the aid of heat, evaporating the solution, and purifying the product by successive precipitations from aqueous solution by means of acetone. To obtain an analytically pure product, the chromium hydroxide must be washed free from sodium, and the malic acid purified from potassium by precipitation of the latter as chloroplatinate. Quantitative yields were obtained by the action of a metallic malate on a solution of a chromium salt, and the best results from the point of view of isolating the product were given by acting on a solution of purified chromium sulphate with lead malate at 100°, filtering off the lead sulphate, removing the excess of lead in solution by treatment with hydrogen sulphide, and precipitating the chromium malate as small, anhydrous, greyish-green, hygroscopic crystals by addition of acetone. The anhydrous salt is soluble only with difficulty in water, but on evaporation of the solution a green, amorphous substance is obtained readily soluble in cold water. This is a hydrated substance of the composition $2[(C_4H_4O_5)_3Cr_2] \cdot 13H_2O$, which has acidic properties corresponding with the replacement of 5H, and salts are formed with metals, for example with lead, having the composition $Pb_5[(C_4H_4O_5)_6Cr_4(OH)_5 \cdot 8H_2O]_2$. These salts in analogy to the chromi-oxalates are termed chromimalates. From the green hydrated chromium malate, and from the chromimalates chromium is not precipitated by the usual reagents. G. F. M.

Oxidation of Lignin Alcohol to Lignic Acid and the Occurrence of Lignic Acid. J. GRÜSS (*Ber. Deut. bot. Ges.*, 1923, 41, 53—58; cf. this vol., i, 541).—The oxidation of lignin alcohol by means of hydrogen peroxide leads to *lignic acid*, isolated as the more soluble α -copper salt, $C_7H_{14}O_5Cu \cdot 5H_2O$, and the less soluble β -copper salt. The former has been isolated from oak-wood attacked

by *Polyporus versicolor*, and from pine-wood attacked by *Trametes radiciperda*. A third copper salt has also been obtained from *mykolignic acid*, which is found in pine-wood infested by fungus; this acid gives *oxymykolignic acid* on oxidation by means of hydrogen peroxide. The copper salts are described in detail. W. S. N.

Synthesis of Anemoninic Acid. ATUSI FUJITA (*J. Pharm. Soc. Japan*, 1923, No. 492, 67—75).—Anemoninic acid, $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{H}$, has been synthesised from δ -furylidenelævulic acid by Baeyer's method. The δ -acid (10 g.), prepared by a somewhat modified method of Kehrer and Hofacker (A., 1897, i, 204), was dissolved in excess of sodium carbonate solution and reduced with 3% sodium amalgam (about 100 g.) to δ -furfuryl-lævulic acid, white plates, m. p. 99° , the semicarbazone of which forms small white plates, m. p. 125° . δ -Furfuryl-lævulic acid (4 g.) was dissolved in warm water (400 c.c.), to which bromine water (3.3 g. bromine) was added at a time. Then the mixture was mixed with moist silver oxide, prepared from 20.5 g. of silver nitrate, and warmed at 70° during three hours. After cooling, it was acidified with dilute hydrochloric acid, concentrated in a vacuum and extracted ten times with acetic ester, from which α -anemoninic acid was obtained as a syrup containing some crystals. By treating with a small quantity of hydrochloric acid (20%), it was changed into the β -isomeride, colourless plates, m. p. 189° . K. K.

Action of Molybdic Acid on the Rotatory Power of Tartaric and Malic Esters. E. DARMOIS (*Compt. rend.*, 1923, 176, 1140—1142).—It has already been shown that molybdic acid causes a change in the rotatory power of tartaric and malic acids, and the subject was further investigated by studying the effect of molybdic acid in methyl and ethyl tartrates and malates in dilute aqueous solution. A progressive change in rotation occurred, the rate of which was greatly accelerated by an increase in temperature, but the final value attained was unaffected, as was also the dispersion. The rate of change in rotation and also the final value were dependent on the relative proportions of molybdic acid and ester. The addition of potassium hydroxide in amount less than one-fourth of the quantity required to form K_2MoO_4 has no effect on the rate of variation of α , but larger amounts cause a rapid acceleration of the change. Ammonium molybdate has a similar effect. With ethyl malate molybdic acid causes practically no change in rotation in the cold, but at 100° the change is rapid. It is concluded that the mutarotation is not due to a progressive esterification of the hydroxyl groups, but rather to a saponification of the esters.

G. F. M.

Alkaline Hydrolysis of the Stereoisomeric Dimethyl Tartrates. ANTON SKRABAL and LUDWIG HERMANN (*Monatsh.*, 1923, 43, 633—643).—A study of the relative rates of hydrolysis of methyl *d*- and *l*-tartrates, racemate, and mesotartrate, by sodium carbonate and by carbonate-hydrogen carbonate mixtures. An improved method for preparing the *d*-ester is described (cf.

Anschütz and Pictet, A., 1880, 876). It is shown that the two-stage hydrolysis of the *d*- and *l*-esters proceeds at the same rate, the ratio of the velocity constants, k_1 and k_2 , for the two stages, depending on the concentration of ester, being smaller if the ester concentration is increased. For 0.05 to 0.1 molar solutions of *d*-ester, at 25°, $k_1 = 4.2 \times 10^{-2}$ and $k_2 = 0.30 \times 10^{-2}$; for 0.005 to 0.01 molar solutions, $k_1 = 6.06 \times 10^{-2}$ and $k_2 = 0.31 \times 10^{-2}$. Almost identical values for k_1 and k_2 were obtained for similar solutions of the *l*- and the *dl*-ester, whilst the *meso*-ester (0.01–0.005 molar) gave $k_1 = 4.3 \times 10^{-2}$ and $k_2 = 0.15 \times 10^{-2}$ (cf. A., 1920, ii, 239). E. E. T.

Alkaline Hydrolysis of Diacetyl-*d*-tartaric [Diacetoxysuccinic] Acid and of its Methyl Ester. ANTON SKRABAL and LUDWIG MEHR (*Monatsh.*, 1923, 43, 645–653).—The velocity of alkaline hydrolysis of diacetyl-*d*-tartaric acid and of its methyl ester have been investigated. In the case of the ester, the methyl groups hydrolyse more rapidly than the acetyl groups. In the two-stage hydrolysis of the methyl groups, the ratio of the velocity constants for the two stages is roughly 2:1. In the two-stage hydrolysis of the acetyl groups in the acid, the corresponding ratio is 3.5:1. E. E. T.

Optical Rotation of Arabinic Acid and of the Alkali Arabinates. MOISEI ABRAMOVITSCH RAKUZIN (*J. Russ. Phys. Chem. Soc.*, 1917, 49, 247–250).—Gum arabic is shown to contain potassium, magnesium, and calcium, and has $[\alpha]_D -24.8^\circ$. Pure arabinic acid prepared from this has $[\alpha]_D -27.86^\circ$, and not, as Scheibler states, -98.5° . The lithium, ammonium, sodium, and potassium salts have $[\alpha]_D -17.81^\circ$, -19.81° , -21.67° , and -23.06° , respectively, $[\alpha]_D$, as in previous cases, increasing with the atomic weight of the substituting metal. R. T.

***n*- α -Sulphobutyric Acid and its Optically Active Compounds.** H. J. BACKER and J. H. DE BOER (*Proc. K. Akad. Wetensch. Amsterdam*, 1923, 26, 79–82).—*n*- α -Sulphobutyric acid can be obtained by the action of ammonium sulphite on α -bromobutyric acid and by sulphonation of ethylmalonic acid, but is best prepared by sulphonation of *n*-butyric acid with sulphur trioxide. The butyrylsulphuric acid formed in the cold changes into sulphobutyric acid on heating. The acid crystallises after a long time in a vacuum over phosphoric oxide in hard, very hygroscopic crystals, m. p. 66° , containing $1\text{H}_2\text{O}$. Aniline sulphobutyrate forms small, glistening plates, m. p. 175° , and the *p*-toluidine salt has m. p. 163° . When these salts are heated with an excess of the amine, the amide of the carboxylic acid is formed. Aniline butyranilide- α -sulphonate crystallises in concentrically grouped, feather-like needles, m. p. 253 – 256° ; *p*-toluidine butyro-*p*-toluidide- α -sulphonate has m. p. 260 – 263° , the corresponding *p*-anisidine compound 242° , and the *p*-phenetidine compound 264 – 266° . When heated with aromatic *o*-diamines, sulphobutyric acid forms derivatives of benziminazole. Benziminazole-2-propylsulphonic acid, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{N} \\ \diagup \text{NH} \end{smallmatrix} > \text{C} \cdot \text{CHEt} \cdot \text{SO}_3\text{H}$, from *o*-phenylenediamine, and methyl-

benziminazole-2-propylsulphonic acid, $\text{C}_6\text{H}_5\text{Me} \begin{smallmatrix} \text{---N} \\ \text{NH} \end{smallmatrix} \text{C} \cdot \text{CHEt} \cdot \text{SO}_3\text{H}$,

from 3 : 4-diaminotoluene, are white, crystalline substances of low solubility and high m. p. with properties similar to those of taurine.

The resolution of α -sulphobutyric acid was accomplished through the strychnine salt. *Strychnine d-sulphobutyrate* crystallises in small, glistening needles containing $2\frac{1}{2}\text{H}_2\text{O}$. The d- and l-barium salts form long needles containing $2\frac{1}{2}\text{H}_2\text{O}$, whilst the r-salt forms small, glistening leaflets containing $2\text{H}_2\text{O}$. The direction of rotation of the barium salts is opposite to that of the free acids. The magnitude of rotation varies with the concentration. The molecular rotation of the barium salt for sodium light is 32.2° in a $2\frac{1}{2}\%$ and 29.9° in a 5% solution. The presence of barium chloride lowers the rotation. E. H. R.

The Second Dissociation Constant of Sulphoacetic and α -Sulphopropionic Acids. H. J. BACKER (*Proc. K. Akad. Wetensch. Amsterdam*, 1923, **26**, 83—87).—Using the values of the first dissociation constants of α -sulphoacetic and α -sulphopropionic acids previously determined (this vol., i, 88), the values of the second dissociation constants have now been determined from the hydrogen-ion concentrations, measured colorimetrically, of the acid salts and of mixtures of the acid and neutral salts. The values found, which can only be regarded as approximations, are, at the ordinary temperature, α -sulphoacetic acid, 7.2 to 9.7×10^{-5} ; α -sulphopropionic acid, 4.2 to 6.0×10^{-5} . E. H. R.

Viscosity of the Systems Water-Bromal and Chloral-Dimethylethylcarbinol. NIKOLAI NIKOLAEVITCH EFREMOV (*J. Russ. Phys. Chem. Soc.*, 1918, **50**, 338—371).—Binary fusion, viscosity, and density diagrams are constructed for the systems bromal-water and chloral-dimethylethylcarbinol. For the former system, maxima exist in the fusion and viscosity diagrams at 50 mol. %, corresponding with the formation of bromal hydrate. The summit of the viscosity isotherms moves from 50 to 42.5 mol. % on changing the temperature from 40° to 100° , and a similar change occurs in the isotherms of the temperature coefficients of viscosity, indicating that some dissociation of the compound occurs at higher temperatures. The minimum boiling-point mixture contains 35—45 mol. % of bromal. Bromal hydrate and its mixtures with bromal or water readily lose water with rise of temperature, causing the separation of the liquid into two layers. The density curves for both the system and chloral-dimethylethylcarbinol exhibit at first a rapid and then a gradual rise up to 100% of the halogen compounds. The viscosity isotherms and temperature coefficient of viscosity curves of the latter system are similar in type to those of the former, and indicate the formation of an equimolecular compound similar in properties to chloral hydrate or ethylate. R. T.

Trimethylacetaldehyde [$\alpha\alpha$ -Dimethylpropaldehyde]. I. ADOLF FRANKE and HERMANN HINTERBERGER (*Monatsh.*, 1923, **43**, 655—660).—The aldehyde is prepared as follows: *iso*Butyl

alcohol is passed, together with carbon dioxide, through a brass tube filled with brass turnings and heated at 500—550°, when it is converted into *isobutyraldehyde*. The latter is converted into $\beta\beta$ -dimethylpropan- $\alpha\gamma$ -diol, from which $\beta\beta$ -dimethylpropyl alcohol is prepared as previously described (A., 1914, i, 7), although better conditions are now detailed. By passing the vapours of the last-named alcohol through a hot tube (as before), $\alpha\alpha$ -dimethylpropaldehyde was obtained, and has been studied from the point of view of its possible resemblance to benzaldehyde rather than to a typical aliphatic aldehyde.

When treated with a little concentrated sulphuric acid, it rapidly polymerises to give a *trimeride* (needles, m. p. 82°) which is distinct from a similar compound described by Richard (A., 1911, i, 6). When heated in alcoholic solution with potassium cyanide, the aldehyde gives a small quantity of an *acid* (needles, m. p. 223°), presumably of the benzoic acid type, and formed as a result of the alkaline properties of potassium cyanide. E. E. T.

The Isomeric Trithioacetaldehydes. FREDERICK GEORGE MANN and (SIR) WILLIAM JACKSON POPE (T., 1923, 123, 1178—1181).

Preparation of the Homologues of Mesityl Oxide by the Action of Gaseous Hydrogen Chloride on Ketones. C. V. GHEORGHIU (*Bull. Acad. Sci. Roumaine*, 1923, 8, 68—71).—An attempt to condense homologues of acetone yielded, in the case of a mixture of acetone with methyl ethyl ketone, mesityl oxide, methylmesityl oxide with a larger amount of $\beta\gamma$ -dimethyl- Δ^{β} -pentene- δ -one and small quantities of γ -methyl- $\Delta\gamma$ -hexene- ϵ -one and $\gamma\delta$ -dimethyl- $\Delta\gamma$ -hexene- ϵ -one. From methyl ethyl ketone, $\gamma\delta$ -dimethyl- $\Delta\gamma$ -hexene- ϵ -one is the chief product. The yield in both cases is small owing to resinification. H. J. E.

Syntheses of α -Diketones by Means of Organo-zinc Derivatives. E. E. BLAISE (*Compt. rend.*, 1923, 176, 1148—1150; cf. this vol., i, 181).—It has been shown previously that the condensation of zinc propyl iodide with oxalylbisoxymethyl chloride gives a mixture of the bisoxalylacetatoxyisobutyrate of propylglyoxal and of dibutyl. After alcoholysis of the mixed products only the latter remains. This forms a crystalline substance, m. p. 55—80°, consisting of a mixture of the internally compensated and the racemic isomerides. They could only be separated by slow crystallisation from methyl alcohol, and mechanical separation of the two kinds of crystals formed. The pure substances melt at 72° and 82°, respectively, and boil at 168°/13 mm. Hydrolysis of the mixed isomerides by means of hydriodic acid was accompanied by reduction, and *propyl n-butyl ketone* was formed, b. p. 163°, giving a *semicarbazone*, m. p. 96°. Hydrolysis by means of a mixture of hydrochloric and acetic acids gave, however, dibutyl in 60% yield. It is a yellow liquid, b. p. 61·5°/14 mm. The dioxime melts at 181—182°, and the disemicarbazone above 250°.

G. F. M.

The Oxidation of Dextrose by Yellow Oxide of Mercury, and the Preparation of Gluconic Acid. A. BLANCHETIÈRE (*Bull. Soc. chim.*, 1923, [iv], 33, 345—348).—Gluconic acid was obtained as its calcium salt in almost theoretical yield by the oxidation of a 10% solution of dextrose with yellow mercuric oxide in presence of calcium carbonate. After boiling for twenty-four hours, the liquid was filtered from the mercurous oxide and mercury formed, concentrated by evaporation on a water-bath, and precipitation of the calcium salt induced by the addition of an excess of alcohol. The pasty mass which separates becomes crystalline on keeping for several days over sulphuric acid. It was further purified by recrystallisation from water and alcohol. The salt contains 1 mol. of water, which it retains somewhat tenaciously, exsiccation at 70—80° in a vacuum being necessary for the production of the anhydrous salt. G. F. M.

Carbohydrate Sulphates. VI. Acetone [*iso*Propylidene] Compounds of Dextrose Sulphates. HEINZ OHLE (*Biochem. Z.*, 1923, 136, 428—448; cf. A., 1922, i, 986, this vol., i, 441).—Purified diisopropylidenedextrose, treated in pyridine solution with chlorosulphonic acid in chloroform, yields the crystalline pyridine salt of diisopropylidene-dextrose sulphate; it has m. p. 163—164° and $[\alpha]_D^{20} -21.9^\circ$ in chloroform ($c=2.9$). The sodium salt has $[\alpha]_D^{20} -14.7^\circ$ in water ($c=3.27$). It forms a crystalline additive product with sodium acetate, having $[\alpha]_D -13.4^\circ$ and decomposing at 221—222°. The brucine salt melts at 248° and has $[\alpha]_D^{20} -27.6^\circ$ in water and -30.98° in chloroform. When recrystallised from alcohol, pyridine diisopropylidene-dextrose sulphate loses one molecule of acetone and yields pyridine isopropylidene-dextrose γ -sulphate, m. p. 134°, $[\alpha]_D^{20} -13.5^\circ$ in water. The sodium salt is amorphous and hygroscopic, but the barium salt crystallises with 5 molecules of alcohol and has $[\alpha]_D -14^\circ$ in water. On boiling an alcoholic solution of the pyridine salt for four hours, the sulphuric acid is removed quantitatively as ethylsulphuric acid, identified as its brucine salt, m. p. 200—201°, $[\alpha]_D -29.7^\circ$ in water and crystallising with $3/4$ mol. of alcohol. *iso*Propylidene-dextrose- γ -sulphuric acid is reconverted into the diisopropylidene compound by shaking the pyridine salt with an equal weight of copper sulphate in fifty volumes of acetone for thirty-six hours. *iso*Propylidene-dextrose is converted by chlorosulphonic acid into isopropylidene-dextrose-6-sulphuric acid, which was isolated either as its crystalline sodium salt, m. p. 157°, $[\alpha]_D^{19} -9.88^\circ$, crystallising with $\frac{1}{2}$ H₂O, as its amorphous barium salt, $[\alpha]_D^{20} -7.2^\circ$ in water, or better as its crystalline strychnine salt, m. p. 178—182° (when dried), and $[\alpha]_D^{20} -24.3^\circ$ in water. On keeping the barium salt at 37° in *N*/10-sulphuric acid solution, it loses acetone and yields dextrose-6-sulphuric acid, identifiable as its brucine salt and identical with Soda's preparation (this vol., i, 441). Strychnine-dextrose-6-sulphate monohydrate crystallises well, but during crystallisation its initial rotation falls from -6.27° to -3.12° , whilst its final value remains at -0.7° . A discussion follows of the mechanism of combination

of acetone with dextrose. Evidence has been obtained of intermediate combination with hydrochloric and with sulphuric acids.

H. K.

Extraction of β -Ethylgalactoside in the Presence of a Large Proportion of Reducing Sugars. J. CHARPENTIER (*J. Pharm. Chim.*, 1923, [vii], 27, 368—371).—Galactose has been identified in the products of the hydrolysis of gum arabic by converting it into β -ethylgalactoside by means of emulsin (cf. Bourquelot and Bridel, A., 1920, i, 530). All attempts to extract the β -ethylgalactoside with ethyl acetate gave a product which was contaminated with a large proportion of arabinose. By the action of hydrocyanic acid, however, in the presence of a trace of ammonia the sugar is converted into a nitrile which is hydrolysed to the acid containing one atom of carbon more than the original sugar. This acid is completely precipitated by basic lead acetate, and the β -ethylgalactoside is recovered from the filtered solution. It was obtained as somewhat voluminous, transparent crystals, melting at 159—160° and giving $[\alpha]_D -4.40^\circ$.

W. T. K. B.

The Acetone [*iso*Propylidene] Compounds of Xylose. OLOF SVANBERG and KNUT SJÖBERG (*Ber.*, 1923, 56, [B], 863—869).—In a recent communication (Freudenberg and Svanberg, A., 1922, i, 1116), the preparation of diisopropylidene-xylose by the action of hydrogen chloride on a suspension of xylose in acetone has been described. The remarkable observations were made that a portion of the catalyst appears to pass into a non-ionised form (and to be lost subsequently during the distillation in a high vacuum) and that the diisopropylidene-xylose is very pronouncedly mutarotatory. The behaviour of the hydrogen chloride, however, is shown to be independent of the presence of xylose and to be due in all probability to the formation of an additive product with mesityl oxide or phorone; this is not very material in the cases of the preparation of crystalline isopropylidene sugars, but if, as in the present instance, the products must be purified by distillation, it may easily happen that the distillates are contaminated with hydrogen chloride. Actually, the observed mutarotation of the specimens of diisopropylidene-xylose is shown to be due to this cause and the consequent hydrolysis of the substance to monoisopropylidene-xylose.

Pure diisopropylidene-xylose, b. p. 85—87°/0.5 mm., $[\alpha]_D^{18} +14.0^\circ$ (constant), is conveniently prepared in 80% yield by agitating xylose with a solution of concentrated sulphuric acid in acetone at the atmospheric temperature and subsequent neutralisation of the mixture with barium and calcium carbonates. The rapidity with which the sugar dissolves depends greatly on the purity and dryness of the solvent. The residues from the preparation of the diisopropylidene compound contain small amounts of *monoiso*propylidene-xylose, colourless needles, m. p. 41—43°, $[\alpha]_D^{18} -19.0^\circ$ in aqueous solution (2—4%). The latter compound is more conveniently prepared by the partial hydrolysis of diisopropylidene-xylose by very dilute hydrochloric acid at 18°, the course of the

change, which is unimolecular, being conveniently followed by polarimetric observation. H. W.

The Structure of Sucrose. MAX BERGMANN (T., 1923, 123, 1277—1279).

Investigation of the Mannan Present in Vegetable Ivory. JOCELYN PATTERSON (T., 1923, 123, 1139—1149).

Cellulose Xanthates. R. WOLFFENSTEIN and E. OESER (*Ber.*, 1923, 56, [B], 785—787).—The action of sodium hydroxide solution (*d* 1.2) and carbon disulphide on different cellulose acetates which are soluble in acetone leads to the formation of a *cellulose xanthate*, $C_6H_5(ONa)_3 \cdot (O \cdot C : S \cdot SNa)_2$, which, in contrast to the product derived from cellulose, appears to be derived from a parent substance containing five active hydroxyl groups. It is a dark brown, resinous material which more readily evolves carbon disulphide on exposure to moist air than does the sodium salt of the more usual cellulose xanthate. It gives salts with the heavy metals which are less stable than the corresponding compounds from alkali-cellulose.

H. W.

"Hydrocellulose." A Summary of the Literature. PERCY HERBERT CLIFFORD (*J. Text. Inst.*, 1923, 14, T.69—77).—A review of the literature dealing with the preparation and properties of "hydrocellulose." Seventy-one references are cited.

J. C. W.

Polysaccharides. XVIII. Lichenin. P. KARRER and B. JOOS (*Biochem. Z.*, 1923, 136, 537—541).—Lichenin from *Cetraria islandica* is closely allied to cellulose. By acetolysis at 120°, it yields octa-acetylcellobiose, and with acetyl bromide at 40° yields acetobromocellobiose. Lichenin acetate is prepared like cellulose acetate, and has a similar rotation, $[\alpha]_D^{20} - 23.8^\circ$ (in chloroform + methyl alcohol, 9 : 1). It yields aceto-1 : 6-dibromoglucose on treatment with phosphorus pentabromide. Lichenin is soluble in dilute alkali and in hot water.

H. K.

Lignin. J. GRÜSS (*Ber. Deut. bot. Ges.*, 1923, 41, 48—52; cf. Klasen, A., 1920, i, 821; 1922, i, 324; Beckmann, Liesche, and Lehmann, A., 1921, i, 546; 1922, i, 233; Paschke, A., 1921, i, 772; 1922, i, 325).—The action of ethyl-alcoholic hydrogen chloride on wood, previously extracted by means of 4% sodium hydroxide solution and boiling water, gives a substance described as *lignin alcohol*, $C_{26}H_{46}O_{10}$, m. p. 160°, *vanadium* derivative, $C_{26}H_{45}O_{10}V_3$, a microcrystalline powder. Numerous colour reactions of lignin alcohol are described (cf. Crocker, A., 1921, i, 839).

W. S. N.

Lignin. EMIL HEUSER and ARNE WINSVOLD (*Ber.*, 1923, 56, [B], 902—909).—Lignin has been considered to be an aromatic compound, whilst, on the other hand, arguments have been advanced in favour of an aliphatic structure, such as that of the cellulose and pentosans of wood. In the authors' opinion, the chemical evidence available is insufficient at the present to enable a definite decision

between these alternatives to be made, but in the present communication a number of experiments are quoted the results of which point to the conclusion that the molecule of lignin contains a benzenoid nucleus with oxidisable side chains.

Treatment of lignin with molten potassium hydroxide has been shown previously to lead to the formation of protocatechuic acid, pyrocatechol, and oxalic acid, whereas cellulose under similar conditions gives large amounts of oxalic acid and small quantities of protocatechuic acid and pyrocatechol. The previous results may be summarised in the statement that lignin and cellulose behave differently towards molten potassium hydroxide, the former giving mainly aromatic compounds, the latter chiefly oxalic acid. If the treatment of lignin is effected in an atmosphere of hydrogen or nitrogen the production of oxalic acid is very greatly diminished whereas that of aromatic compounds, particularly pyrocatechol, considerably increased. The formation of pyrocatechol from lignin is doubtless a secondary change due to the further decomposition of protocatechuic acid primarily formed. The latter substance by itself requires a high temperature (360°) to effect the complete removal of carbon dioxide, but in the presence of potassium hydroxide the change occurs at 240° . If air is present, the yield of pyrocatechol is small (1–3%), but oxalic acid is formed in considerable quantity (14–16%). The displacement of the yields in favour of pyrocatechol can also be greatly influenced by the presence of iron, which doubtless acts catalytically. Protocatechuic and oxalic acids are not present in the product, so that the decomposition of the former is also accelerated by the catalyst. Actually, a part of the pyrocatechol which is produced also suffers further change under these conditions, since the yield of the substance is only 23% of the weight of lignin taken.

Protocatechuic acid is converted by molten potassium hydroxide at 240 – 280° in the presence of air into pyrocatechol (2.5%) and oxalic acid (about 20%), whilst 70% of it remains unchanged. In an atmosphere of hydrogen, the yields are pyrocatechol (19%), oxalic acid (0%), unchanged protocatechuic acid (77%), whilst in the presence of iron and hydrogen they are pyrocatechol (26%) and unchanged protocatechuic acid (0%).

The behaviour of ligninsulphonic acid towards molten potassium hydroxide is generally similar to that of lignin prepared by Willstätter's method.

The communication concludes with an extended, adverse criticism of the method proposed by Schmidt (A., 1921, i, 912; 1922, i, 206; this vol., i, 274) for the estimation of lignin in wood (the results of which are not in harmony with those obtained by the customary methods) and of the introduction of the conception of "skeleton substance."

H. W.

Humic Acids. IV. Preparation and Properties of Artificial and Natural Humic Acids. WILHELM ELLER [and, in part, H. SAENGER, K. WENZEL, H. SEILER, and H. PIEPER] (*Annalen*, 1923, 431, 133–161).—An extension of previous work on the

subject (A., 1920, i, 733). Phenols are oxidised in alkaline solution by exposure to the air, by addition of hydrogen peroxide, by addition of potassium persulphate, or by electrolysis. In respect to the humic acids to which they give rise, the phenols investigated fall into four classes. (1) Hydroxyquinol gives a humic acid, $(C_6H_4O_3)_x$, which is also produced from hydroxyquinol triacetate; methylquinol is converted into the homologue, $(C_7H_6O_3)_x$. (2) Pyrogallol is oxidised to a humic acid, $(C_{48}H_{30}O_{25})_x$; if insufficient alkali or persulphate is used, purpurogallin and a *hexahydroxydiphenyl*, m. p. 230° , are formed, either of which gives the same humic acid on continued oxidation. It is not, however, possible to obtain a pure humic acid by the oxidation of phloroglucinol, its triacetate, its diethyl ether, or its carboxylic acid. (3) Salicylic acid, gentisic acid, and 2 : 4 : 2' : 4'-tetrahydroxydiphenyl, in contrast to the phenols of the previous classes, undergo oxidation with elimination of carbon dioxide and production of a humic acid containing 56.37—56.57% carbon, 2.49—2.58% hydrogen, for which no formula has yet been devised. (4) The oxidation of phenol, *o*-cresol, resorcinol, or 3 : 5 : 3' : 5'-tetrahydroxydiphenyl leads to a product of variable composition. Nevertheless, it is shown that the properties (*loc. cit.*) of any of these phenol-humic acids are the same as those of the natural humic acids.

It is known that humic acids decompose at 80° (A., 1921, i, 506); this is doubtless the reason why humic acids prepared from carbohydrates by previous workers vary in composition. Indeed, it is now shown that if the temperature of reaction does not exceed 70° , the action of 45—50% aqueous sulphuric acid on sucrose, lactose, or dextrose leads to the formation of a humic acid, $(C_7H_7O_3)_x$ (cf. Bottomley, A., 1915, i, 648), the composition of which is constant. A homogeneous product is not, however, obtained by the action of sulphuric acid on cellulose. Humic acids from carbohydrates show slight differences in their solubility, when compared with natural humic acids or those derived from phenol. Moreover, both natural and phenol-humic acids absorb atmospheric oxygen when moistened with alkali hydroxide solution; when they are warmed to about 100° with phenylhydrazine carbamate, nitrogen is evolved. These reactions are not, however, given by humic acids derived from carbohydrates (cf. following abstract).

W. S. N.

Humic Acids. V. Action of Nitric Acid on Humic Acids.

WILHELM ELLER, HARRY MEYER, and HANS SAENGER (*Annalen*, 1923, 431, 162—177; cf. preceding abstract).—The similarity between the natural humic acids and those derived from phenols is shown to extend to their derivatives. The action of cold concentrated nitric acid on quinol-humic acid gives *seminitrohumic acid*, $(C_{12}H_7O_6 \cdot NO_2)_x$, a brownish-red, amorphous, hygroscopic powder, which is soluble in water, but tends to form colloidal solutions; the aqueous solution has an acid reaction, but does not decompose alkali carbonates. A product identical in composition and properties is obtained by the action of cold concentrated nitric

acid on natural humic acid; the insoluble material formed in this reaction is held to be an adsorption-compound of the nitro-acid and inorganic salts. Seminitrohumic acid causes the elimination of nitrogen when warmed with phenylhydrazine carbamate at 70°; its aqueous solution gives an intense red coloration when warmed with potassium cyanide solution. The action of hot, concentrated nitric acid leads to the formation of oxalic acid, carbon dioxide, and hydrogen cyanide.

When quinol-humic acid is treated with boiling concentrated nitric acid, oxidation and nitration occur simultaneously, with formation of a yellow, amorphous, very hygroscopic powder, *nitrohydroxyhumic acid*, the composition of which varies. In contrast to nitrohumic acid, it is insoluble in alcohol.

When quinone is treated with boiling concentrated nitric acid, nitration and polymerisation both occur, the product, *nitroquinone-humic acid*, being a reddish-yellow, amorphous, hygroscopic powder the composition and properties of which are intermediate between those of nitrohumic acid and nitrohydroxyhumic acid. When it is heated with phenylhydrazine carbamate, nitrogen is evolved at 80°. It forms a colloidal aqueous suspension.

The product of the action of cold concentrated nitric acid on sucrose-humic acid is a faintly yellowish-brown, amorphous powder, $(C_{21}H_{21}O_{14}N_2)_x$, which is only stable to air and sunlight after drying; it is soluble in alkalis or ammonia, and in water, alcohol, or acetone when freshly prepared, or on warming. In contrast to the other humic acids described, it decolorises aqueous potassium permanganate solution.

W. S. N.

Humic Acids. VI. Action of Chlorine on Humic Acids.

WILHELM ELLER, ERNST HERDIECKERHOFF, and HANS SAENGER (*Annalen*, 1923, **431**, 177—186).—The action of chlorine gas at 50—70°, in the absence of air and sunlight, on an aqueous suspension of quinol-humic acid gives a golden-yellow, infusible, amorphous powder, *chlorohumic acid*, $C_{10}H_5O_6Cl_5$, which, when heated, decomposes below 100°, more rapidly at higher temperatures. When chlorohumic acid is heated with phenylhydrazine carbamate, nitrogen is evolved at 70°. Since it forms true solutions in ether, phenol, or glacial acetic acid, the molecular weight can be determined; in the formation of chlorohumic acid it is suggested that the six-membered rings in humic acid (A., 1921, i, 506) become converted into five-membered rings. The action of chlorine under the same conditions on natural humic acid gives identically the same product, but from sucrose-humic acid a pale-yellow, amorphous powder, decomp. 150° $(C_{21}H_{21}O_{13}Cl_4)_x$, is produced the properties of which are compared with those of the other humic acids as follows. The chloro-derivative from sucrose-humic acid is incompletely soluble in alcohol, and insoluble in ether, phenol, or acetic acid; the chloro-acids from phenols or natural acids very readily form true solutions in these solvents. The chloro-acid from sucrose is stable to boiling water; the other chloro-acids are immediately decomposed with elimination of carbon dioxide. The chloro-acids

from natural or phenol-humic acids are immediately decomposed by means of cold concentrated alkali hydroxide solution, whereas the acid derived from sucrose is stable. W. S. N.

Conversion of Alanine into Pyruvic Acid by the Direct Action of Oxygen. L. J. SIMON and LÉON PIAUX (*Compt. rend.*, 1923, 176, 1227—1229).—Whilst oxidising agents convert alanine into acetaldehyde, carbon dioxide, and ammonia, the direct action of oxygen itself on a solution of the sodium salt in presence of small amounts of copper causes the formation of pyruvic acid to the extent of a maximum of about 8%, when 0.25 atom of copper is present for each molecule of alanine. With greater proportions of copper, the amount of pyruvic acid produced progressively decreases, and as this decrease is not due to the further oxidation of pyruvic acid, it is clear that two quite distinct reactions are involved, one giving rise to pyruvic acid, and the other to acetaldehyde. These results lend support to the suggestion of Neubauer and Fromherz that pyruvic acid is an intermediate product in the biochemical transformation of amino-acids into alcohols.

G. F. M.

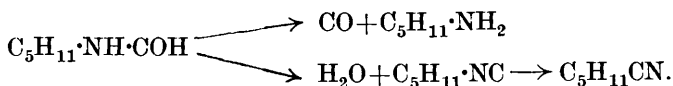
The Optical Activity of Leucine and its Salts with Alkali Metals. M. A. RAKUZIN (*J. Russ. Phys. Chem. Soc.*, 1917, 49, 92—93).—The molecular rotation of leucine salts is higher than that of the parent acid, and increases with the atomic weight of the metal. Thus $[\alpha]_D$ for leucine in aqueous solution is -3.39° ; lithium salt, -8.35° ; ammonium salt, -10.34° ; sodium salt, -20.21° ; potassium salt, -23.22° (cf. this vol., i, 494).

G. A. R. K.

Optical Rotation of *l*-Aspartic Acid and its Alkali Salts. M. A. RAKUZIN (*J. Russ. Phys. Chem. Soc.*, 1917, 49, 245—247).—The specific rotation of aspartic acid is found to be $[\alpha]_D +3.63^\circ$, not, as stated, $+4.36^\circ$. The lithium, ammonium, sodium, and potassium salts have $[\alpha]_D -4.86^\circ$, -7.60° , -9.09° , and -14.20° , respectively, $[\alpha]_D$ increasing with the atomic weight of the substituting metal.

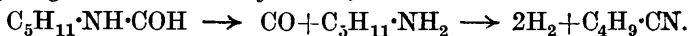
R. T.

Decomposition of the Formamides of Aliphatic Amines. A. MAILHE (*Compt. rend.*, 1923, 176, 1159—1161; cf. this vol., i, 458).—The catalysis of the formyl derivatives of aliphatic amines over alumina at $400-410^\circ$ proceeds in the same way as that of the corresponding aromatic compounds, with the formation of the amine and liberation of carbon monoxide. At the same time, a certain amount of nitrile is formed due to the dehydration of the amine. Thus *isoamyl*formamide gave a mixture of *isoamyl*amine and *isovaleronitrile*:



Catalysis over nickel at 360° furnishes carbon monoxide and dioxide, hydrogen, methane, olefines, and an alkaline condensate, b. p.

120—130°, consisting mainly of *isobutyronitrile* produced by the dehydrogenation of *isoamylamine*,

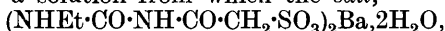


A portion of the *isoamylamine* is resolved into ammonia and *isoamylene*, which in its turn is decomposed further into methane, ethylene, etc. The hydrogenation of *isoamylformamide* over nickel at 200—210° gives a certain amount of secondary amine, *methylisoamylamine*, b. p. 108°, but the water produced hydrolyses some of the formamide to the primary amine, and the product is therefore a mixture of the two amines. G. F. M.

Carbamide and Guanidine Derivatives of Aliphatic Sulphonic Acids. RUDOLF ANDREASCH (*Monatsh.*, 1923, 43, 485—491).—A continuation of previous work (A., 1880, 877; 1883, 664). Sulphoacetylcarbamide, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{SO}_3\text{H}$, which cannot itself be obtained, forms well-defined salts. The potassium and ammonium salts are obtained by treating chloroacetylcarbamide with potassium and ammonium sulphite, respectively. If carbamide (10 g.), chloroacetic acid (16 g.), and phosphoryl chloride (15 g.) are heated together for three hours at 100°, a 75% yield of chloroacetylcarbamide results.

The *potassium* salt (needles, $+1\text{H}_2\text{O}$) of *sulphoacetylmethylcarbamide*, $\text{NHMe}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{SO}_3\text{H}$, is similarly obtained from chloroacetylmethylcarbamide (cf. Frerichs, A., 1899, i, 795, 796).

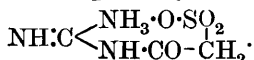
Chloroacetylethylcarbamide, obtained from ethylcarbamide and chloroacetyl chloride, forms needles, m. p. 138°, and with potassium sulphite gives a solution from which the salt,



is obtained after evaporating in presence of barium acetate and extracting the potassium acetate with alcohol.

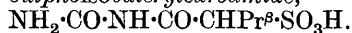
Potassium sulphoacetylphenylcarbamide is obtained from chloroacetylphenylcarbamide and potassium sulphite.

Chloroacetylguanidine hydrochloride, after treatment with potassium hydroxide and sulphite, yields *sulphoacetylguanidine*,



s-Diphenylcarbamide reacts slowly with chloroacetyl chloride to give a *chloroacetyl* derivative, m. p. 180°.

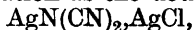
The successive actions of chloroacetyl chloride and ammonium sulphite on dicyanodiamidine sulphate give needles, m. p. 108°, probably the *ammonium* salt ($+2\text{H}_2\text{O}$) of *sulphoacetyldicyanodiamidine*, $\text{NH}_2\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{SO}_3\text{H}$. Ammonium sulphite converts "bromural" (bromo*isovaleryl*carbamide) into the *ammonium* salt of *sulphoisovalerylcarbamide*,



isoValerylcarbamide was isolated as well, but was probably present in the commercial bromural used. E. E. T.

The Action of Potassium Cyanide on Monochloroamine. W. F. SHORT (*Chem. News*, 1923, 26, 100—101).—A method is

described for the preparation of dicyanimide from a solution of hypochlorite and ammonia by the addition of potassium cyanide. It was removed from solution as the double silver salt,

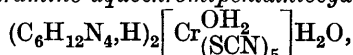


from which the dicyanimide hydrochloride could be recovered. Cold hydrochloric acid converted the silver compound into a cyanocarbamide, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CN}$. After precipitation of the silver by hydrogen sulphide, and concentration of the solution in a vacuum, an insoluble, amorphous polymeride of dicyanimide separated as a jelly-like mass.

W. E. G.

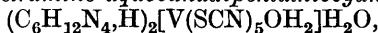
Complex Thiocyanates of Tervalent Elements. G. SCAGLIARINI and G. TARTARINI (*Gazzetta*, 1923, 53, i, 139—143).—The authors have successfully repeated Rosenheim and Cohn's attempts (A., 1901, i, 455) to prepare chromithiocyanates with the value of the ratio $\text{Cr} : \text{SCN}$ other than 1 : 6, advantage being taken of Bjerrum's suggestion to effect the reactions in hot solutions containing an acid (A., 1922, i, 19). The hexathiocyanates of chromium are so stable that energetic chemical reagents are necessary to decompose them, and the chromithiocyanic acid from which they are derived is a resistant complex of pronounced acid character. Vanadium, iron, and aluminium form, however, less stable hexa-acid salts, which allow more readily of the gradual demolition of the complex anion. Thus a dilute solution of ammonium vanadithiocyanate contains at least a penta-aquo-salt, which may be rendered evident by conversion into the slightly soluble hexamethylenetetramine salt.

Hexamethylenetetramine aquochromipentathiocyanate,



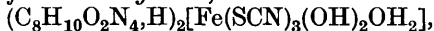
forms violet crystals, and *hexamethylenetetramine chromihexathiocyanate*, $(\text{C}_6\text{H}_{12}\text{N}_4, \text{H})_3[\text{Cr}(\text{SCN})_6]$, pale violet crystals.

Hexamethylenetetramine aquovanadipentathiocyanate,



forms brick-red crystals and the *aquoferripentathiocyanate*, $(\text{C}_6\text{H}_{12}\text{N}_4, \text{H})_2[\text{Fe}(\text{SCN})_5\text{OH}_2]$, dark green, almost black crystals.

Caffeine aquoferritriithiocyanate,



forms mosaic gold, tabular crystals.

T. H. P.

The Catalytic Reduction of Aliphatic Azines. II. Reduction of Dimethylketazine and isoButyraldazine in the Presence of Glacial Acetic Acid. K. A. TAIPALE (*Ber.*, 1923, 56, [B], 954—962).—It has been found by the author (the communication will be published later) that dimethylketazine can be hydrogenated in the presence of platinum black to the corresponding symmetrical secondary hydrazine, and that the method can be extended to other aliphatic ketazines and aldazines, giving thus a method for the preparation of the difficultly accessible aliphatic hydrazohydrocarbons. Reduction, however, occurs very slowly, and the yields do not exceed 60% of those theoretically possible. It is found in the case of dimethylketazine that these disadvantages

can be largely avoided if the reaction is effected in glacial acetic acid solution. Under definite conditions, the change occurs with sufficient rapidity, and the yield of hydrazine attains 90%. The corresponding primary and secondary amines are formed as by-products and, in contrast to the action with the ketazine alone or in the presence of a neutral solvent, ammonia is produced in small amount. As the quantity of acetic acid is increased, the yields of the hydrazine diminish.

With *isobutyraldazine* the process is not so successful. The rapidity of hydrogenation is increased, but the yield of the hydrazine is diminished, whereas that of amines and ammonia is increased. In this case, also, increasing amounts of by-products are formed as the dilution of the solution increases. On the other hand, undue concentration of the solution causes gradual cessation of the change owing to the separation of solid acetates. The difficulty is most readily avoided by operating in alcoholic or ethereal solution with addition of a quantity of acetic acid which is approximately equivalent to the azine used.

The following compounds call for mention. *Diisopropylhydrazine dihydrochloride*, $\text{CHMe}_2\cdot\text{NH}\cdot\text{NH}\cdot\text{CHMe}_2\cdot 2\text{HCl}$, and the corresponding monohydrochloride, m. p. 203—204° after softening at 200°, and *monoperchlorate*, m. p. 145—146°. *Diisopropylsemicarbazide*, $\text{NH}_2\cdot\text{CO}\cdot\text{NPr}^\beta\cdot\text{NHPr}^\beta$, m. p. 103—104°. *Monobenzoyldiisopropylhydrazine*, $\text{NHPr}^\beta\cdot\text{NBzPr}^\beta$, m. p. 44·5°. *Diisobutylhydrazine dihydrochloride*, $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{NH}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CHMe}_2\cdot 2\text{HCl}$, and the corresponding monohydrochloride have m. p. 175° when heated rapidly. The *monoperchlorate*, m. p. 159° (decomp.), when rapidly heated, and the *dibenzoyl* derivative, small needles, m. p. 79—80°, are described. *Diisobutylsemicarbazide* crystallises in hexagonal plates, m. p. 132°.

Diisobutylamine chloroaurate forms yellow crystals, decomp. 199—200°. H. W.

[No reference is made to the papers by Lochte, Bailey, and Noyes, A., 1922, i, 328; this vol., i, 26.]

Bismuth Cacodylate. P. CLAUSMANN (*Bull. Soc. chim.*, 1923, [iv], 33, 447—448).—A crystalline bismuth cacodylate of the composition $(\text{AsMe}_2\text{O}_2)_3\text{Bi}\cdot 8\text{H}_2\text{O}$, was obtained by dissolving the theoretical amount of bismuth oxide in a hot concentrated aqueous solution of cacodylic acid, filtering, and allowing the salt to crystallise. It forms colourless, hexagonal crystals, m. p. 82°. The whole of the water of crystallisation is not eliminated even at 120°, and above this temperature decomposition occurs. The salt is not so readily hydrolysed as the salts of bismuth with mineral acids. A similar compound cannot be obtained by double decomposition between a bismuth salt and an alkali cacodylate.

G. F. M.

An Electrolytic Method for the Preparation of Mercury Dimethyl. J. LEWIS MAYNARD and HENRY C. HOWARD, jun. (*T.*, 1923, 123, 960—964).

Further Experiments on the Catalytic Dehydrogenation of Hexahydroaromatic Hydrocarbons. N. ZELINSKY (*Ber.*, 1923, 56, [B], 787—788).—*o*-Dimethylcyclohexane is almost completely dehydrogenated to *o*-xylene when passed three times over platinum black at 300—310°; under similar conditions at 310°, *m*-dimethylcyclohexane yields *m*-xylene quantitatively. Four successive passages of *p*-dimethylcyclohexane over palladium black at 310° gives *p*-xylene in 96% yield, whereas menthane is largely transformed into *p*-cymene by two successive treatments at 300—305°. H. W.

The Preparation of Aromatic Chloromethyl Derivatives. G. BLANC (*Bull. Soc. chim.*, 1923, [iv], 33, 313—319).—Chloromethyl derivatives of aromatic hydrocarbons were obtained, in most cases in good yield, by the action of hydrogen chloride on trioxymethylene, or, more conveniently, 40% formaldehyde solution, and the hydrocarbon in presence of zinc chloride at about 60°. Thus from benzene an 80% yield of benzyl chloride together with *p*-dichloromethylbenzene were obtained. With larger quantities of zinc chloride and a more slowly conducted reaction, considerable amounts of diphenylmethane were obtained. From toluene, 1-methyl-4-chloromethylbenzene was prepared in a similar manner, whilst *m*-xylene gave 1:3-dimethyl-4-chloromethylbenzene, b. p. 115°/15 mm., and 1:3-dimethyl-4:6-dichloromethylbenzene, m. p. 93°. From ethylbenzene *p*-chloromethylethylbenzene was obtained, b. p. 95—96°/15 mm., and cumene gave a 75% yield of *p*-chloromethylisopropylbenzene, b. p. 100°/14 mm. Cymene was converted into 1-methyl-2-chloromethyl-4-isopropylbenzene, b. p. 120°/12 mm., identified by conversion into the corresponding aldehyde, b. p. 128°/15 mm., and oxidation of the latter with silver nitrate to 1-methyl-4-isopropylbenzoic acid, m. p. 69°. The condensation with naphthalene was carried out in presence of light petroleum as a diluent, and a good yield of 1-chloromethylnaphthalene, a colourless liquid having an irritating action on the skin, and boiling at 145—146°/6 mm., was obtained. G. F. M.

The Influence of Nitro-groups on the Reactivity of Substituents in the Benzene Nucleus. VII. Reactions of 2:5- and 4:5-Dinitro-*m*-xylenes. KATHLEEN IBBOTSON and JAMES KENNER (*T.*, 1923, 123, 1260—1268).

The Cryoscopy of Diphenyl in Acetic Acid. A. BERLANDE (*Bull. Soc. chim.*, 1923, [iv], 33, 466—468).—Experiments on the cryoscopic determination of the molecular weight of diphenyl using glacial acetic acid as solvent are described. The cryoscope employed was not hermetically sealed, and consisted of a stoppered test-tube immersed in an ice-bath, and the stirring was affected by means of the thermometer. The results were too low when the concentration of the solution was such that the freezing-point depression was less than about 0.5°, owing to the progressive hydration of the solvent, which itself caused a lowering of the freezing point of two- to three-hundredths of a degree in ten to

fifteen minutes and only when the depression caused by the diphenyl was sufficiently great to render this negligible, were approximately accurate results obtained.

G. F. M.

Röntgen Ray Spectroscopy of Organic Compounds. KARL BECKER and HERTA ROSE (*Z. Physik*, 1923, **14**, 369—373).—The following parameters have been determined from crystals of the respective organic substances by X-ray analysis: dibenzyl, $a:b:c = 2.082:1:1.211$, $\beta = 119^\circ$; stilbene, $a:b:c = 1.077:1:1.415$, $\beta = 118^\circ 40'$; benzil, $a:c = 1:1.652$; triphenylmethane, $a:b:c = 1.140:1:0.578$; triphenylcarbinol, $a:c = 1:0.534$; mannitol, $a:b:c = 1.275:1:0.562$; sucrose, $a:b:c = 1.225:1:0.920$, $\beta = 105.74^\circ$. The respective numbers of molecules in the unit cell and the corresponding calculated values of the densities are: dibenzyl, 2, 1.185; stilbene, 4, 1.246; benzil, 3, 1.415; triphenylmethane, 3, 1.103; triphenylcarbinol, 6, 1.234; mannitol, 2, 1.555; sucrose, 2, 1.574. In the case of stilbene, the value of a deduced from X-ray measurements is one half that deduced from goniometric measurements. In the respective cases of triphenylmethane, triphenylcarbinol, and mannitol, the following ratios were found between the respective axial lengths as determined by X-ray and goniometric measurements: a , 2:1; c , 3:4; a , 2:1.

J. S. G. T.

Dinitronaphthalenes. V. VESELÝ and K. DVOŘÁK (*Bull. Soc. chim.*, 1923, [iv], **33**, 319—333).—The preparation of the following hitherto inaccessible or unknown dinitronaphthalenes is described: 1:6-Dinitronaphthalene was obtained from 1-nitro-6-aminonaphthalene by replacing the amino-group successively with the diazonium group, and the nitro-group according to the method recently described (A., 1922, i, 690). It melted at 161—162°, and was identical with the compound prepared by Graebe and Drews (A., 1884, 1036). 1:7-Dinitronaphthalene was similarly obtained from 1-nitro-7-aminonaphthalene. It forms small, yellow crystals, m. p. 156°. In like manner 1:4-dinitronaphthalene was obtained from 1-nitro-4-aminonaphthalene. It forms small needles, m. p. 129°. The same reaction applied to 1-nitro- β -naphthylamine gave only a diazo-oxide, but 1:2-dinitronaphthalene was obtained from *ar*-1:2-dinitrotetrahydronaphthalene (one of the nitration products of "tetralin") by bromination with 2 mols. of bromine, and heating the dibromo-derivative at 180°, when 2 mols. of hydrogen bromide were eliminated with formation of 1:2-dinitronaphthalene, which forms long, slightly brown needles, m. p. 158°. The hitherto very inaccessible 1:3-dinitronaphthalene was prepared in a similar way from *ar*-1:3-dinitrotetrahydronaphthalene. The partial reduction of 1:6- and 1:7-dinitronaphthalenes with alcoholic stannous chloride resulted in each case in the reduction of the α -nitro-group, and 6-nitro- α -naphthylamine, red needles, m. p. 167°, and 7-nitro- α -naphthylamine, red needles, m. p. 121—122°, were isolated from the respective reaction products. Their *acetyl* derivatives form yellow crystals melting at 232—233° and 206—207°, respectively. By diazotisation the former naphthyl-

amine was converted into 6-nitro- α -naphthol, yellow needles, m. p. 179°. Partial reduction of the above two dinitronaphthalenes with ammonium sulphide, on the other hand, led to the reduction of the β -nitro-group, and formation of 5-nitro- β -naphthylamine, and 8-nitro- β -naphthylamine, m. p. 104—105°, respectively. The 1:2- and 1:3-dinitronaphthalenes did not behave in a perfectly analogous fashion. Stannous chloride reduced the α -nitro-group in the 1:3-compound giving 3-nitro- α -naphthylamine, m. p. 136—137°, *acetyl* derivative, m. p. 255°, but the β -nitro-group of the 1:2-compound is attacked with formation of 1-nitro- β -naphthylamine, m. p. 126—127°. Ammonium sulphide reduces 1:3-dinitronaphthalene mainly to the same 3-nitro- α -naphthylamine, together with a small amount of the 4-nitro- β -naphthylamine, red needles, m. p. 95°, *acetyl* derivative, 237—238°. The decomposition of the diazonium salt of 3-nitro- α -naphthylamine gave 3-nitro- α -naphthol, yellow needles, m. p. 167—168°. With 1:2-dinitronaphthalene, ammonium sulphide gave only tarry products. The α -nitro-group in 1:2-dinitronaphthalene is very mobile, and was replaced by numerous other groups, for example, on boiling with sodium hydroxide 2-nitro- α -naphthol, m. p. 127—128°, was formed. Alcoholic ammonia caused the replacement of the nitro- by the amino-group, with formation of β -nitro- α -naphthylamine, m. p. 141—142°, and on boiling with aniline 2-nitro-1-anilinonaphthalene, orange crystals, m. p. 110—111°, was produced. G. F. M.

The Crystalline Structure of Anthracene. (SIR) W. H. BRAGG (*Proc. Physical Soc.*, 1923, **35**, 167—169).—The dimensions of the crystal unit of anthracene have been determined, and the major length of the molecule is found to lie along the *c* axis. The differences between the lengths of the *c* axis for naphthalene and anthracene is 2.5, which corresponds exactly with the width of the benzene ring. The calculated specific gravity is 1.255, which is in agreement with an experimental determination of this constant. The crystals of naphthalene and anthracene show great similarities; the same planes are in each case the best reflectors, and it is only in the length of the *c* axis that there is any great difference. The cell contains two molecules in each case, and since the symmetry number is four, a molecule in the crystal must possess a twofold symmetry. This symmetry has been confirmed by the results.

W. E. G.

Compounds of Picric Acid with Hydrocarbons. NIKOLAI N. EFREMOV (*J. Russ. Phys. Chem. Soc.*, 1918, **50**, 373—421).—Binary fusion diagrams are constructed for mixtures of picric acid with various substances. At 50 mol. % formation of the following picrates occurs: Acenaphthene picrate, m. p. 160.8°; acenaphthylene picrate, m. p. 165.3°; phenanthrene picrate, m. p. 132.8°. α - and β -Chloronaphthalene picrates, m. p. 125.7° and 81.5°, respectively; α - and β -bromonaphthalene picrates, m. p. 130° and 83.5°, respectively; α -benzyl-naphthalene picrate, m. p. 97°, and retene picrate, m. p. 120.9°. Unstable picrates are also formed with

stillbene, transition point, 92.8° , and α -nitronaphthalene, transition point, 54.7° . Nitroacenaphthene, diphenyl, dibenzyl, diphenylmethane, and triphenylmethane do not form picrates. R. T.

Compounds of Picryl Chloride with Hydrocarbons. NIKOLAI N. EFREMOV (*J. Russ. Phys. Chem. Soc.*, 1918, **50**, 421—440).—Binary fusion diagrams are constructed for mixtures of picryl chloride with various hydrocarbons and with picric acid. Equimolecular compounds form in every case with the former, whilst with the latter solid solution, but not compound formation is observed. The following compounds were obtained: Anthracene picryl chloride, m. p. 141.6° ; acenaphthene picryl chloride, m. p. 113.2° ; acenaphthylene picryl chloride, m. p. 109.4° ; retene picryl chloride, m. p. 53.5° ; naphthalene picryl chloride, m. p. 91.2° ; phenanthrene picryl chloride, m. p. 82.4° , and fluorene picryl chloride, m. p. 64.6° . R. T.

Compounds of Picramide with Hydrocarbons. NIKOLAI N. EFREMOV (*J. Russ. Phys. Chem. Soc.*, 1918, **50**, 441—459).—Binary fusion diagrams are constructed for mixtures of picramide with various hydrocarbons and with picric acid. In the latter case, no compound formation occurs, the components forming solid solutions up to 16% of picric acid and 11.5% of picramide. The following equimolecular compounds are formed: Naphthalene picramide, m. p. 168.8° ; anthracene picramide, m. p. 158.8° ; phenanthrene picramide, m. p. 160.2° ; acenaphthene picramide, m. p. 195.4° ; retene picramide, m. p. 125.1° ; and an unstable equimolecular compound, transition point, 127.5° , exists for fluorene. R. T.

Some Reactions of Tetranitroaniline. CECIL WHITFIELD DAVIES and THOMAS CAMPBELL JAMES (*Aberystwyth Studies*, 1922, **4**, 213—216).—Tetranitroaniline does not form compounds with hydrocarbons in dry benzene or acetone solution. With phenols, there is a slight colour change but only with β -naphthol was a definite compound obtained, $C_6H(NO_2)_4 \cdot NH_2 \cdot C_{10}H_7 \cdot OH$, deep red needles, beginning to decompose at 110° , m. p. 140° . With primary amines, tetranitroaniline rapidly condenses with elimination of the 3-nitro-group. With aniline, 2:4:6-trinitro-3-aminodiphenylamine is formed, orange-yellow crystals, m. p. 188° . *o*-Toluidine gives 2:4:6-trinitro-3-aminophenyl-*o*-tolylamine, dark red crystals, m. p. 200° ; 2:4:6-trinitro-3-aminophenyl-*m*-tolylamine forms brick-red crystals, m. p. 181° , and 2:4:6-trinitro-3-aminophenyl-*p*-tolylamine, orange crystals, m. p. 220° . 2:4:6-Trinitro-3-aminophenyl- β -naphthylamine forms bright red crystals, m. p. 212° ; from acetone it forms bright yellow crystals containing 1 mol. of acetone which are lost at 70° . When trinitroaniline is warmed with *n*-amyl alcohol, 2:4:6-trinitro-3-aminophenyl amyl ether is obtained, yellow crystals, m. p. 168° . Trinitro-*m*-phenylenediamine is formed when tetranitroaniline is warmed with aqueous ammonia. E. H. R.

Separation of *o*- and *p*-Nitroacetanilides. KENKICHI MATSUO and the KÔTÔ SEIYAKU KABUSHIKI KAISHA (Japan. Pat. 40523).—The nitration product of acetanilide is a mixture of about 70% *p*-nitroacetanilide and 30% of the ortho-isomeride. When the mixture is treated with hot water of about 80°, the ortho-isomeride is dissolved, whilst the para-isomeride remains insoluble. By filtering, subsequent treatment with hot water if necessary, and washing with hot or cold water, the para-compound, m. p. 208°, is isolated almost quantitatively. The ortho-compound, m. p. 90—93°, is obtained from the mother-liquor and washings by cooling. Formerly it was considered that the para-isomeride is liable to decomposition by treatment with hot water in the presence of acid; the author, however, finds that this compound is stable towards hot water even in the presence of an acid, but the ortho-compound is decomposed to some extent into *o*-nitroaniline by treatment with hot water for a long time in the presence of an acid. K. K.

The Action of Ferrous Chloride on the Hydrochlorides of some Aromatic Amines. WILLIAM MURDOCH CUMMING (*J. Soc. Chem. Ind.*, 1923, 42, 166—168T).—The addition of ferrous chloride solution to solutions of the hydrochlorides of certain aromatic amines causes the precipitation of the hydrochlorides, without the formation of double salts. *o*- and *p*-Toluidine hydrochlorides crystallise in a variety of forms according to the conditions of crystallisation, and all these modifications were obtained by using ferrous chloride as precipitant, but after keeping in the mother-liquors for two days the various forms of the ortho-compound were almost completely converted into the rhombic form, and of the para-compound into the rhombohedral form, which modifications appear therefore to be the most stable forms of the hydrochlorides. The phenylenediamine hydrochlorides were not precipitated by ferrous chloride, except when an excess of concentrated hydrochloric acid was present. Ferrous chloride precipitates anhydrous benzidine monohydrochloride from solutions of the dihydrochloride, but from *o*-toluidine dihydrochloride solutions it precipitates a dihydrochloride crystallising with $1\frac{1}{2}$ mols. of water. Both these salts are much less soluble in water than the normal dihydrochlorides. G. F. M.

The Effect on the Reaction between Halogenonitrohydrocarbons and Aniline of Different Substituents in the Latter. B. LINKE (*Ber.*, 1923, 56, [B], 848—851).—The velocity of reaction between chloronitrohydrocarbons and substituted anilines, occurring in accordance with the general scheme, $2\text{PhNH}_2 + \text{C}_6\text{H}_4\text{Cl}\cdot\text{NO}_2 = \text{NH}_2\text{Ph}\cdot\text{HCl} + \text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NHPh}$, has been investigated in alcoholic solution by determining the hydrochloric acid liberated after definite intervals of time as silver chloride. 4-Chloro-1-nitrobenzene, 4-chloro-1:3-dinitrobenzene, and 2-chloro-1:3:5-trinitrobenzene have been used on the one hand, and *o*-, *m*-, and *p*-nitro-, chloro-, bromo-, and iodoanilines, the aminophenols, toluidines, phenylenediamines, aminobenzoic acids, aminobenzenesulphonic acids in addition to *p*-phenetidine, on the other.

The reactivity of the amines is diminished by the presence in them of iodine, bromine, chlorine, nitro-, sulphonic, or carboxylic groups, the effect of the two latter being less pronounced than that of the other four. The action of the substituent is least marked when it is in the meta-position to the amino-group, and most marked in the ortho-position. With regard to the other substituents investigated (OH, Me, and NH_2), the most pronouncedly restrictive action is observed, as in the previous cases, when they are in the ortho-position, but the least action when they are in the para-position. The action of the amino-group is less marked than that of any other substituent.

The following compounds have been incidentally prepared: 2-Iodo-2':4'-dinitrodiphenylamine, golden-yellow, fibrous aggregates, m. p. 164—165°; 3-iodo-2':4'-dinitrodiphenylamine, orange-coloured, rhombic crystals, m. p. 135°; 4-iodo-2':4'-dinitrodiphenylamine, orange-coloured crystals, m. p. 185°; 2-iodo-2':4':6'-trinitrodiphenylamine, orange-coloured, rhombic needles, m. p. 206°; 3-iodo-2':4':6'-trinitrodiphenylamine, golden-yellow platelets, m. p. 150—152°; 4-iodo-2':4':6'-trinitrodiphenylamine, golden-yellow, fibrous aggregates, m. p. 196°; 2-chloro-2':4':6'-trinitrodiphenylamine, orange-coloured, rhombic crystals, m. p. 160—161°; 2-bromo-2':4':6'-trinitrodiphenylamine, small, orange-coloured, rhombic leaflets or needles, m. p. 187—189°; 2-methyl-2':4'-dinitrodiphenylamine, red, microcrystalline needles, m. p. 158—159°; 3-methyl-2':4':6'-trinitrodiphenylamine, carmine-red aggregates, m. p. 119°. H. W.

The Mutual Replacement of Ammonia and Aniline in Amino-derivatives of Triphenylmethane. PAVEL IVANOVITSCH PETRENKO-KRITSCHENKO and A. GANDELMAN (*J. Russ. Phys. Chem. Soc.*, 1917, **49**, 413—417).—Triphenylmethylaniline, $\text{NHPh}\cdot\text{CPh}_3$, is converted by heating in a sealed tube with alcoholic ammonia into triphenylmethylamine, which can be reconverted into the former substance by heating with excess of aniline. Triphenylmethylcarbinol cannot be an intermediate product in these reactions, as on similar treatment with ammonia or aniline these substances are not produced. Triphenylmethylaniline can be more easily converted into triphenylmethylamine by boiling with a solution in acetic acid of ammonium acetate. The reverse reaction does not, however, appear to take place. Triphenylmethylcarbinol, when treated in this way with ammonium or aniline acetate, gives fair yields of the corresponding amines. R. T.

Oxidations and Reductions Caused by Salts of Uranium under the Influence of Light. Antioxygen Action of Phenols. JULES ALOY and VALDIGUIÉ (*Compt. rend.*, 1923, **176**, 1229—1231).—Oxidations and reductions brought about by uranium compounds under the influence of light are closely related to the changes which the uranium salt itself undergoes. Thus when alcohol or dextrose is added to a 1% solution of uranium acetate, the former is oxidised and the latter reduced to the violet oxide, $\text{U}_3\text{O}_8\cdot 2\text{H}_2\text{O}$. If, in addition, methylene-blue is added to the above solution, the

dextrose is oxidised and the methylene-blue reduced, the uranium salt playing the rôle of an oxido-reducing catalyst. Aldehydes and the lower fatty alcohols can all be similarly oxidised, and the progress of the reaction can be followed by the reduction of the uranium acetate or of methylene-blue. The phenols, although readily oxidisable in ordinary circumstances, behave anomalously, owing to the antioxygen character of these substances, and they are neither oxidised themselves nor do they permit the oxidation of other substances to proceed. A red coloration is produced on adding the uranium compound to the phenol solution, but no other apparent change occurs. The solution does, however, contain a certain amount of uranous salt and the violet oxide can be precipitated from it by heating at 100°.


G. F. M.

Binary Systems of α - and β -Forms of Chloroacetic Acid with Phenols. IV. EFISIO MAMELI and GLAUCO COCCONI (*Gazzetta*, 1923, **53**, i, 149—158; cf. A., 1913, ii, 571).—With the various phenols examined, neither the α - nor β -form of chloroacetic acid forms additive compounds, the two acids behaving as acids of medium strength.

The fusion curve, and the position of the eutectic, for the systems phenol- β -chloroacetic acid and *o*-cresol- β -chloroacetic acid agree with those given by Kendall (A., 1916, i, 599) for the corresponding systems containing the α -form of the acid. Data are given also for the binary systems formed by each of these acids with *m*- and *p*-cresols, α - and β -naphthols, thymol, and guaiacol.

T. H. P.

Action of Organo-magnesium Compounds on Aminophenols. E. PUXEDDU (*Gazzetta*, 1923, **53**, i, 99—105).—The action of magnesium ethyl bromide on 3-amino-*p*-cresol or amino- β -naphthol differs from that on a compound containing an amino- or a phenolic group alone. In either case, gas is generated, two molecules of the Grignard reagent reacting with one molecule of the aminophenol, probably with formation of an additive compound, OH, MgEtBr

pound of the type  $\text{NH}_2, \text{MgEtBr}$. When treated with acetyl chloride, these products yield the corresponding diacetyl derivatives.

The acetyl derivative of 3-acetylamino-*p*-cresol, $\text{OAc} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{NHAc}$, forms crystals, m. p. 157°.

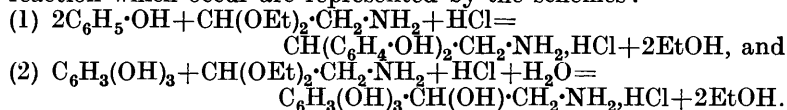
T. H. P.

Imino-aryl Ethers. II. The Thermal Decomposition of *N*-Arylaryliminoaryl Ether Hydrochlorides. ARTHUR WILLIAM CHAPMAN (T., 1923, **123**, 1150—1155).

Nitro-derivatives of *m*-Cresol. GEORGE PHILIP GIBSON (T., 1923, **123**, 1269—1277).

The Reaction of Aminoacetals with Phenols and Phenolic Ethers. O. HINSBERG (*Ber.*, 1923, **56**, [B], 852—857).—The introduction of the groups $-\text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_2$ or $\cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{NH}_2$ into the aromatic nucleus is of considerable importance in pharmacological chemistry. It can be effected by allowing aminoacetal or its *N*-alkylated substitution products to react with phenols

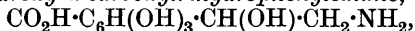
or phenolic ethers in the presence of hydrochloric or acetic and sulphuric acids as condensing agents. The two main types of reaction which occur are represented by the schemes :



The former reaction generally predominates with monohydroxy-, the latter with polyhydroxy-phenols, but its course can be altered in either case by suitable adjustment of the experimental conditions.

β -Amino- α -di-4-hydroxyphenylethane, $CH(C_6H_4 \cdot OH)_2 \cdot CH_2 \cdot NH_2$, is prepared by the action of concentrated hydrochloric acid at 100° on a mixture of aminoacetal and phenol. It crystallises in colourless needles, which are stable towards air, m. p. 105° ; the *hydrochloride*, a colourless, hygroscopic mass, and the *chloroplatinate*, brownish-yellow needles, are described. β -Amino- α -di-4-hydroxy-2-methyl-3-isopropylphenylethane, from aminoacetal and thymol, forms colourless needles, m. p. 220° ; it yields a *hydrochloride* (+ $2H_2O$), colourless needles. β -Amino- α -di-2-hydroxy-1-naphthylethane, colourless needles, m. p. 124° , and its *hydrochloride*, colourless needles, are described.

Methylaminoacetal reacts with two molecular proportions of pyrocatechol in the presence of concentrated hydrochloric acid at the atmospheric temperature to give β -methylamino- α -di-o-dihydroxyphenylethane, $(C_6H_3[OH]_2)_2CH \cdot CH_2 \cdot NHMe$, colourless needles, m. p. 143° , which yields a *hydrochloride*, colourless needles, sparingly soluble in hydrochloric acid. If, however, molecular proportions of methylaminoacetal and pyrocatechol are heated with hydrochloric acid and water in a sealed tube at 100° , r - β -methylamino- α -hydroxy- α -o-dihydroxyphenylethane, $(HO)_2C_6H_3 \cdot CH(OH) \cdot CH_2 \cdot NHMe$, is obtained; the free base is unstable when exposed to air, but yields a stable *hydrochloride* which is freely soluble in water. r - β -Amino- α -hydroxy- α -o-dihydroxyphenylethane is obtained as the *hydrochloride* from pyrocatechol and aminoacetal. Pyrogallol and aminoacetal yield the unstable r - β -amino- α -hydroxy- α -tri-hydroxyphenylethane (the *hydrochloride* crystallises in colourless needles). r - β -Amino- α -hydroxy- α -carboxytrihydroxyphenylethane,



is isolated as the *hydrochloride* from the product of the action of gallic acid on aminoacetal.

β -Amino- α -diphenylethane, which could not be obtained in the crystalline condition, is the main product of the action of aminoacetal on phenetole in the presence of sulphuric and acetic acids. β -Methylamino- α -bis-o-dimethoxyphenylethane is non-crystalline; it gives a *hydrochloride*, small, colourless needles, m. p. 102° . β -Amino- α -hydroxy- α -trimethoxyphenylethane, from aminoacetal and pyrogallol trimethyl ether, gives a *hydrochloride*, colourless crystals, m. p. 187° , and a *chloroplatinate*, pale yellow plates. β -Amino- α -bistrimethoxyphenylethane *hydrochloride* forms large, colourless crystals, m. p. 199° ; the free base has little tendency towards crystallisation.

H. W.

Catalytic Ammonolysis of β -Naphthol and Chlorobenzene in the State of Vapour. A. M. HOWARD and ALEXANDER LOWY (*J. Ind. Eng. Chem.*, 1923, 15, 397—401).— β -Naphthol and chlorobenzene vapours mixed with ammonia were passed at definite temperatures over various contact materials. For β -naphthol, alumina was the best catalyst, and yields of 90—95% of β -naphthylamine were obtained under suitable conditions. The activity of the catalyst increased very rapidly from 400° to an optimum temperature range of 430—450°, and the best yields of the primary amine were obtained when the β -naphthol was heated at 191—193° in the vapour of boiling dimethylaniline, and a slow stream of ammonia gas was bubbled through. If the rate of flow of the vapour mixture was too great, equilibrium was not attained during its passage over the catalyst, and lower yields resulted. Using pure ammonia, the catalyst did not depreciate materially in activity during a run of sixteen hours' duration. About 5% of $\beta\beta$ -dinaphthylamine was obtained as a by-product. Experiments were conducted with titania and thoria as catalysts, but the results were inferior to the above. In the experiments with chlorobenzene, some conversion to aniline was effected with reduced nickel or iron catalysts at 380° and 450°, respectively, but the catalysts were soon poisoned, and the original yields of about 7% rapidly fell off to mere traces. Reduced cobalt, copper, and platinum black gave still less satisfactory results. G. F. M.

Boric Acid Compounds of some Organic Substances containing more than One Hydroxyl Group. Boron as a Quinquevalent Element. P. H. HERMANS (*Proc. K. Akad. Wetensch. Amsterdam*, 1923, 26, 32—42).—By the action of boric acid on $\beta\delta$ -dimethylpentane- $\beta\delta$ -diol, a compound is obtained which crystallises with great facility, m. p. 100—102°, and must have the formula $\text{CH}_2\langle\begin{smallmatrix} \text{CMe}_2\cdot\text{O} \\ \text{CMe}_2\cdot\text{O} \end{smallmatrix}\rangle\text{B}\cdot\text{OH}$. It has a saffron-like odour, and is a weak acid no stronger than boric acid. It was supposed from the latter observation that the strong acids which are formed by addition of many polyhydroxy-compounds to boric acid solutions must have a different constitution from the above compound. In confirmation of this view, weakly acidic boric acid compounds similar to the above were obtained from $\beta\delta$ -dimethylhexane- $\beta\delta$ -diol and pinacone. Evidence of the formation of compounds with trimethylene glycol, ordinary glycol, and *cis*-cyclohexane-1 : 2-diol was also obtained, but the compounds could not be crystallised. All these compounds appear to be partly split up into their components in aqueous solution. In the case of the *cis*-cyclohexane-1 : 2-diol boric acid compound, a crystalline potassium salt was obtained. This has an alkaline reaction and the potassium can be titrated quantitatively in presence of methyl-orange. A dipotassium derivative of this compound was also obtained. Crystalline potassium salts of the boric acid compounds of *cis*-hydrindene-1 : 2-diol, *cis*-cyclopentane-1 : 2-diol, *cis*-tetrahydronaphthalene-1 : 2-diol, and -2 : 3-diols were also obtained, but they could not always be obtained free from potassium hydroxide on account of their high

solubility in water and in alcohol. These compounds provide a method for separating *cis*- from *trans*-cyclic-1 : 2-diols, as the latter do not give such compounds.

The crystalline potassium salt of pyrocatecholboric acid prepared by Böeseken, Haeften, and Obreen (A., 1918, i, 219) has been analysed again, as its composition was uncertain. It is now found to be $C_{12}H_8O_4BK$ and the only plausible structure is $\left[C_6H_4 \begin{smallmatrix} \text{O} \\ < > \\ \text{O} \end{smallmatrix} \right]_2 BK$.

The boron is here quinquevalent or, from another point of view, has the co-ordination number four. Although this salt has an alkaline reaction, the potassium cannot be titrated quantitatively; pyrocatecholboric acid is therefore a stronger acid than the other diol compounds described above. It is probable that other complex acids stronger than boric acid have a structure similar to that proposed for pyrocatecholboric acid. Free *pyrocatecholboric acid* can be obtained by heating the aniline salt in a vacuum, and can be purified by sublimation in a vacuum at 200° .

The boric acid compound of *cis*-cycloheptane-1 : 2-diol (cf. Derx, A., 1922, i, 651) forms an oil with a saturated solution of boric acid. On addition of aniline to the oil, it crystallises, forming an unstable aniline salt, $C_{20}H_{36}O_4NB$. This appears to be *aniline di-cis-cycloheptane-1 : 2-diolborate*. Scheibe's potassium borodicitrate and Jahn's zinc borodisalicylate are also probably derivatives of quinquevalent boron. The structure of these compounds is further discussed by Böeseken (this vol., ii, 406). E. H. R.

Ethylene and Trimethylene Ethers of Dihydroxybenzenes.

I. MORITZ KOHN and FRANZ WILHELM (*Monatsh.*, 1923, **43**, 545—555).—Molecular amounts of ethylene bromide and aqueous potassium hydroxide when refluxed with a large excess of resorcinol yield *diresorcinol ethylene ether*, $C_2H_4(O \cdot C_6H_4 \cdot OH)_2$, in fair yield as colourless, thin needles, m. p. 163° ; the *benzoyl* derivative has m. p. 115 — 116° . With methyl sulphate and potassium hydroxide the *dimethyl ether*, $C_2H_4(O \cdot C_6H_4 \cdot OMe)_2$, m. p. 61 — 63° , is formed, which is identical with the product obtained from resorcinol monomethyl ether and ethylene bromide in presence of sodium ethoxide. In a similar manner, trimethylene bromide refluxed with aqueous potassium hydroxide and resorcinol in large excess yields *diresorcinol trimethylene ether*, $C_3H_6(O \cdot C_6H_4 \cdot OH)_2$, long needles, m. p. 118° ; *benzoyl* derivative, m. p. 97 — 98° . With methyl sulphate and potassium hydroxide it yields the dimethyl ether, $C_3H_6(O \cdot C_6H_4 \cdot OMe)_2$, m. p. 39 — 41° , identical with the product from resorcinol monomethyl ether and trimethylene bromide in presence of sodium ethoxide. Ethylene bromide and aqueous potassium hydroxide refluxed with a large excess of pyrocatechol yield, however, only the cyclic ethylene ether, $C_6H_4 \cdot O_2 \cdot C_2H_4$, previously obtained by Vorländer (A., 1895, i, 17), and not the unknown bisdipyrocatechol trimethylene ether. Using trimethylene bromide, however, *dipyrocatechol trimethylene ether* is readily obtained in rhombic needles [*a* : *b* : *c* = 0.5047 : 1.06178], m. p. 123 — 125° , benzoyl derivative, m. p. 91 — 93° . On methylation, it yields a dimethyl ether identical with Gattermann's diguaiacol-trimethylene ether, obtained from

guaiacol and trimethylene bromide in presence of sodium ethoxide, m. p. 107—109° (111—112° ?) (A., 1908, i, 35).

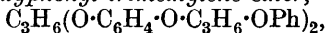
Quinol in large excess when refluxed with aqueous alkali hydr-oxide and ethylene dibromide or trimethylene dibromide yields, respectively, Vorländer's diquinol ethylene ether and the new substance, *diquinol trimethylene ether*, m. p., respectively, 222—224° (Vorländer 219—220°), and 142—144°. The *ethylene* derivative forms a *dimethyl ether*, m. p. 148—150°, and a *benzoyl* derivative, m. p. 186°; the *trimethylene* derivative forms a *dimethyl ether*, m. p. 84—85°, and a *benzoyl* derivative, m. p. 138—139°. The methyl ethers are identical with the products obtained from quinol monomethyl ether and ethylene dibromide or trimethylene bromide, respectively, in presence of sodium ethoxide. F. A. M.

Ethylene and Trimethylene Ethers of the Dihydroxy-benzenes. II. MORITZ KOHN and LEOPOLD SAFRIN (*Monatsh.*, 1923, 49, 557—568; cf. preceding abstract).—*Phenyl o-hydroxyphenyl ethylene ether*, $\text{OPh}\cdot\text{C}_2\text{H}_4\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, is obtained on refluxing β -bromophenetole with a large excess of pyrocatechol and a little water, and adding the calculated amount of aqueous potassium hydroxide during half an hour; it forms crystals, m. p. 86·5°. Methylation by means of methyl sulphate yields the corresponding *phenyl o-anisyl ethylene ether*, $\text{OPh}\cdot\text{C}_2\text{H}_4\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$, long needles, m. p. 86—87°, which is identical with the product formed from guaiacol and β -bromophenetole in presence of sodium ethoxide. The *benzoyl* derivative, $\text{OPh}\cdot\text{C}_2\text{H}_4\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{OBz}$, forms colourless prisms, m. p. 60—61°.

On treatment of the original phenyl *o*-hydroxyphenyl ethylene ether with a further molecule of β -bromophenetole in presence of sodium ethoxide, the substance *pyrocatechol bisphenoxyethyl ether* is formed, $\text{C}_6\text{H}_4(\text{O}\cdot\text{C}_2\text{H}_4\cdot\text{OPh})_2$, forming platelets, m. p. 116—117°. The action of ethylene bromide on phenyl *o*-hydroxyphenyl ethylene ether in presence of sodium ethoxide yields the *bis- β -phenoxy-o-ethoxyphenyl ethylene ether*, $[\text{OPh}\cdot\text{C}_2\text{H}_4\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{O}]_2\text{C}_2\text{H}_4$, short, thin needles, m. p. 106—107°; if trimethylene bromide is used in place of ethylene bromide, the product is the *trimethylene bis- β -phenoxy-o-ethoxyphenyl ether*, $[\text{OPh}\cdot\text{C}_2\text{H}_4\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{O}]_2\text{C}_3\text{H}_6$, needles, m. p. 91°; the latter substance is also formed by the action of β -bromophenetole on dipyrocatechol trimethylene ether in presence of sodium ethoxide.

By refluxing phenyl γ -bromopropyl ether with a large excess of pyrocatechol in presence of a little water and the calculated quantity of potassium hydroxide, there is formed *phenyl o-hydroxyphenyl trimethylene ether*, $\text{OPh}\cdot\text{C}_3\text{H}_6\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, thick prisms, m. p. 56—57°; the *methoxy-ether* has m. p. 55—56°; the *benzoyl* derivative, needles, m. p. 60—61°. It reacts with a second molecule of phenyl γ -bromopropyl ether in presence of sodium ethoxide to form *pyrocatechol bisphenoxypropyl ether*, $\text{C}_6\text{H}_4(\text{O}\cdot\text{C}_3\text{H}_6\cdot\text{OPh})_2$, needles, m. p. 51°; or using β -bromophenetole in place of phenyl γ -bromopropyl ether, the product is *pyrocatechol β -phenoxyethyl γ -phenoxypropyl ether*, $\text{OPh}\cdot\text{C}_2\text{H}_4\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{C}_3\text{H}_6\cdot\text{OPh}$, prisms, m. p. 66·5—67·5°; the latter substance is also obtained by the converse

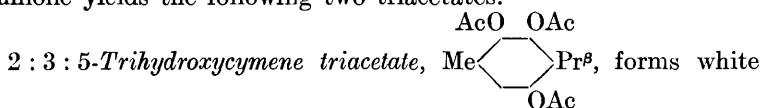
method from phenyl *o*-hydroxyphenyl ethylene ether and phenyl γ -bromopropyl ether. Two molecules of phenyl *o*-hydroxyphenyl trimethylene ether may be united by means of ethylene dibromide or trimethylene dibromide in presence of sodium ethoxide to yield, respectively, the substances *bis*- γ -phenoxy-*o*-propoxyphenyl ethylene ether, $C_2H_4(O \cdot C_6H_4 \cdot O \cdot C_3H_6 \cdot OPh)_2$, needles, m. p. 102—103°, and *bis*- γ -phenoxy-*o*-propoxyphenyl trimethylene ether,



needles, m. p. 61—62°. The latter product is also formed from two molecules of phenyl γ -bromopropyl ether and one molecule of pyrocatechol trimethylene ether in presence of sodium ethoxide.

F. A. M.

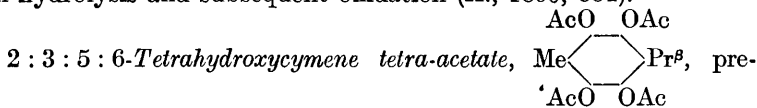
Investigations on Phenols Derived from Cymene. G. BARGELLINI (*Atti R. Accad. Lincei*, 1923, [v], 32, i, 231—235).—Thiele (A., 1898, i, 469) has shown that a new hydroxyl group may be introduced into the molecule of a quinol by treating the corresponding quinone with acetic anhydride in presence of a small amount of sulphuric acid. Application of this reaction to thymoquinone yields the following two triacetates.



crystals, m. p. 135—137°, and, on hydrolysis and subsequent oxidation, gives the 3-hydroxythymoquinone described by Mazzara (A., 1891, 297).



in white needles, m. p. 83—85°, and yields 6-hydroxythymoquinone on hydrolysis and subsequent oxidation (A., 1890, 884).



When dihydroxythymoquinone is reduced in alcoholic solution by means of hydrogen in presence of platinum black, the red solution absorbs hydrogen and is completely decolorised, but in contact with the air it rapidly reddens, the tetrahydroxycymene probably formed undergoing oxidation to the original dihydroxythymoquinone (cf. Henderson and Boyd, T., 1910, 97, 1663).

T. H. P.

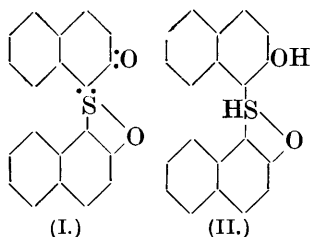
Photo-sensitiveness of certain Urethanes. A. KORCZYNSKI (*Gazzetta*, 1923, 53, i, 94—99).—Urethanes have been prepared by the action of diphenylcarbamide chloride on the following phenols : *p*-chloro-, bromo-, and iodo-phenols, *o*- and *p*-nitrophenols, 4-chloro-

and 4-bromo-2-nitrophenols, 4:6-dibromo- and 4:6-di-iodo-2-nitrophenols, 4-chloro-6-bromo-2-nitrophenol, 2:6-dichloro-4-nitrophenol, and 2:4:6-trichlorophenol. Photo-sensitiveness is shown by the compounds obtained from the halogenated nitrophenols with an ortho-nitro-group and a para-halogen atom, but not by those obtained from the halogenated or nitro-phenols; in the former case, introduction of a second halogen atom in the second ortho-position leaves the photo-sensitiveness unchanged. The photochemical change occurring in these compounds is more destructive than the similar phenomenon observed, for instance, with *o*-nitrobenzaldehyde (Ciamician and Silber, A., 1901, i, 390, 547; 1902, i, 434), since the nitroso-compound cannot be isolated; no marked change occurs, however, in the diphenylaminic portion of the molecule. The fact that the condensation of 2:4-dinitrophenol or of picric acid with diphenylcarbamide chloride yields, not the corresponding carbamic ester, but a non-homogeneous, resinous mass, is explainable by the occurrence of a photochemical reaction.

[With ST. GRZYBOWSKI.]—4-Chlorophenyl N-diphenylcarbamate, $C_6H_4Cl \cdot O \cdot CO \cdot NPh_2$, forms colourless needles, m. p. 97° ; the 4-bromophenyl ester, colourless needles, m. p. 99° ; the 4-iodophenyl ester, m. p. $126-127^\circ$; the 2:4:6-trichlorophenyl ester, colourless needles, m. p. 143° ; the 2-nitrophenyl ester, colourless crystals, m. p. $108-109^\circ$; the 4-nitrophenyl ester, colourless needles, m. p. 112° ; the 2:6-dichloro-4-nitrophenyl ester, colourless needles, m. p. 132° ; the 4-chloro-2-nitrophenyl ester, m. p. $124-125^\circ$, is photo-sensitive; the 4-chloro-6-bromo-2-nitrophenyl ester, m. p. 140° , is photo-sensitive; the 4:6-dibromo-2-nitrophenyl ester, m. p. 139° , is photo-sensitive; the 4:6-di-iodo-2-nitrophenyl ester, m. p. $174-175^\circ$; the 4-bromo-2-nitrophenyl ester forms lustrous, colourless needles, m. p. $129-130^\circ$, and is photo-sensitive, both in the crystalline condition and in solution in neutral solvents such as benzene, toluene, ethyl or amyl alcohol, and also in absence of oxygen. T. H. P.

The Isomerism of β -Naphthol Sulphide and the Analogous Isomerism of Aromatic *o*-Hydroxysulphides.

RUDOLF LESSER and GEORG GAD (*Ber.*, 1923, 56, [B], 963-978).—The isomerism of β -naphthol sulphides has been examined in detail by Smiles and his co-workers (T., 1911, 99, 973; 1912, 101, 710; 1146, 1420; 1913, 103, 340, 901; 1914, 105, 1396, 1739, 1744), and by Hinsberg (A., 1915, i, 237, 808; 1916, i, 723). The former



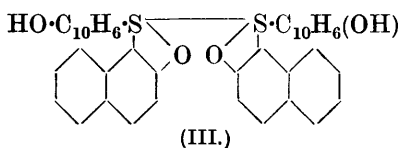
the naphthalene nuclei, the latter that it is caused by the structure of the sulphur atom itself. It is now shown, however, that the isomerism is not of an abnormal type, since if the constitution (I) assigned by Hinsberg to the dehydrosulphide is adopted it is readily possible that this may pass on reduction into the compound II without rupture of the "thionylum" ring (the term is applied by the authors to the structure,

$-\text{CH} \begin{smallmatrix} \nearrow \text{S} \\ \searrow \text{CH} \end{smallmatrix} \text{O}$). This constitution is in complete harmony with the behaviour of the *isosulphide*. The ability to form dehydro-compounds, and hence also *isosulphides*, is not restricted to naphthalene derivatives, but is common to aromatic *o*-hydroxy-sulphides which have a substituent in the para-position to the hydroxy-group and a tertiary carbon atom in the ortho-position to the sulphur atom.

During the course of the work it has been frequently necessary to chlorinate phenols in order to introduce a substituent into the para-position. This has been effected by sulphuryl chloride, but it has been observed that reaction does not occur, at any rate under the usual conditions, if the phenol contains a negative substituent in the ortho-position to the hydroxy-group as in *o*-chlorophenol, *o*-nitrophenol, salol, *o*-hydroxydiphenyl, *o*-chloro-*s*-m-xyleneol. The general assumption that sulphuryl chloride only chlorinates phenols in the para-position is shown to be incorrect, since ortho-derivatives are simultaneously produced in varying amounts. The chlorides of sulphur do not react with phenols which contain a negative substituent in the ortho-position to the hydroxy-group and a substituent in the para-position such as dichloro-*s*-m-xyleneol, *p*-chloro-*o*-nitrophenol, *o*-chloro-*p*-nitrophenol, and *o*-nitro-*p*-cresol.

With regard to the nomenclature of the group, the authors propose to retain the terms "dehydrosulphide" and "*isosulphide*," and to distinguish between the dehydro-compounds which contain a single and double thionylum ring by appending in brackets the expressions "quinoid form" (as in formula I) and "spiran form" (as in formula IV).

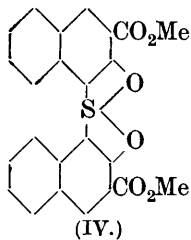
β -Naphthol sulphide, its dihydro-compound, and the *isosulphide* are prepared in the usual manner. The latter is oxidised by iodine to diiso- β -naphthol sulphide (annexed formula III), m. p. 141—142°, which is identical with the compound obtained by Hinsberg by the action of hydrogen peroxide on the *iso*-sulphide. It is converted by



benzoyl chloride and sodium hydroxide into the corresponding *dibenzoate*, yellow platelets ($+\text{C}_6\text{H}_6$), m. p. 202—203°, which is reduced by zinc dust and hydrochloric acid to *o*-mono-benzoyliso- β -naphthol sulphide, pale yellow prisms, m. p. 111—112°, which is reconverted by iodine into the parent dibenzoate. The isomeric *S*-monobenzoyliso- β -naphthol sulphide, pale yellow platelets, m. p. 181°, is prepared from the *isosulphide* and benzoyl chloride in the presence of pyridine, and is converted into *dibenzoyliso*- β -naphthol sulphide, colourless platelets, m. p. 179—180°, which is also obtained from the *O*-benzoyl compound or from the *isosulphide* itself. *Monobenzoyl*- β -naphthol sulphide crystallises in colourless, lustrous platelets, m. p. 190°, whereas the corresponding *p*-bromo-benzoyl derivative forms small, colourless needles, m. p. 195°.

6-Bromo-2-naphthol sulphide, long, colourless needles, m. p. 245—246°, is prepared by the action of sulphur chloride on 6-bromo- β -naphthol suspended in carbon disulphide. The corresponding *dibenzoyl* compound crystallises in colourless, felted needles, m. p. 270°. The sulphide is oxidised by potassium ferricyanide in alkaline solution to *dehydro-6-bromo-2-naphthol sulphide* (*quinoid form*), ruby-red, cubic crystals, m. p. 176—177° [*mono-p-nitro-phenylhydrazone*, orange-yellow needles, m. p. 254° (decomp.)], which is reduced by zinc dust in the presence of benzene and hydrochloric acid to *iso-6-bromo-2-naphthol sulphide*, pale yellow platelets, m. p. 156—157° (*dibenzoyl* derivative, small, colourless needles, m. p. 184—185°).

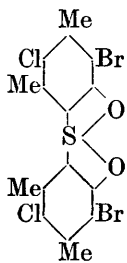
Methyl 2-hydroxynaphthalene-3-carboxylate 1-sulphide forms lemon-yellow crystals, m. p. 227—228° (*dibenzoate*, colourless platelets, m. p. 231—232°); it is oxidised by bromine to the *dehydro*-compound (*spiran form*) (annexed formula IV), dark red crystals, m. p. 245—246°, which is reduced by zinc dust and hydrochloric acid in the presence of benzene to *methyl iso-2-hydroxynaphthalene-3-carboxylate-1-sulphide*, yellow crystals, m. p. 227—228°, which appears to pass below its melting point into the normal sulphide; the corresponding *dibenzoyl* derivative forms yellow crystals, m. p. 176°.



s-m-Xylenol, dissolved in chloroform, is converted by the theoretically necessary amount of sulphuryl chloride into a mixture of 2-chloro-*s-m-xylenol*, long, colourless prisms, m. p. 115—116°, and minor quantities of 6-chloro-*s-m-xylenol*, colourless needles, m. p. 49—50°; an excess of the reagent produces *dichloro-s-m-xylenol*, m. p. 95—96°. The *p*-chloro-derivative is converted by sulphur chloride in the presence of chloroform into 2-chloro-*s-m-xylenol 4-sulphide*, small, colourless needles, m. p. 214—215°, which

is transformed successively by bromine in the presence of alkali hydroxide into 2-chloro-6-bromo-*s-m-xylenol 4-sulphide*, colourless, lustrous needles, m. p. 215—216°, and *dehydro-2-chloro-6-bromo-s-m-xylenol sulphide* (*spiran form*) (annexed formula), coarse, dark red crystals, m. p. 195° (the mother-liquors from the crystals contain 2-chloro-4:6-dibromo-*s-m-xylenol*, long, asbestos-like needles, m. p. 158°). The *dehydro*-compound is converted by zinc dust and hydrochloric acid in the presence of benzene into *iso-2-chloro-6-bromo-s-m-xylenol 4-sulphide*, pale yellow prisms, m. p. 177°, which is oxidised smoothly by iodine in the presence of sodium hydrogen carbonate solution to *däiso-2-chloro-6-bromo-s-m-xylenol sulphide*, pale yellow, cubic crystals, m. p. 127° (decomp.).

p-Xylenol is converted by sulphuryl chloride in the presence of chloroform into *chloro-p-xylenol*, needles, m. p. 74—75°, after previous softening, which is transformed by sulphur chloride into *chloro-p-xylenol sulphide*, colourless needles, m. p. 180—181°. *Chlorothymol sulphide*, [S : OH : C₃H₇ : Cl : Me = 2 : 3 : 4 : 6 : 1], forms

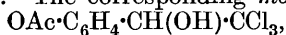


large, glassy crystals, m. p. 110—111°. *ψ-Cumenol sulphide* crystallises in colourless, lustrous needles, m. p. 127—128°. The sulphides described in this paragraph are oxidisable to coloured dehydro-compounds.

The following phenolic sulphides do not contain a substituent in the ortho-position to the sulphur atom and do not yield dehydro-compounds: *m-Xylenol sulphide*, almost colourless prisms, m. p. 96—98°; *6-chloro-m-cresol sulphide*, colourless, lustrous needles, m. p. 180—181°. H. W.

Aldol Condensation between Chloral and Phenols. H. PAULY and HEINRICH SCHANZ (*Ber.*, 1923, 56, [B], 979—985).—Aldol condensations between aldehydes and phenols have only been observed previously between exceptionally reactive members of these classes of compounds. The type of change, however, appears to be general, since chloral is found to react in this manner with a number of phenols. The phenolic hydroxy-group remains intact in the new compounds.

Chloral hydrate and phenol are melted together, and so much powdered potassium carbonate is added to the mixture that litmus paper is just turned blue, after which it is preserved for six weeks at the atmospheric temperature, during which time *4-hydroxyphenyltrichloromethylcarbinol*, $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OH})\cdot\text{CCl}_3$, needles, m. p. 87°, slowly separates. The corresponding *monoacetate*,



crystallises in needles, m. p. 173°. The constitution of the condensation product is deduced from the observation that it is converted by phenol in the presence of glacial acetic and concentrated sulphuric acids into the previously described $\beta\beta\beta$ -trichloro- $\alpha\alpha$ -bis-*p*-hydroxyphenylethane, m. p. 202°. Under similar conditions, *p*-cresol gives *p*-tolyltrichloromethylcarbinol, colourless needles, m. p. 147—148°, and guaiacol yields *4-hydroxy-3-methoxyphenyltrichloromethylcarbinol*, colourless needles, m. p. 118—119° (*monoacetate*, slender needles, m. p. 124°). The constitution assigned to the latter substance is deduced from its conversion into vanillin. *Trichlorodiguaiacylthane* is prepared from the guaiacolcarbinol and guaiacol or from chloral and guaiacol in the presence of glacial acetic and concentrated sulphuric acids; it is non-crystalline and does not exhibit a definite melting point. It separates from carbon tetrachloride in colourless needles (+1CCl₄), m. p. 98°, and from chloroform (+1CHCl₃) in slender needles. It is converted by reduction with zinc dust into *4:4'-dihydroxy-3:3'-dimethoxystilbene* (?), slender needles, m. p. 200°. Pyrocatechol and chloral yield *2:3*-(or *3:4*)-*dihydroxyphenyltrichloromethylcarbinol*, small, colourless needles, m. p. 128—129°, whereas resorcinol and chloral hydrate give *2:4*-*dihydroxyphenyltrichloromethylcarbinol*, colourless needles, m. p. 176°. H. W.

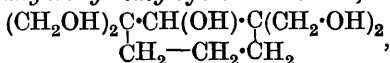
The Action of Magnesium on a Mixture of Bromoallene with Cuminol. K. VOLKOV (*J. Russ. Phys. Chem. Soc.*, 1917, 49, 259—263).—*Cumylallylcarbinol*, $\text{C}_6\text{H}_4\text{Pr}^\beta\cdot\text{CH}(\text{C}_3\text{H}_5)\cdot\text{OH}$, b. p.

140°/17.5 mm., d_4^{25} 0.9470, n_D^{25} 1.51385, is prepared by the addition of magnesium to a mixture of cuminaldehyde, $C_6H_4Pr^{\beta}\cdot CHO$, and α -bromoallene. The carbinol on oxidation with potassium permanganate yields a mixture of β -hydroxy- β -cumylpropionic and *p*-isopropylcinnamic acids.

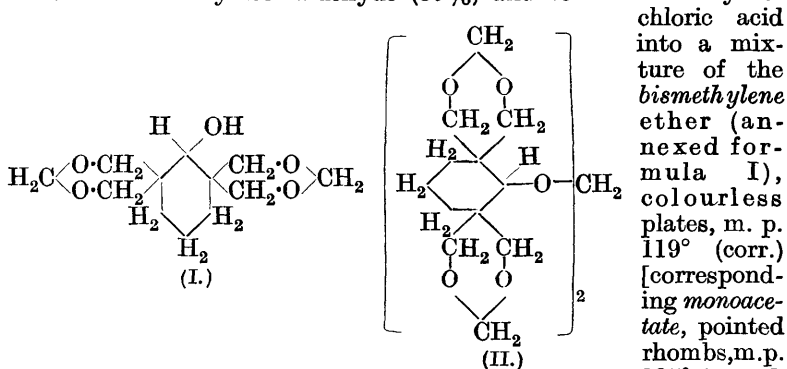
R. T.

Synthesis of Keto-alcohols and Polyhydroxy-alcohols from Cyclic Ketones and Formaldehyde. C. MANNICH and W. BROSE (*Ber.*, 1923, 56, [B], 833—844).—Tollens's method for the production of polyhydroxy-alcohols by the action of an excess of formaldehyde on aliphatic aldehydes and ketones in the presence of milk of lime has been extended to cyclic ketones, including *cyclohexanone*, *o*- and *p*-methyl*cyclohexanones*, *cyclopentanone*, menthone, carvone, and camphor. With the three substances last mentioned, a condensation could not be effected. In the case of *cyclohexanone* and its *o*- and *p*-methyl derivatives, the action follows the expected course, two hydroxymethyl groups being introduced at each carbon atom vicinal to the ketonic group and the latter suffering reduction to the secondary alcoholic group when excess of formaldehyde is employed. When smaller quantities of the latter are taken it is possible to control the action in such a manner that keto-alcohols are produced. With *cyclopentanone*, on the other hand, the reaction follows a rather different course, yielding either condensation products of high molecular weight or a tetrahydroxy-keto-alcohol according to the proportion of formaldehyde employed.

2 : 2 : 6 : 6-Tetrahydroxymethylcyclohexane-1-ol,



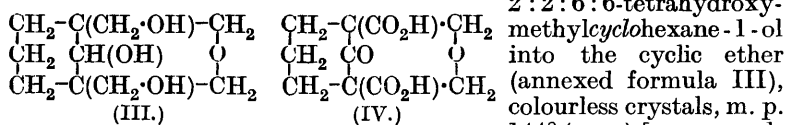
colourless, quadratic plates, m. p. 131° (corr.), is prepared by allowing a homogeneous mixture of *cyclohexanone*, formaldehyde, and water to remain in contact with slaked lime at 30° during several days. It gives a *penta-acetate*, needles, m. p. 75° (corr.). It is converted by formaldehyde (30%) and concentrated hydro-



and the *compound* (annexed formula II), colourless, lustrous leaflets,

x*

m. p. 242° (corr.). Hydrogen chloride at 150—160° converts



ing triacetate, colourless plates, m. p. 72° (corr.)], which is oxidised by concentrated nitric acid to the dicarboxylic *keto-acid* (annexed formula IV), colourless needles, m. p. 218° (corr.). The latter substance is converted by phenylhydrazine into the *compound*, $\text{C}_{16}\text{H}_{16}\text{O}_4\text{N}_2$, small, colourless needles, m. p. 251° (corr.).

*cyclo*Hexanone is converted by four molecular proportions of formaldehyde into 2 : 2 : 6 : 6-tetrahydroxymethylcyclohexane-1-one, colourless, four-sided, double pyramids, m. p. 143° (corr.) [corresponding *tetra-acetate*, colourless prisms, m. p. 140° (corr.)]. The presence of the ketonic group cannot be established directly, since the compound could not be caused to react with phenylhydrazine, semicarbazide, or hydroxylamine, and the possibility of a cyclic structure is therefore not excluded. Indirectly, however, this can be effected, since the corresponding *bismethylene ether*, colourless prisms, m. p. 150° (corr.), is reduced by alcohol and a large excess of sodium to the bismethylene ether of tetrahydroxymethylcyclohexanol which is identical with the product (formula I) described above. The *bisbenzylidene ether* of 2 : 2 : 6 : 6-tetrahydroxymethylcyclohexane-1-one, long, colourless needles, m. p. 230·5° (corr.), is readily prepared from the parent substance, benzaldehyde, and hydrochloric acid and is resolved into its components by treatment with boiling mineral acid.

2-Hydroxymethylcyclohexane-1-one is prepared from equimolecular proportions of *cyclo*hexanone and formaldehyde. It is a colourless liquid, b. p. 114—115°/16 mm., which is sensitive towards both acids and alkalis. It gives a *monoacetate*, a colourless liquid, b. p. 134—136°/15 mm. (prepared by the aid of acetyl chloride in the presence of pyridine), and a *phenylhydrazone*, small, colourless prisms, m. p. 129°.

p-Methylcyclohexanone and formaldehyde (5·5 molecular proportions) give 4-methyl-2 : 2 : 6 : 6-tetrahydroxymethylcyclohexane-1-ol, small, colourless needles, m. p. 150° (corr.), which is further characterised by its conversion by acetic anhydride and sodium acetate into the *penta-acetate*, leaflets, m. p. 139° (corr.).

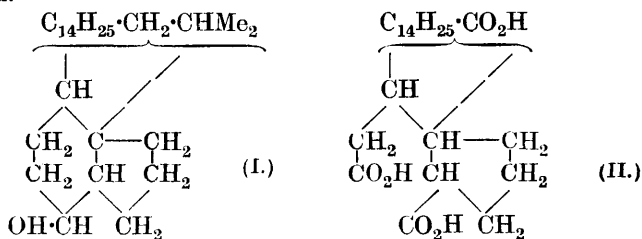
The product obtained by the similar condensation of *o*-methylcyclohexanone with formaldehyde could not be caused to crystallise, and was therefore treated with benzaldehyde and concentrated hydrochloric acid, whereby the *bisbenzylidene ether* of 2-methyl-2 : 6 : 6-trihydroxymethylcyclohexane-1-ol was obtained in colourless prisms, m. p. 133° (corr.). Treatment of the ether with hot aqueous hydrochloric acid leads to the production of 2-methyl-2 : 6 : 6-trihydroxymethylcyclohexane-1-ol, short, colourless prisms, m. p. 100° (corr.).

Treatment of *cyclopentanone* with a large excess of formaldehyde

and slaked lime causes the slow formation of insoluble, amorphous condensation products. With 4—6 molecular proportions of aldehyde and moderate quantities of slaked lime, 2 : 2 : 5 : 5-*tetrahydroxymethylcyclopentane-1-one*, colourless plates, m. p. 143° (corr.), is produced. The presence of four hydroxy-groups is established by the isolation of a *tetrabenzooate*, colourless needles, m. p. 144° (corr.). The compound, however, does not appear to react with phenylhydrazine, semicarbazide, hydroxylamine, or hydrogen cyanide; attempts to reduce it to the corresponding secondary alcohol were unsuccessful. It yields a *bismethylene ether*, m. p. 182° (corr.), and a *bisbenzylidene ether*, long, colourless needles, m. p. 206·5° (corr.). The bismethylene ether is reduced by sodium and boiling alcohol to the *bismethylene ether* of 2 : 2 : 5 : 5-*tetrahydroxymethylcyclopentane-1-ol*, colourless plates, m. p. 81° (corr.), which gives a *monoacetate*, prisms, m. p. 106° (corr.).

H. W.

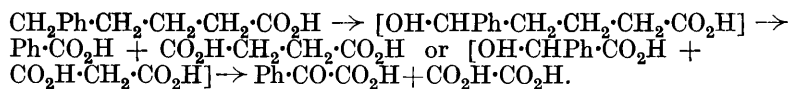
Conversion of Coprosterol into *iso*Lithobilianic Acid. A. WINDAUS and TH. RIEMANN (*Z. physiol. Chem.*, 1923, **126**, 277—280).—Coprosterol, (I), when oxidised yields an acid, $C_{27}H_{46}O_4$. It is now shown that this acid on further oxidation yields *iso*-lithobilianic acid, (II), m. p. 262° (dimethyl ester, m. p. 204°), and the constitution assigned to these substances has thus been confirmed.



W. O. K.

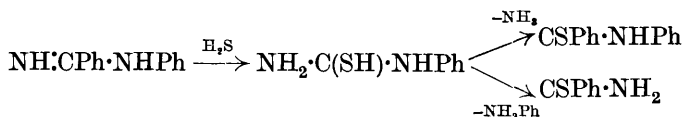
The Oxidising Action of Alkaline Potassium Permanganate on Normal Phenyl-fatty Acids. EUGENI STEPANOVITSCH PRSHEVALSKI (*J. Russ. Phys. Chem. Soc.*, 1917—1918, **49**, 567—572).—The oxidation of phenylated fatty acids in the animal organism has been shown by Dakin (A., 1908, ii, 964; 1910, ii, 795) and by Knoop (A., 1905, ii, 46) to take place at the β -carbon atom. It is now shown that hot alkaline permanganate in all cases attacks the carbon atom next to the phenyl group, a hydroxyl group being introduced; this may then be further oxidised to a keto- and finally to a carboxyl-group, forming benzoic acid; the remainder of the side-chain is oxidised to carbon dioxide or a dibasic acid. On the other hand, after the entrance of the first hydroxyl group into the molecule, the next carbon atom may be attacked and oxidised to carboxyl, forming a hydroxy- or keto-acid (mandelic or phenylglyoxylic acid), the remainder of the side-chain being oxidised to carbon dioxide or a dibasic acid. Thus, phenylacetic

acid yields benzoic and phenylglyoxylic acids; phenylpropionic acid gives mainly mandelic acid, also some benzoic and oxalic acid; the latter are the main products from phenylbutyric acid, in addition to some phenylglyoxylic acid; phenylvaleric acid gives the same three products in addition to succinic acid. The oxidation of phenylvaleric acid is thus an illustration of both the suggested processes :

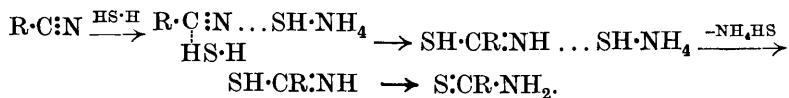


G. A. R. K.

The Mechanism of Chemical Reactions. I. Reduction of Amides and Oxidation of Amines. KARL KINDLER [and, in part, F. BURGHARD, F. FINNDORF, W. DEHN, O. GIESE, and P. KÖRDING] (*Annalen*, 1923, **431**, 187—230).—It is already known that the addition of hydrogen sulphide to a nitrile group which is not attached to a negative residue (Ph or CN) cannot be effected unless ammonium hydrogen sulphide is present (Bernthsen, A., 1877, i, 616). This is not due to the intermediate production of an amidine : $\text{R}\cdot\text{C}\cdot\text{N} \xrightarrow{+\text{NH}_3} \text{NH}\cdot\text{CR}\cdot\text{NH}_2 \xrightarrow{\text{H}_2\text{S}} \text{NH}_3 + \text{S}\cdot\text{CR}\cdot\text{NH}_2$, because the action of alcoholic hydrogen sulphide, saturated at -10° , on benzonitrile and dimethylamine at $80-90^\circ$ leads only to the formation of thiobenzamide in 100% yield; if the reaction proceeded according to the above scheme, an *N*-alkylthioamide would also be produced, since hydrogen sulphide acts on phenylbenzenylamidine, for example (Bernthsen, A., 1878, 788), as follows :



The promotion of this reaction by means of ammonium hydrogen sulphide is therefore considered to be due to the intermediate formation of molecular compounds :



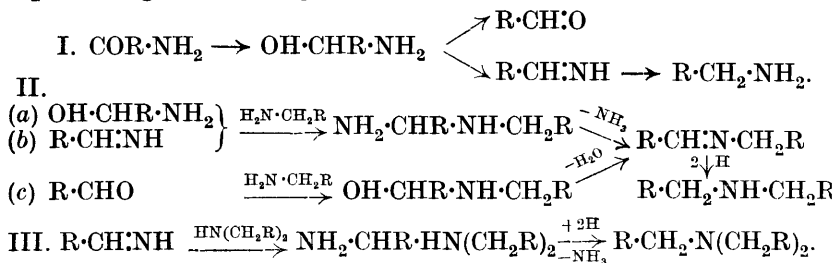
This view is confirmed by the fact that alkali hydrogen sulphides are even more efficient catalysts than ammonium hydrogen sulphide. Thus benzyl cyanide, heated for one and a half days at 70° with alcoholic hydrogen sulphide saturated at -10° , does not give phenylthioacetamide, but if ammonia, dimethylamine, sodium hydroxide, or potassium hydroxide is added, the yield of thioamide is 77, 81, 89, and 91%, respectively. The conversion is seldom quantitative, because the reaction is reversible; the same equilibrium : $\text{RCN} + \text{H}_2\text{S} \rightleftharpoons \text{R}\cdot\text{CS}\cdot\text{NH}_2$ (89% theory) is attained in the presence of alcoholic sodium hydrogen sulphide, starting

from phenylthioacetamide. In the presence of alkali hydrogen sulphide or dimethylammonium hydrogen sulphide in dry benzene solution, the following thioamides are prepared from the relevant nitriles in the yields stated. Thioacetamide, 66%; thiopropionamide, 43%; thio-*p*-toluamide, 78%; thio- β -naphthoamide, 88%; phenylthioacetamide, 83%; thioamide of acetylmandelic acid, $\text{CO}_2\text{Me}\cdot\text{CHPh}\cdot\text{CS}\cdot\text{NH}_2$, 70%; *phenylthiopropionamide*, m. p. 87° , 64%. Aliphatic and aliphatic-aromatic selenoamides are produced in the same way. Phenylacetonitrile reacts at 80° with alcoholic hydrogen selenide, saturated at -10° , containing sodium hydrogen selenide, giving an almost quantitative yield of *phenylselenoacetamide*, glistening, white crystals, m. p. $92-92.5^\circ$; *selenoacetamide*, m. p. $126-126.5^\circ$, is obtained in the same way, yield 17%, from acetonitrile.

The action of phosphorus pentasulphide on amides (Hofmann, A., 1878, 396) occurs in two stages. If the reaction is conducted in cold carbon disulphide solution, using *N*-dimethylbenzamide, the oily additive product, $\text{NH}_2\cdot\text{CR}\cdot\text{O}\dots(\text{S}_2)\text{P}\cdot\text{S}\cdot\text{P}(\text{S}_2)\dots\text{O}\cdot\text{C}(\text{NH}_2)\text{R}$ (cf. Pfeiffer, *Organischer Molekülverbindungen*, 1922, 156), may be isolated. This is decomposed by means of water into the amide, phosphoric acid, and hydrogen sulphide, but gives *thiobenzodimethylamide*, m. p. 67° (corr.), b. p. $180-182^\circ/18\text{ mm.}$, in 93% yield, on being repeatedly extracted by means of warm xylene. The formation of the thioamide is considered to take place by an interchange of oxygen and sulphur atoms in the additive compound, followed by dissociation. The following thioamides are formed with especial readiness in the presence of potassium sulphide. Thioacetamide, 75%; phenylthioacetamide, 48%; phenylthiopropionamide, 45%; *N*-methylthiobenzamide, 78%; *phenylthioacetethylamide*, colourless plates, m. p. $62.5-63^\circ$ (corr.), 75%; *phenylthioacetodimethylamide*, colourless crystals, m. p. $80-81^\circ$ (corr.), 80%; β -*phenylthiopropionodimethylamide*, red oil, 83%.

The reduction of phenylacetamide by means of sodium and amyl alcohol leads to the formation, not only of β -phenylethylamine, but also of di-(β -phenylethyl)amine. Moreover, secondary and even tertiary amines are produced when thioamides are reduced by means of aluminium amalgam in moist ethereal or alcoholic solution. Thus in ethereal solution the following amines are formed from the corresponding thioamides. 88% Benzylamine, 7% dibenzylamine, and traces of tribenzylamine. 84% *p*-Methylbenzylamine, 15% di-(*p*-methylbenzyl)amine. 26% β -Phenylethylamine, 66% di-(β -phenylethyl)amine. 35% γ -Phenylpropylamine, 65% di-(γ -phenylpropyl)amine, $(\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{NH}$, b. p. $245^\circ/35\text{ mm.}$, hydrochloride, m. p. 203° (corr.) (cf. Rupe and Glenz, this vol., i, 100). In alcoholic solution, 69% benzylamine, 21% dibenzylamine, and traces of tribenzylamine; 74% *p*-methylbenzylamine, 15% secondary amine; 22% β -phenylethylamine, and 21% secondary amine are produced. To explain these results, the intermediate formation of an aminoalcohol, $\text{OH}\cdot\text{CHR}\cdot\text{NH}_2$, or aminothioalcohol, $\text{SH}\cdot\text{CHR}\cdot\text{NH}_2$, is postulated, the production of a primary, secondary, or tertiary amine from an amide being then

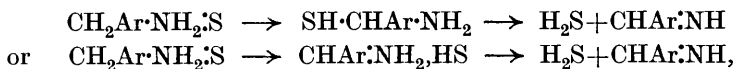
expressed by the following scheme, the reduction of a thioamide proceeding in an analogous manner :



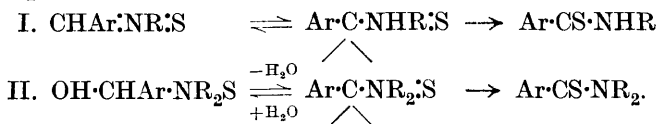
In accordance with this explanation, secondary and tertiary amines are not formed in acid solution; the aminothio-alcohol, being unstable to acids, undergoes fission to an aldehyde or to an aldimine, the latter being further reduced to a primary amine. Thus the electrolytic reduction of phenylthioacetamide in alcoholic hydrogen chloride solution leads to a 63% yield of β -phenylethylamine, and the reduction of thiobenzamide in dilute acetic acid solution by means of iron powder in an atmosphere of carbon dioxide gives benzaldehyde in a yield corresponding quantitatively with the amount of unrecovered thioamide. Moreover, the reduction of phenylthioacetamide by means of aluminium amalgam in moist ethereal solution containing ethylamine gives β -phenylethylamine, di-(β -phenylethyl)amine, and β -phenylethylethylamine, *hydrochloride*, whilst β -phenylethyldimethylamine is formed in the presence of dimethylamine. *N*-Monoalkyl or dialkyl amides or thioamides also pass first into the aminoalcohol or aminothioalcohol. Hence the electrolytic reduction of thiobenzanilide in 80% sulphuric acid solution at 15–20°, using a current density 0.15 amp./sq. cm., gives about 10% benzalaniline besides considerable amounts of aniline and benzaldehyde, whilst under similar conditions *N*-benzothiodimethylamide gives benzyldimethylamine, dimethylamine, and about 40% benzaldehyde. The preparation of tertiary amines from thiodialkylamides may, however, be accomplished by reduction in 60% sulphuric acid solution, using a current density 0.3 amp./sq. cm. Thiobenzodimethylamide, phenylthioacetodimethylamide, and β -phenylthiopropionodimethylamide give, respectively, benzyldimethylamine, 100%, β -phenylethyldimethylamine, 100%, and γ -phenylpropyldimethylamine, 73%. Benzylmethylamine, *p*-methoxybenzylmethylamine, and β -phenylethylmethylamine are obtained in yields of 79, 84, and 83%, respectively, by the reduction of the corresponding thioamides in concentrated hydrochloric acid solution. The reduction by means of aluminium amalgam of thioacetanilide, in ethereal solution, of thiobenzomethylamide, and of thiobenzodimethylamide, in alcoholic solution, gives ethylaniline, 100%, benzylmethylamine, 70%, and benzyldimethylamine, 60%, respectively.

Benzylamine is oxidised to benzamide by means of cold alkaline potassium permanganate (cf. Bamberger and Scheutz, A., 1901,

i, 587), but at 100° only benzoic acid and ammonia are produced; hence benzaldoxime is not an intermediate product. The parallel conversion of amines into thioamides by heating with sulphur (Wallach, A., 1891, 189) proceeds more readily, but has only been accomplished in the arylmethylamine series. Hence the reaction might be supposed to proceed through an aldimine:



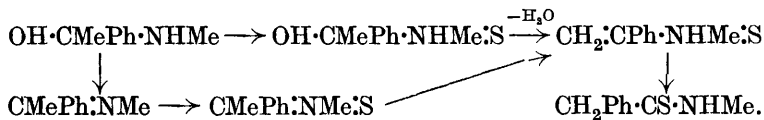
but for the fact that tertiary amines, which cannot be converted into aldimines, undergo this reaction. Thus benzyldimethylamine gives thiobenzodimethylamide when heated for four hours at 180° with sulphur (2 atoms). That in the oxidation of amines an amino-alcohol is primarily formed is supported by the fact (Pickard and Carter, T., 1901, '79, 520) that amino-alcohols can be oxidised to amides; moreover, both amino-alcohols and aminothio-alcohols may be converted into thioamides by heating with sulphur (see below). This is not merely dehydrogenation: $\text{OH}\cdot\text{CHR}\cdot\text{NR}_2 + \text{S} = \text{R}\cdot\text{CO}\cdot\text{NR}_2 + \text{H}_2\text{S}$, since the corresponding amides do not react with sulphur under similar conditions. Indeed, whether the amino-alcohol or the aldimine is the intermediate product, the formation of a compound of bivalent carbon must be postulated:



The aldehyde or ketone and ammonia or the amine are mixed in equivalent proportions, with cooling, and the mixture is heated with sulphur for three hours at 170–180°. Benzaldehyde and ammonia give thiobenzamide. *p*-Tolualdehyde and methylamine give *thio-p-tolumethylamide*, m. p. 55°. Benzaldehyde and β -naphthylamine give *thiobenzo- β -naphthylamide*, m. p. 106–107°. Benzaldehyde and dimethylamine give thiobenzodimethylamide; benzaldehyde and diethylamine give *thiobenzodiethylamide*, b. p. 194°/18 mm. Anisaldehyde and dimethylamine give *thio-p-methoxybenzodimethylamide*, m. p. 68·5°. Phenylacetaldehyde and dimethylamine give phenylthioacetodimethylamide. Similar compounds are produced by the action of sulphur on aldimines and ketimines; these are prepared by heating an equimolecular mixture of a primary amine and an aldehyde or ketone at 80–90° for three to four hours, and distilling the product under reduced pressure. Benzylidenemethylamine gives *N*-methylthiobenzamide. *p*-Methoxybenzylidenemethylamine, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{NMe}$, b. p. 129–130°/18 mm., gives *p*-methoxythiobenzomethylamide, m. p. 108–109°. Benzylidenedianiline gives thiobenzanilide and α -phenylethylidenemethylamine, $\text{CMePh}\cdot\text{NMe}$, b. p. 96°/10 mm., gives phenylthioacetomethylamide.

Phenylthioacetodimethylamide is produced when acetophenone and dimethylamine are heated with sulphur. Similarly, *p*-acetylanisole and dimethylamine give *p*-methoxyphenylthioacetodimethyl-

amide, m. p. 75—76°, whilst the products when diethylamine is used are, respectively, *phenylthioacetodiethylamide*, b. p. 184°/12 mm., and *p-anisylthioacetodiethylamide*, b. p. 220°/12 mm. In these reactions, the migration of an alkyl group must occur. It is suggested that the intermediate hydramine or ketimine forms an amine sulphide; this is followed by dehydration or migration of a hydrogen atom, giving an ethylene derivative, which then undergoes molecular rearrangement to the thioamide:



It is indicated that amino-alcohols may be intermediate products in the interconversion of amines and amides in plants and animals.

Use is made of thioamides in the synthesis of hordenine and hydrastinine. *p*-Nitrophenylacetodimethylamide, when treated with phosphorus pentasulphide and potassium sulphide, gives *p*-nitrophenylthioacetodimethylamide, yellowish-green prisms or leaflets, m. p. 131° (corr.), yield 90%, which on electrolytic reduction in 60% sulphuric acid solution gives *p*-amino- β -phenylethyldimethylamine, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NMe}_2$, colourless crystals, m. p. 40—42° (corr.), b. p. 137—138°/6 mm., *hydrochloride*, m. p. 261° (corr.). By diazotisation and warming in aqueous solution, hordenine is obtained in 95% yield. When the *N*-methylammonium salt of homopiperonylic acid is heated at 185—195° for two hours in an atmosphere of methylamine, an 85% yield of *homopiperonylmethylamide*, m. p. 106° (corr.), is obtained. This is treated with phosphorus pentasulphide and potassium sulphide, giving *homopiperonylthiomethylamide*, m. p. 136° (corr.), yield 82%, which is converted by electrolytic reduction in alcoholic hydrochloric acid solution into piperonylmethylamine, yield 80%, from which hydrastinine is obtained by the method of Decker and Becker (A., 1913, i, 290).

W. S. N.

The Resolution of *p*- and *m*-Nitrophenoxypropionic Acids. E. FOURNEAU and G. SANDULESCO (*Bull. Soc. chim.*, 1923, [iv], 33, 459—465).—The resolution of *o*-nitrophenoxypropionic acid by means of cinchonine, strychnine, and yohimbine has already been described (*loc. cit.*, 1922, 31, 988), but the methods which were successful with the ortho-acid do not give uniformly good results with the meta- and para-acids. The cinchonine and cinchonidine salts of the para-acid are oily or gummy and fail to crystallise, whilst the crystallisation of the strychnine and brucine salts is good, but no resolution occurs. On the other hand, *l-p*-nitrophenoxypropionic acid was obtained in good yield by the fractional crystallisation of the yohimbine salt. It melts at 89—90° and has $[\alpha]_D -53.7^\circ$. The *d*-acid was obtained by means of the quinidine salt. For the resolution of the meta-acid strychnine gave the best results amongst the various alkaloids tried. The salt of the *l*-acid crystallised out, and had a constant rotation after three

recrystallisations, $[\alpha]_D -25^\circ$. The free *l-m*-nitrophenoxypionic acid had m. p. $101-102^\circ$, and $[\alpha]_D -51.87^\circ$. G. F. M.

Researches on Residual Affinity and Co-ordination. XVI. Normal and Acid Salicylatotetramminocobaltic Salts. GILBERT T. MORGAN and J. D. MAIN SMITH (T., 1923, 123, 1096—1108).

Silver Derivative of Amino-thiolbenzoic Acid. A. FELDT (U.S. Pat. 1439624).—Interaction of a silver salt, in particular silver nitrate, with 4-amino-2-thiolbenzoic acid yields the compound, $\text{AgS}\cdot\text{C}_6\text{H}_3(\text{NH}_2)\cdot\text{CO}_2\text{H}$, a colourless powder, m. p. 205° .

CHEMICAL ABSTRACTS.

Oxalic Acid Derivatives of Benzo- and *p*-Tolu-acetodinitriles. ERICH BENARY, HELENE SOENDEROP, and ERICH BENNEWITZ (*Ber.*, 1923, 56, [B], 910—917).—A continuation of previous work (cf. Benary and Schmidt, A., 1921, i, 776).

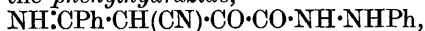
Ethyl γ -imino- β -cyano- α -keto- γ -phenylbutyrate,



lustrous plates, decomp. $165-167^\circ$, is prepared by the action of benzoacetodinitrile, ethoxalyl chloride, and pyridine in the presence of anhydrous ether. (The substance described under this name by von Meyer [A., 1914, i, 999] is actually the corresponding *N*-derivative.) It is converted by phenylhydrazine in acetic acid solution (50%) into 4-cyano-1 : 3-diphenylpyrazole-5-carboxyphenylhydrazide, $\text{Ph}\cdot\text{C}\cdot\text{C}(\text{CN})\begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix}\text{NPh} \gg \text{C}\cdot\text{CO}\cdot\text{NH}\cdot\text{NHPh}$, needles, m. p. $215-216^\circ$, which is

converted by prolonged treatment with *N*-sodium hydroxide solution into 4-carbamido-1 : 3-diphenylpyrazole-5-carboxyphenylhydrazide, m. p. 269° . The cyano-compound is oxidised by potassium permanganate in the presence of acetone to 4-cyano-1 : 3-diphenylpyrazole-5-carboxylic acid, $\text{Ph}\cdot\text{C}\cdot\text{C}(\text{CN})\begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix}\text{NPh} \gg \text{C}\cdot\text{CO}_2\text{H}$, colourless needles,

m. p. $216-217^\circ$ (decomp.), which is converted by sodium hydroxide solution (10%) into 1 : 3-diphenylpyrazole-4 : 5-dicarboxylic acid, m. p. 197° (decomp.). Ethyl γ -imino- β -cyano- α -keto- γ -phenylbutyrate is transformed by alcoholic ammonia into the corresponding amide, $\text{NH}\cdot\text{CPh}\cdot\text{CH}(\text{CN})\cdot\text{CO}\cdot\text{CO}\cdot\text{NH}_2$, lustrous leaflets, m. p. $212-213^\circ$ (decomp.) after progressive decomposition above 198° , and by the calculated quantity of cold *N*-sodium hydroxide solution into the imino-lactone, $\text{C}_{11}\text{H}_8\text{O}_3\text{N}_2$, lustrous, quadratic leaflets, m. p. 272° (decomp.). The latter substance is transformed by phenylhydrazine into the phenylhydrazide,



matted needles, m. p. $279-280^\circ$ (decomp.). Ammonium γ -imino- β -cyano- α -keto- γ -phenylbutyrate, m. p. $181-183^\circ$ (decomp.), was obtained in one instance from the products of the action of water at $60-70^\circ$ on the ester and was converted into the copper salt, a dark green, voluminous precipitate from which γ -imino- β -cyano- α -keto- γ -phenylbutyric acid, an unstable compound, m. p. 132° (decomp.), is isolated by the action of hydrogen sulphide in the presence of ether.

Benzoacetodinitrile is converted by oxalyl chloride in the presence of ether and pyridine into *oxalylbisbenzoacetodinitrile*, $C_{20}H_{14}O_2N_4$, m. p. 217—218° (decomp.).

p-Toluoacetodinitrile, ethoxalyl chloride, and pyridine in the presence of anhydrous ether give *ethyl γ -imino- β -cyano- α -keto- γ -p-tolylbutyrate*, $NH_2C(C_6H_4Me) \cdot CH(CN) \cdot CO \cdot CO_2Et$, long, colourless needles, m. p. 132—133° (decomp.), which is converted by phenylhydrazine into *4-cyano-1-phenyl-3-p-tolylpyrazole-5-carboxyphenylhydrazide*, $C_{24}H_{19}ON_5$, lustrous needles, m. p. 224—225°, and *4-carbamido-1-phenyl-3-p-tolylpyrazole-5-carboxyphenylhydrazide*, $C_{24}H_{21}O_2N_5$, small needles, m. p. 266—268°. Oxidation of the cyanohydrazide by potassium permanganate in the presence of acetone leads to the formation of *4-cyano-1-phenyl-3-p-tolylpyrazole-5-carboxylic acid*, microscopic needles, m. p. 208—209°. Ethyl γ -imino- β -cyano- α -keto- γ -p-tolylbutyrate is converted by alcoholic ammonia into *γ -imino- β -cyano- α -keto- γ -p-tolylbutyramide*, m. p. 195—196° (decomp.) after darkening and incipient decomposition at 175°, and by *N*-sodium hydroxide solution into the *imino-lactone*, $C_{12}H_{10}O_3N_2$, slender needles, decomp. 301°. *Ammonium γ -imino- β -cyano- α -keto- γ -p-tolylbutyrate*, m. p. 165—166° (decomp.), is obtained as in the case of the corresponding phenyl compound and is similarly transformed into the *copper salt* and the *free acid*, m. p. 149° (decomp.).

The compounds obtained by von Meyer (*loc. cit.*) from *p*-toluoacetodinitrile are to be regarded as *N*-derivatives.

C-Oxalylbisdiacetodinitrile, $C_{10}H_{10}O_3N_4$, four-sided prisms which slowly become carbonised above 195°, is obtained from diacetodinitrile, pyridine, and oxalyl chloride in the presence of anhydrous ether.

H. W.

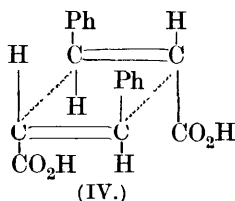
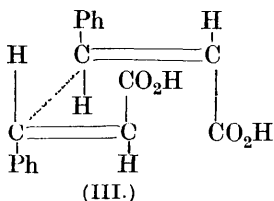
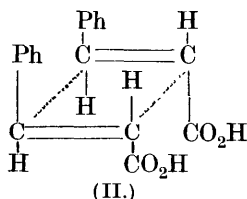
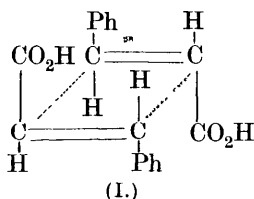
The Constitution of the Truxillic and Truxinic Acids and the Action of Sunlight on the Cinnamic Acids and their Salts.

A. W. K. DE JONG (*Ber.*, 1923, 56, [B], 818—832).—The action of sunlight on the normal and acid salts of *trans*-cinnamic acid has been investigated, the material being spread evenly over glass plates placed in shallow wooden boxes and not further covered. Under these conditions, lithium *trans*-cinnamate gives β - and ϵ -truxinic acids, the sodium and potassium salts yield only β -truxinic acid, whereas methyl *trans*-cinnamate gives α -truxillic acid. Among salts of the bivalent metals, the stable strontium salt and the copper, cadmium, manganese, ferrous, and cobaltous salts do not give truxillic and truxinic acids. β -Truxinic acid is exclusively obtained from the magnesium and nickel salts and from the barium salt after desiccation at 100°. The metastable strontium and the stable barium salts yield β -truxinic and ϵ -truxillic acids, whereas the metastable barium and the stable lead salts give β - and δ -truxinic acids. δ -Truxinic acid in large amount and only a small quantity of β -truxinic acid are obtained from the metastable lead salt, so that it does not appear improbable that the occurrence of the β -acid is due to the partial transformation of the salt into the stable form. Exclusive production of ϵ -truxillic acid is not observed.

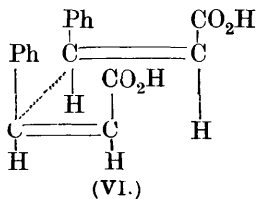
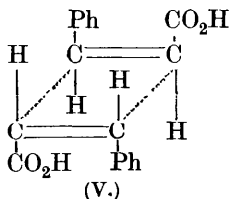
The strontium and barium salts after being heated during eight days do not yield α -truxillic acid when illuminated; truxinic or truxillic acids are not obtained from the double salt derived from calcium benzoate and calcium *trans*-cinnamate.

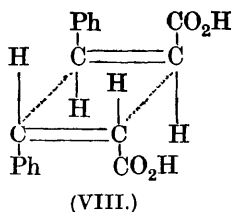
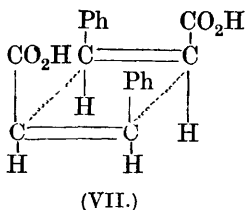
Among the hydrogen salts, the lithium and ammonium compounds yield β -truxinic and α -truxillic acids; the production of the latter acid is probably due to the salts becoming moist and sticky, and thus converted into a mixture of free acid and normal salt. β -Truxinic acid is alone obtained from the strontium and barium compounds. The sodium and caesium salts yield β - and δ -truxinic acids, whereas β -truxinic and ϵ -truxillic acids are derived from the potassium compound.

The author seeks an explanation of the polymerisation of the cinnamic acids in the hypothesis that the cinnamic acid molecules are held by the partial valencies of the double bond in such a manner that the latter are always parallel to one another. In the case of the *trans*-cinnamic acid four possibilities present themselves as shown by the formulæ



The production of α -truxillic (I), β -truxinic (II), ϵ -truxillic, (III) and δ -truxinic (IV) acids is thus readily explained. Considerations of symmetry show this property to decrease in the given sequence and the stability must consequently diminish in the same order. This is in good accord with the known properties of the α - and β -cinnamic acids, and the non-occurrence of the other two possible forms. Similarly, four forms are possible for the *cis*-cinnamic acids as shown in the scheme :





The symmetry and consequently the stability diminish in the given order. The formulæ V, VI, and VII represent, therefore, the nuclei of the acids, m. p. 68° , 58° , and 42° , respectively.

Illumination of the normal calcium salt gives β -truxinic acid and a new acid, m. p. 214° , which is only formed in very small quantity.

The following salts of cinnamic acid are described. The normal strontium compound crystallises when its aqueous solution is rapidly cooled in small, metastable needles which rapidly pass in contact with the solution into larger needles of the stable salt. Similarly, metastable *barium* cinnamate ($+2\text{H}_2\text{O}$) crystallises in lustrous, thin, hexagonal leaflets from its highly concentrated solution which pass into small needles of the stable form. The metastable form of lead cinnamate, small needles, is converted more slowly into the stable modification.

The following acid salts have not been described previously. They are all anhydrous. The *lithium* salt, $\text{C}_9\text{H}_7\text{O}_2\text{Li}\cdot\text{C}_5\text{H}_5\text{O}_2$, the *rubidium*, *cæsium*, *strontium*, and *barium* salts. The corresponding calcium salt could not be prepared. For the purposes of comparison, the following benzoates have been prepared; the *barium* salt, $(\text{Ph}\cdot\text{CO}_2)_2\text{Ba}\cdot 2\text{Ph}\cdot\text{CO}_2\text{H}$, small, slender needles; the *strontium* salt, $(\text{Ph}\cdot\text{CO}_2)_2\text{Sr}\cdot\text{Ph}\cdot\text{CO}_2\text{H}$, slender needles; the *calcium* salt, $(\text{Ph}\cdot\text{CO}_2)_2\text{Ca}\cdot\text{Ph}\cdot\text{CO}_2\text{H}$. The ratio of acid to normal salt is not affected in the two latter instances by the presence of an excess of acid.

H. W.

The Dinaphthanthracene Series. V. ERNST PHILIPPI and REINHARD SEKA [with MOLLY HAUSENBICHL] (*Monatsh.*, 1923, 43, 615—619; cf. A., 1921, i, 728).—Pyromellitic anhydride readily condenses with *p*-xylene at 75° in presence of aluminium chloride to give a mixture of 4 : 6-*di-p*-xylylisophthalic and 2 : 5-*di-p*-xylyltetraphthalic acids. The recrystallised mixture (m. p. 298°) is converted by concentrated sulphuric acid into 1 : 4 : 8 : 11-tetramethyl-5 : 7 : 12 : 14-dinaphthanthradiquinone, greenish-yellow needles, darkening at 340° and charring at 385° without melting. This substance does not give a vat colour with alkali hyposulphite, but on oxidation with nitric acid passes into 5 : 7 : 12 : 14-dinaphthanthradiquinone-1 : 4 : 8 : 11-tetracarboxylic acid (darkening at 280° and charring at 325°), which dyes cotton pale rose-red shades and, with hyposulphite, affords a deep red vat colour, the latter becoming blue in presence of alkali (cf. Seer, A., 1912, i, 571).

E. E. T.

The Dinaphthanthracene Series. VI. ERNST PHILIPPI and REINHARD SEKA [with WILHELM FIGDOR and RUDOLF NEMECZEK] (*Monatsh.*, 1923, **43**, 621—631; cf. preceding abstract, and Fairbourne, T., 1921, **119**, 1573).—Pyromellitic anhydride condenses with *o*-xylene in presence of aluminium chloride to give a mixture of 4 : 6-*di*-*mp*-dimethylbenzoylisophthalic and 2 : 5-*di*-*mp*-dimethylbenzoyltetraphthalic acids, separable into a sparingly soluble acid (m. p. 312°) and a soluble acid (m. p. 250°). The corresponding mixture of acid chlorides loses hydrogen chloride when treated with aluminium chloride, but no isolable compound results.

Pyromellitic anhydride and anisole condense to give a mixture (m. p. 200—250°) of 4 : 6-*di*-*p*-methoxybenzoylisophthalic and 2 : 5-*di*-*p*-methoxybenzoyltetraphthalic acids, which may be separated by crystallisation from water. The 2 : 5-acid (sparingly soluble) melts at 311°, the 4 : 6-acid (more soluble) at 285°, with previous discoloration. Neither acid is convertible by means of sulphuric acid into a dinaphthanthradiquinone.

Pyromellitic anhydride condenses with quinol dimethyl ether to give a poor yield of the two expected *di*-2 : 4-dimethoxybenzoylisophthalic and -tetraphthalic acids (green product, m. p. about 220°).

Anthracene-2 : 3-dicarboxylic anhydride and benzene on condensation give an ill-defined product, melting indefinitely at 130°, and giving, on oxidation, 2-benzoylanthraquinone-3-carboxylic acid, m.p. (indef.) 275°. Magnesium phenyl bromide converts anthracene-dicarboxylic anhydride into the corresponding diphenylphthalide derivative (yellow, m. p. 260°), and this, on oxidation, gives the corresponding anthraquinone derivative (yellow, m. p. 200°).

Bromination of dinaphthanthradiquinone at 300° gives a mixture of products, of which the isolable one is a *dibromo*-derivative, sintering at 358° and melting at 363°. Nitration of the diquinone gives a *dinitro*-derivative, darkening and charring at 380—400°. E. E. T.

The Symmetric and Mixed Esters of Carboxycamphoracetic Acid and their Saponification Products. A. HALLER and L. PALFRAY (*Compt. rend.*, 1923, **176**, 1193—1197).—The following esters of carboxycamphoracetic acid having the general

formula $C_8H_{14} \begin{smallmatrix} \diagup C(CO_2R') \cdot CH_2 \cdot CO_2R \\ \diagdown CO \end{smallmatrix}$ were prepared in the manner

previously described (A., 1905, i, 601) by the action of the corresponding iodoacetic ester on the sodium camphorcarboxylic ester:—*Diethyl* ester, b. p. 199—200°/14 mm., $[\alpha]_D + 59.43^\circ$; *phenyl*(R)-*methyl*(R') ester, b. p. 233—235°/13 mm., m. p. 83°, $[\alpha]_D + 41.38^\circ$; *benzyl*(R')*methyl*(R) ester, b. p. 265—270°/16 mm., $[\alpha]_D + 46.1^\circ$. On saponification by alkalis or mineral acids, only the acetic ester (R) group is removed provided the temperature is kept below 150°, the carboxylic ester (R') group proving exceptionally stable. The above-mentioned diethyl ester furnishes therefore a *carbethoxy*-

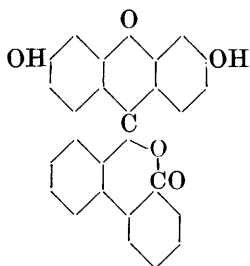
camphoracetic acid of the constitution $C_8H_{14} \begin{smallmatrix} \diagup C(CO_2Et) \cdot CH_3 \cdot CO_2H \\ \diagdown CO \end{smallmatrix}$,

forming large crystals, m. p. 117—118°. The dimethyl ester similarly gives the corresponding *monomethyl* ester, m. p. 177—178°,

and the above phenyl methyl ester gives the same product. The benzyl methyl ester gives the benzylcarboxylate, which forms an uncrystallisable oil. The action of hydrochloric acid on the esters at 180—190° under pressure effects the hydrolysis of both ester groups with simultaneous elimination of carbon dioxide and formation of *camphoracetic acid*, $C_8H_4 \begin{smallmatrix} \text{CH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H} \\ \text{CO} \end{smallmatrix}$, m. p. 84—85°, $[\alpha]_D + 72.35^\circ$.

G. F. M.

Condensation of Diphenic Anhydride with Resorcinol.



FRITZ BISCHOFF and HOMER ADKINS (*J. Amer. Chem. Soc.*, 1923, **45**, 1030—1033).—Diphenic anhydride and resorcinol are condensed by heating at 135—150° with zinc chloride, to give the 9-lactone of 2'-(3'':6'':9'':tri-hydroxyxanthenyl)diphenyl-2-carboxylic acid (annexed formula), an amorphous, ruby-red glass, which reacts with bromine in alcoholic solution to give the corresponding 2'':4'':5'':7'':tetra-bromo-derivative, a pinkish-yellow solid. Both these compounds give acetylated products which are insoluble in alkalis.

W. S. N.

The Sodium Salts of Phenolphthalein. HENRY BASSETT and PHILIP HALTON (*T.*, 1923, **123**, 1291—1304).

The Molecular Configurations of Polynuclear Aromatic Compounds. III. Diphenyl-3 : 5 : 3' : 5'-tetracarboxylic Acid. HAROLD BURTON and JAMES KENNER (*T.*, 1923, **123**, 1043—1045).

Derivatives of 2 : 4-Dinitrobenzaldehyde. III. THOMAS B. DOWNEY and ALEXANDER LOWY (*J. Amer. Chem. Soc.*, 1923, **45**, 1060—1065; cf. *A.*, 1920, i, 440; 1921, i, 337).—A number of Schiff bases derived from 2 : 4-dinitrobenzaldehyde are described; the intermediate condensation product with *o*-tolidine is formed in a 95% aqueous alcoholic solution, but the Schiff base is produced in the presence of acetic acid. A number of triphenylmethane derivatives have been prepared by the condensation of 2 : 4-dinitrobenzaldehyde (1 mol.) with a tertiary alkylated aromatic amine or substituted aromatic amine or phenolic substance (2 mols.).

The *additive* compound of 2 : 4-dinitrobenzaldehyde and *o*-tolidine, $C_6H_3(NO_2)_2 \cdot CH(OH) \cdot NH \cdot C_6H_3Me \cdot C_6H_3Me \cdot NH_2$, deep purple plates, m. p. 232°, is converted by acetic acid in acetone solution into 2 : 4-dinitrobenzylidene-*o*-tolidine, yellowish-red crystals, m. p. 282° (decomp.), which reacts with acetic anhydride to give 2 : 4-dinitrobenzylideneacetyl-*o*-tolidine, orange-yellow needles, m. p. 231.5°. The following Schiff bases are also described: 2 : 4-dinitrobenzylidene-*op*-dichloroaniline, $C_6H_3(NO_2)_2 \cdot CH:N \cdot C_6H_3Cl_2$, bright orange plates, m. p. 185°; 2 : 4-dinitrobenzylidene-*o*-chloroaniline, yellow needles, m. p. 167.5°; 2 : 4-dinitrobenzylidene-*p*-chloroaniline, yellow needles, m. p. 161.5°; 2 : 4-dinitrobenzylidene-*p*-aminoazobenzene, red prisms, m. p. 229°. The following triphenylmethane derivatives

are described: 2'' : 4''-*dinitro-4 : 4'-dihydroxytriphenylmethane*, $C_6H_3(NO_2)_2 \cdot CH(C_6H_4 \cdot OH)_2$, pale yellow solid, m. p. 204°, which gives a *tetrabromo-derivative*, yellow needles, m. p. 234°; 4 : 4'-*di-chloro-2 : 4'-dinitrotriphenylmethane*, m. p. 190·5°; *op-dinitrophenyl-di-o-4'-cresolmethane*, m. p. 200·5°; *op-dinitrophenyldi-guaiacol-methane*, m. p. 221°; *op-dinitrobenzylidenedi-4-salicylic acid*, m. p. 268·5°, all of which are yellow solids. 2'' : 4''-*Dinitro-4 : 4'-dimethylaminotriphenylmethane*, yellow needles, m. p. 151·5°; the corresponding *bisdiethylamino-compound*, an unstable, dirty green solid, and the *benzylethylamino-compound*, a brownish-yellow solid. The last three compounds give colour bases and dyes. The formation of *op-dinitrophenyldi-4'-resorcinolmethane*, yellow, amorphous solid, chars above 280°, red *calcium salt*, is accompanied by the production of 3 : 6-*dihydroxy-9-op-dinitrophenylxanthene*, a yellowish-red, amorphous solid, which chars above 280°, which is also formed if the condensation is carried out in the presence of zinc chloride at 95—130°, or of sulphuric acid at 60°; it yields a *calcium salt* and a *tetrabromo-derivative*, red prisms, decomp. 290° (cf. *J.S.C.I.*, 1923, 490A).
W. S. N.

The Isomerism of the Oximes. XI. Carbethoxy-derivatives. OSCAR LISLE BRADY and GERALD PATRICK McHUGH (T., 1923, 123, 1190—1198).

Peroxides of Monoximes. R. CIUSA and E. PARISI (*Gazzetta*, 1923, 53, i, 143—149).—*m*-Nitrobenzaldoxime peroxide, obtained either by passing a slow current of nitrogen trioxide into an ethereal solution of the oxime or by oxidising the latter by means of amyl nitrite, has m. p. 131°, as stated by Ponzio (A., 1906, i, 593), and not 105°, as given by Minunni and Ciusa (A., 1906, i, 187), or 124°, as given by Franzen and Zimmermann (A., 1906, i, 388). The action of nitrogen trioxide on the oxime dissolved in ether yields, in addition to the peroxide, (1) a substance, probably *m*-nitrobenzonitrolic acid, $NO_2 \cdot C_6H_4 \cdot C(NO_2) \cdot N \cdot OH$, which reddens sodium carbonate solution and is converted by this reagent into a mixture of di-*m*-nitrobenzildioxime peroxide, m. p. 184°, and 3 : 4-di-*m*-nitrophenylfurazan, m. p. 168°; (2) *m*-nitrobenzoic acid; (3) a compound, m. p. 147—150°, which is identical with that described by Bamberger and Scheutz (A., 1901, i, 548) as *m*-nitrobenzenylazoxime, but is more probably 3 : 4-di-*m*-nitrophenylfurazan; (4) di-*m*-nitrobenzildioxime. *m*-Nitrobenzaldoxime peroxide is also obtainable in small proportion by oxidising the oxime with either potassium ferricyanide or sodium hypochlorite.

When heated at 50° in suspension in benzene, the peroxide yields di-*m*-nitrobenzaldoxime peroxide, 3 : 4-di-*m*-nitrophenylfurazan, *m*-nitrobenzoic acid in large proportion, and a small proportion of a compound which crystallises in colourless, rhombic plates, m. p. 124°, but has not yet been identified. T. H. P.

Dehydration of Phenylhydrobenzoin. STEFAN DANILOV (*J. Russ. Phys. Chem. Soc.*, 1917, 49, 282—289).—The dehydration with 40% sulphuric acid of phenylhydrobenzoin results in a mixture of

triphenylvinyl alcohol and triphenylacetaldehyde, in the proportions 4:1. Garder (*Bull. Acad. roy. Belg.*, [iii], **34**, 94), who used phosphoric oxide for the dehydration, obtained the same products, but erroneously identified the second of them as triphenylethylene oxide. Triphenylacetaldehyde has been described by Schmidlin (A., 1910, i, 368) as a substance of m. p. 218°, but it appears that he was mistaken in considering the substance he obtained as triphenylacetaldehyde, and the compound now obtained melts at 105—106°. Oxidation with chromic anhydride converted it into a mixture of triphenylacetic acid and triphenylcarbinol, whilst alcoholic potash gave triphenylmethane. *Triphenylacetaldoxime*, colourless rhombic prisms, m. p. 190°, and the *semi-carbazone*, m. p. 223°, and *phenylhydrazone*, m. p. 142°, of triphenylacetaldehyde were prepared. By the reduction with sodium amalgam of the phenylhydrazone, triphenylethylamine, m. p. 130—131°, was obtained. Aluminium amalgam converts the aldehyde into *triphenylethanol*, m. p. 110—111°, the *phenylurethane* of which, m. p. 205—206°, was prepared. Phosphoric oxide acts on the aldehyde to give triphenylvinyl alcohol, showing that a tendency exists for the aldehyde to isomerise to a ketonic form. R. T.

The Behaviour of certain Aromatic Hydroxyaldehydes.

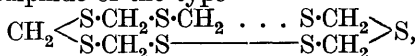
A. WINDAUS and H. SCHIELE (*Ber.*, 1923, **56**, [B], 846—848).—Benzaldehyde is converted by iodine and dilute potassium hydroxide solution at the atmospheric temperature into benzoic acid in good yield. Under similar conditions, salicylaldehyde loses the aldehydic group as formic acid and yields iodophenol; it is preferable to use an excess of iodine which causes the almost exclusive production of 2:4:6-tri-iodophenol, whereas a mixture of iodophenols is otherwise produced. The behaviour of *p*-hydroxybenzaldehyde is similar. *m*-Hydroxybenzaldehyde, on the other hand, gives an *iodo-m-hydroxybenzoic acid*, needles, m. p. 219—220° (*methyl ester*, colourless needles, m. p. 49°), in which the position of the iodine atom has not been established. 6-Hydroxy-*m*-tolualdehyde and β -naphthol-1-aldehyde behave similarly to *o*- and *p*-hydroxybenzaldehydes, the former giving 3:5-di-iodo-4-hydroxytoluene, m. p. 61—61.5°, and the latter yielding α -iodo- β -naphthol, m. p. 92.5°.

Catalytic hydrogenation of salicylaldehyde dissolved in glacial acetic acid at the atmospheric temperature and pressure in the presence of spongy platinum gives *o*-cresol; under similar conditions, β -naphthol-1-aldehyde is converted into α -methyl- β -naphthol. H. W.

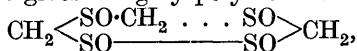
Isomerism of Thioaldehydes. EMIL FROMM and CARLTHEO SCHULTIS (*Ber.*, 1923, **56**, [B], 937—947).—Baumann and Fromm have shown in a series of communications that thioaldehydes occur usually in trimeric, but also in other polymeric forms, and that under the most varied conditions it is possible to obtain only a single trithioformaldehyde or trithioacetone, whereas many other aldehydes give two isomeric trithioaldehydes. The substances have been regarded as cyclic sulphides, and their occurrence in different modifications has been explained in accordance with the principles

of *cis-trans*-isomerism. This conception appeared adequate until Hinsberg (A., 1912, i, 546; 1913, i, 818; 1914, i, 185, 797) announced the discovery of a second β -trimethylene trisulphide, and of a third (δ)-trithiobenzaldehyde, the existence of which is not explicable by the theory of stereoisomerism. A repetition of Hinsberg's work has shown that the compounds described by him do not exist.

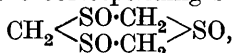
The crude product obtained by the action of hydrogen sulphide on formaldehyde in the presence of hydrochloric acid has the same melting point (216°) as pure trimethylene trisulphide. The compounds, however, are not identical. The crude material is a highly polymerised disulphide of the type



which loses a small amount of sulphur when recrystallised and yields pure trimethylene trisulphide, m. p. 216°, in accordance with the scheme: $(\text{H}_2\text{CS})_x + \text{S} \rightarrow x/3(\text{H}_2\text{CS})_3 + \text{S}$. It is converted by concentrated hydriodic acid into the highly polymerised dimercaptan, $\text{HS} \cdot \text{CH}_2 \cdot \text{S} \cdot \text{CH}_2 \cdot \text{S} \dots \text{CH}_2 \cdot \text{S} \cdot \text{CH}_2 \cdot \text{SH}$, decomp. 247°, which loses small amounts of hydrogen sulphide when recrystallised and gives trimethylene trisulphide, m. p. 216°. The latter cannot be transformed by any known method into the mercaptan or disulphide. The products also behave differently when oxidised. The crude material gives a highly polymerised sulfoxide,



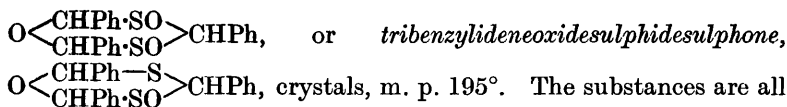
which is reduced to the mercaptan, decomp. 247°, whereas the pure trisulphide yields the corresponding sulfoxide,



decomp. 270°, which, when reduced with hydriodic acid, gives trimethylene trisulphide, m. p. 216°, and its *di-iodide*, $\text{C}_3\text{H}_6\text{S}_3\text{I}_2$, small, dark red leaflets, m. p. 100–110°, and *tetraiodide*, $\text{C}_3\text{H}_6\text{S}_3\text{I}_4$, dark violet prisms, decomp. 100–105°, but not the substance, decomp. 247°.

With tribenzylidene trisulphides the relationships are more complicated but Hinsberg's main error appears to consist in the supposition that the pure α - and β -varieties yield different oxidation products when treated with hydrogen peroxide. This is, however, impossible since in the presence of even a deficiency of the reagent the α -form is converted into the β -modification and the oxidation products are therefore necessarily derived from the latter. The products obtained by treating tribenzylidene trisulphide with suitable amounts of hydrogen peroxide are *tribenzylidene trisulphoxide*, $\text{SO} \left\langle \begin{array}{c} \text{CHPh} \cdot \text{SO} \\ \text{CHPh} \cdot \text{SO} \end{array} \right\rangle \text{CHPh}$, small needles, m. p. 240°, *tribenzyl-*

idene trisulphone, $\text{SO}_2 \left\langle \begin{array}{c} \text{CHPh} \cdot \text{SO}_2 \\ \text{CHPh} \cdot \text{SO}_2 \end{array} \right\rangle \text{CHPh}$, a white, chalky powder which does not melt below 340° (the *sodium* salt, $\text{C}_{21}\text{H}_{17}\text{O}_6\text{S}_3\text{Na}$, *potassium* salt, $\text{C}_{21}\text{H}_{17}\text{O}_6\text{S}_3\text{K}$, additive compound with pyridine, $\text{C}_{21}\text{H}_{18}\text{O}_6\text{S}_3 \cdot \text{C}_5\text{H}_5\text{N}$, slender needles, and the *dimethyl* derivative, m. p. 248°, are described), and *tribenzylideneoxidisedisulphoxide*,



The substances are all stable towards aqueous solutions of alkali hydroxides, by means of which they can be separated from one another. Since this treatment also causes the production of benzaldehyde and sulphur dioxide, there are always components of the crude product which are unstable towards alkali, but have not been investigated further. The tetroxide and pentoxide which have been described by Hinsberg are mixtures of these three or four products. Reduction of the trisulphoxide by hydriodic acid gives a product which usually contains iodine and has m. p. $180-215^\circ$ according to the degree of purity. When recrystallised, it yields pure β -tribenzylidene trisulphide, m. p. 216° . The product is invariably crude β -trithiobenzaldehyde and not the new δ -isomeride, as assumed by Hinsberg.

If α - or β -tribenzylidene trisulphide is oxidised with a large excess of hot hydrogen peroxide, a product, decomp. 295° , is obtained which, in consequence of its insolubility, cannot be recrystallised. It is a mixture which is resolved by treatment with aqueous alkali hydroxide solution into tribenzylidenetrisulphone, tribenzylideneoxidedisulphoxide, benzaldehyde, and sulphur dioxide.

H. W.

The Oxidation of 1 : 3-Dimethylcyclohexan-4-one, and the Synthesis of cyclopentane Diketones. MARCEL GODCHOT (*Compt. rend.*, 1923, 176, 1151—1153).—The oxidation of 1 : 3-dimethylcyclohexan-4-one with cold 3% aqueous permanganate furnished a 70% yield of δ -acetyl- γ -methylvaleric acid together with a small amount of β -methyladipic acid formed by the further oxidation of the ketonic acid. The δ -acetyl- γ -methylvaleric acid is a colourless liquid, b. p. $177^\circ/20$ mm., with n_D^{17} 1.4599, and d^{17} 1.078. Its semicarbazone melts at 136° , and the ethyl ester boils at $130^\circ/18$ mm., and has d^{17} 0.9715, and n_D^{17} 1.4334. The internal condensation of this ester by means of sodium ethoxide gave a 75% yield of a β -diketone, 2-acetyl-1-methylcyclopentan-3-one, $\text{CH}_2-\text{CO} > \text{CH} \cdot \text{COMe}$, an agreeably smelling liquid, b. p. $89-90^\circ/12$ mm., and having d^{16} 1.029, and n_D^{16} 1.4756. It gives an intense violet coloration with ferric chloride, and forms with semicarbazide a disemicarbazone, $\text{C}_{10}\text{H}_{18}\text{O}_2\text{N}_6$, m. p. 240° (decomp.), and a carbamylpyrazole, m. p. 120° , arising from the anhydrisation of the monosemicarbazone. On treatment with sodium and methyl iodide, the β -diketone was converted into 2-acetyl-1 : 2-dimethylcyclopentan-3-one, a colourless liquid, b. p. $99-100^\circ/14$ mm., and having d^{17} 1.020, and n_D^{17} 1.4585. Its monosemicarbazone melts at 240° . On treatment with aqueous alkali hydroxide, it is converted into δ -acetyl- γ -methylhexoic acid, b. p. $164^\circ/10$ mm., with d^{15} 1.055, and n_D^{15} 1.4631; the ethyl ester has b. p. $134-135^\circ/13$ mm., d^{13} 0.9865, and n_D^{13} 1.4488.

G. F. M.

Action of Ammonium Cyanide on Diketones. H. D. DAKIN and C. R. HARRINGTON (*J. Biol. Chem.*, 1923, **55**, 487—494).—A study of the action of ammonium cyanide on α -diketones, with a view to the synthesis of homologues of diaminosuccinic acid, has shown that the reaction does not result, as expected, in the formation of aminonitriles, but usually leads to a fission of the carbon chain between the two carbonyl groups. Thus, benzil is converted practically quantitatively into benzamide and benzaldehyde cyanohydrin, the same products being also formed by the action of ammonia on benzil dicyanohydrin; anisil, piperil, and furil undergo analogous decompositions; *m*-dinitrobenzil yields *m*-nitrobenzamide and an oil which is probably a condensation product between *m*-nitrobenzaldehyde or its cyanohydrin and dinitrobenzil, and is converted into a glyoxaline derivative when heated with sodium hydroxide and acidified; diacetyl and phenylglyoxal appear to give glyoxaline derivatives. The following ketones are practically unaffected by ammonium cyanide: benzoin, distyryl ketone, benzoylacetone. E. S.

The Electrolytic Oxidation of Benzene to *p*-Benzoquinone, and the Electrolytic Reduction of Quinone. A. SEYEWETZ and G. MIRON (*Bull. Soc. chim.*, 1923, [iv], **33**, 449—459).—A study was made of the conditions governing the electrolytic oxidation of benzene with the object of securing a maximum yield of *p*-benzoquinone. The optimum conditions whereby a yield of 65% of *p*-benzoquinone was obtained were found to lie within very narrow limits, and are summarised as follows: Electrodes of pure lead with a very homogeneous surface, separated by a diaphragm of porous pot unattackable by sulphuric acid. A current density of 4 amperes per sq. dm., under 3.2—3.5 volts. An electrolyte consisting of a solution containing 25% of sulphuric acid, 33% of acetic acid, with which is emulsified two-thirds of its volume of benzene in presence of 1.0—1.5% of finely divided lead sulphate as catalyst. The temperature must be maintained at 24°, and as soon as the benzene contains 1% of benzoquinone in solution it must be transferred from the anodic compartment to the cathode, otherwise a destruction of the *p*-benzoquinone commences, which rapidly diminishes the yield. The emulsion is produced by means of a helicoid stirrer rotating at 1,200 revolutions per minute inside the anodic compartment. The yield of *p*-benzoquinone rapidly falls with rise in temperature, and becomes zero at 55°. Traces of silica dissolved in the electrolyte cause a notable decrease in the yield. The reduction of the *p*-benzoquinone to quinol when the benzene solution is transferred to the cathodic compartment is practically quantitative. The optimum temperature is 40°, and the presence of 1% of vanadic acid as catalyst is advantageous. The quinol is dissolved by the aqueous electrolyte as it is formed, and the concentration can be allowed to increase to the saturation point without any disadvantage. The benzene thus freed from *p*-benzoquinone is then returned to the oxidising cell and the process is thus rendered continuous. G. F. M.

Synthesis of 4-Hydroxy-1 : 2-dimethylantraquinone.
 ARTHUR FAIRBOURNE and JOHN MILDRED GAUNTLETT (T., 1923, 123, 1137—1139).

A New Class of Free Organic Radicles. II. ROLAND SCHOLL [with HERBERT HÄHLE] (*Ber.*, 1923, 56, [B], 918—936; cf. A., 1921, i, 872).—Further investigation of the benzoyloxanthronyls has led the authors to a somewhat modified conception of their constitution. They are now regarded as members of a class of nitrogen-free organic radicles which were hitherto without analogues. They are distinguished from the triarylmethyls and the metallic ketyls by their slight sensitiveness to free oxygen and, in particular, by their ability to react with three atoms of bromine or to acquire three hydroxyl groups when titrated with permanganate until colourless. They appear to behave as tervalent radicles, but this is only apparent, since only two of the three equivalents of bromine or hydroxyl are retained, whereas the third removes the hydroketyl hydrogen in the second phase of the reaction in the form of hydrogen bromide or water, so that ultimately only one valency is saturated. In reality, therefore, they are univalent radicles. This is directly shown by the reaction with permonosulphuric acid, whereby only one hydroxyl group is introduced. Incidentally, this group also indirectly removes the hydroketyl hydrogen as water, so that ultimately in the final product one valency less is saturated than in chlorobenzoyloxanthronyl. Both processes, however, are characteristic of a univalent radicle. Towards chromic acid, the oxanthronyls appear to behave as bivalent radicles, probably as a consequence of the formation of peroxides.

The benzoyloxanthronyls are, however, univalent radicles of a peculiar type, and contain the characteristic arrangement of atoms indicated in the annexed formula. The

$$\text{OC} < \begin{matrix} \text{C}_6\text{H}_3 \\ \text{C}_6\text{H}_4 \end{matrix} > \begin{matrix} \text{---} \text{C} \text{---} \text{O} \\ \text{---} \text{C} \text{---} \text{O} \end{matrix} \text{H}$$

hydrogen atom closes an internally-complex, seven-membered ring and shares its affinity with the two carbonyl oxygen atoms, so that these make demands on the two radicle-carbon atoms intermediate between those of carbonyl oxygen atoms and ordinary hydroxy-oxygen. The affinity of the free radicle valency is therefore not concentrated on a single tervalent carbon atom as in the triaryl-methyls or the simple metallic ketyls, but is distributed, generally in a non-uniform manner, over two carbon atoms. The benzoyloxanthronyls therefore contain two carbon atoms which may be regarded as together being septavalent. They are distinguished from the "true" carboxylic acids according to the conception of Hantzsch by their radicle nature, and before all by the firmness of retention and non-ionisability of the hydrogen atom.

1-*p*-Chlorobenzoyl-9-oxanthronyl is prepared according to the method of Schaarschmidt (A., 1915, i, 566, 696; 1916, i, 408) by treatment of 1-*p*-chlorobenzoylantraquinone with aluminium bronze and concentrated sulphuric acid, but satisfactory results are only obtained if the pure ketone is used as initial material. Reduction can also be effected with stannous chloride and glacial

acetic acid or by ferrous sulphate in glacial acetic and hydrochloric acids. The molecular weight of the substance in freezing nitrobenzene corresponds with the simple formula, $C_{21}H_{12}O_3Cl$. The sulphate, $C_{21}H_{12}O_3Cl \cdot 2H_2SO_4$ (cf. Schaarschmidt, *loc. cit.*), has now been isolated in the homogeneous condition in the form of dark emerald-green needles. Oxygen does not appear to react with the compound dissolved in nitrobenzene in the dark during four hours at the atmospheric temperature, and attacks it but slowly when the temperature is raised. In daylight, the substance disappears, but only twice as rapidly as when it is illuminated under carbon dioxide. In either case, the reaction is one of dehydrogenation of the *p*-chlorobenzoyloxanthronyl to *p*-chlorobenzoylanthraquinone. Under carbon dioxide, the oxanthronyl itself, and possibly the solvent, act as hydrogen acceptors, whereas in the presence of oxygen this rôle is played by the gas and the primarily formed hydroperoxide, the presence of which cannot be established at any stage of the reaction.

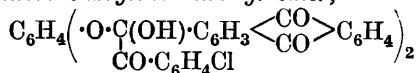
The product of the action of bromine on *p*-chlorobenzoyloxanthronyl has been isolated by cautiously adding the latter to an excess of the halogen. Analyses of the not perfectly homogeneous product indicate the composition $C_{21}H_{11}O_3ClBr_2$. The product is transformed into bromine and *p*-chlorobenzoylanthraquinone when heated with water or acetic acid.

p-Chlorobenzoyloxanthronyl dissolved in nitrobenzene can be sharply titrated with acid permanganate solution, three equivalents of oxygen being required for the decolorisation of each molecule; the primary product has not been isolated, but chlorobenzoylanthraquinone and iodine are obtained when it is treated with potassium iodide and steam.

Titration of *p*-chlorobenzoyloxanthronyl with chromic acid can be effected when the former is dissolved in nitrobenzene and the latter in glacial acetic acid, or both are dissolved in concentrated sulphuric acid. In either case, one atomic proportion of oxygen is required for each molecule of the ketone.

p-Chlorobenzoyloxanthronyl is rapidly converted by nitric acid or nitrogen peroxide into *p*-chlorobenzoylanthraquinone; on the other hand, it appears to be stable in nitrobenzene solution towards nitric oxide.

Quinolbis-p-chlorobenzoyloxanthronyl ether,



is prepared as a white powder with a pale yellow tint by the action of *p*-benzoquinone on *p*-chlorobenzoyloxanthronyl in the presence of glacial acetic acid. It is perfectly stable at the atmospheric temperature even in the presence of air. It begins to dissociate at about 100°, and at 130–140° exhibits the dark bluish-violet colour proper to the oxanthronyl, whilst *p*-benzoquinone sublimes. In solution, dissociation commences at the atmospheric temperature so that they show the same colours as very dilute solutions of the radicle itself. The addition of the quinone appears to take place in two stages; the union of molecular proportions of the components

occurs slowly, after which the second molecule of the radicle is rapidly added.

H. W.

Ethyl Fenchylxanthate. SERGEI S. NAMETKIN and (MLLE) A. S. SELIVANOVA (*J. Russ. Phys. Chem. Soc.*, 1917, **49**, 417—425).—Ethyl fenchylxanthate gives on decomposition a mixture of *cyclofenchene* and *fenchene*. Pure fenchyl alcohol is shown to melt at 49°, not at 45°, as is generally accepted, the lower m. p. being due probably to the presence of an isomeric *isofenchyl* alcohol.

R. T.

A Method for Resolving some Racemic Alcohols into their Optically Active Components. A. WINDAUS, F. KLÄNHARDT, and R. WEINHOLD (*Z. physiol. Chem.*, 1923, **126**, 308—312).—The double compound of the alcohol with digitonin is formed (cf. this vol., i, 590), and on recrystallising this compound resolution is obtained, and the alcohol is then obtained free from digitonin by distillation in a vacuum or in steam. In this way, resolution has been effected of *dl-α-terpineol*, *dl-ac-tetrahydro-β-naphthol*, and of *carvomenthol*. Phenylmethylcarbinol, on the other hand, remained inactive.

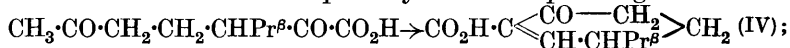
W. O. K.

Homologues of Camphor. I. S. S. NAMETKIN and (MLLE) ANNA M. CHUCHRIKOVA (*J. Russ. Phys. Chem. Soc.*, 1918, **50**, 254—263).—6-*Methylcamphor*, b. p. 213—213·5°/767 mm., m. p. 168—168·5, is synthesised in the following way. Methylfenchyl alcohol is prepared by the action of magnesium methyl iodide on fenchone, and converted into methylfenchene by dehydration with potassium hydrogen sulphate. Boiling with glacial acetic acid converts methylfenchene into *acetylmethylisoborneol*, b. p. 110°/14 mm., d_4^{20} 0·9714, n_D^{20} 1·4634, and this, on hydrolysis, gives *methylisoborneol*, m. p. 191—192°, b. p. 219—219·5°/753 mm. Its *phenylurethane*, m. p. 101—102°, and *hydrogen phthalate*, m. p. 167—168°, were prepared. By means of strong nitric acid *methylisoborneol* is converted into *methylcamphor*, the *semicarbazone* of which, m. p. 251°, and *oxime*, m. p. 131—132°, were prepared. *Methylborneol*, b. p. 219—220°/758 mm., m. p. 183—184°, was prepared by acting on *methylcamphor* with sodium in alcoholic solution, and its *phenylurethane*, white needles, m. p. 108°, and *hydrogen phthalate*, m. p. 186°, were prepared. Oxidation of *methylcamphor* with alkaline potassium permanganate gives *methylciscamphoric acid*, m. p. 185—186°, which on heating is changed into the *anhydride*, m. p. 205—206°.

R. T.

Catalytic Oxidations with Platinum Black. I. **Oxidation of Buchu-camphor.** GUIDO CUSMANO (*Gazzetta*, 1923, **53**, i, 158—164).—When exposed in ethereal solution to the action of oxygen or air in presence of platinum black, buchu-camphor is rapidly converted principally into four compounds, forming two pairs of related compounds: (a) $C_{10}H_{18}O_4$ (I) and $C_{10}H_{16}O_3$ (II); these compounds, previously unknown, retain the cymene skeleton, and the first of them is readily converted into the second, which exhibits the phenolic behaviour of buchu-camphor and is named

provisionally oxybuchu-camphor. (b) $C_{10}H_{18}O_4$ (III) and $C_{10}H_{14}O_3$ (IV). Compound (IV) is an acid and was described by Semmler and Mackenzie (A., 1906, i, 373), who obtained it by the internal dehydration of an open-chain acid occurring among the products of oxidation of buchu-camphor by means of permanganate :



this open-chain acid may possibly represent an intermediate stage in the formation of compound (IV) by the action of lead peroxide, in presence of dilute sulphuric acid, on compound (III), to which is ascribed the formula $OH \cdot CHMe \cdot CH_2 \cdot CH_2 \cdot CHPr^{\beta} \cdot CO \cdot CO_2H$. This action of lead peroxide results also, at the same time, in elimination from acid (III) of carbon dioxide, with formation of another acid, which may have either the formula $OH \cdot CHMe \cdot CH_2 \cdot CH_2 \cdot CHPr^{\beta} \cdot CO_2H$, or a lactonic or ketonic structure. In addition to the above four products, the oxidation of buchu-camphor by oxygen in presence of platinum black yields small proportions of an oxythymoquinone and of another compound, not yet characterised.

The compound $C_{10}H_{18}O_4$ (I) crystallises in colourless, irregularly hexagonal laminæ of vitreous lustre, m. p. 126° (decomp.).

Oxybuchu-camphor, $C_{10}H_{16}O_3$, formed from the preceding compound either by heating it at its melting point or by decomposing its potassium salt by means of carbon dioxide, crystallises in colourless, transparent rhombs, m. p. $75-76^\circ$, has a faint, pleasant odour resembling that of thymol, volatilises unchanged, and in alcoholic solution gives a violet-black coloration with ferric chloride.

The acid, $C_{10}H_{18}O_4$ (III, see above), forms long, colourless, lustrous, acicular crystals containing water of crystallisation, which is lost in a desiccator. It is monobasic and forms crystalline ammonium and barium salts and a sparingly soluble silver salt.

For compound (IV), even when prepared as described by Semmler and Mackenzie (*loc. cit.*), the m. p. 190° is found, these authors giving m. p. 182° .
T. H. P.

Chemical Actions of Light. G. SCAGLIARINI and GIUSEPPINA SALADINI (*Gazzetta*, 1923, 53, i, 135-139).—The indirect auto-oxidations of certain compounds have been investigated.

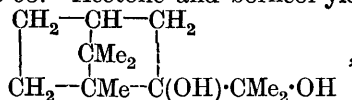
Fenchone and toluene, exposed for some months to the action of light in presence of oxygen and water, yielded carbon dioxide and benzoic and acetic acids. Under similar conditions, fenchone and alcohol gave carbon dioxide, acetic acid, a small proportion of oxalic acid, and a compound, b. p. 83° , containing 49.39% C and 11.32% H. Pinene and oxalic acid yielded a large proportion of resin, together with acetic acid.

Acetone and geraniol gave a compound,



as a liquid, b. p. $208-210^\circ/14 \text{ mm.}$, $d_{20} 0.96$. Acetone and menthol gave the compound $\begin{array}{c} CHMe \cdot CH_2 \cdot C(OH) \cdot CMe_2 \cdot OH \\ | \\ CH_2 \cdot CH_2 - CH \cdot CHMe_2 \end{array}$, b. p. $197-$

200°/15' mm., d 0.95. Acetone and borneol yielded the *compound*



b. p. 160°/20 mm., d 0.99.

T. H. P.

The Action of Hypochlorous Acid on Bornylene. GEORGE GERALD HENDERSON and JOHN ALEXANDER MAIR (T., 1923, 123, 1155—1161).

Pinocamphane. S. S. NAMETKIN and ANNA JARZEV (*Ber.*, 1923, 56, [B], 832—833).—Pinocamphone is converted by hydrazine hydrate at 190—200° into the corresponding *hydrazone*, a colourless liquid of unpleasant odour, b. p. 134—135°/22 mm.; d_4^{20} 0.9917, n_D^{20} 1.5155, which is transformed by potassium hydroxide in the presence of platinised clay or by sodium ethoxide, at 170—180° into *pinocamphane* (annexed formula), b. p. 163.5—164°/747 mm., 164.5—165°/763 mm., d_4^{20} 0.8558, n_D^{20} 1.4611. The product does not appear to be identical with the dihydropinene obtained previously by the authors by the catalytic hydrogenation of *l*- α -pinene by Sabatier's method.

H. W.

West Australian "Sandalwood Oil." B. SANJIVA RAO and J. J. SUDBOROUGH (*J. Ind. Inst. Sci.*, 1923, 5, 163—176).—The so-called West Australian sandalwood oil is derived from a tree (*Fusanus spicatus*, R.Br.) quite different from *Santalum album*, Linn., from which genuine East Indian sandalwood oil is obtained. It has d 15/15°, 0.957—0.972; n_D^{25} 1.5019—1.510; $[\alpha]_D^{25}$ -0.25° to -7.7°; total alcohols as santalol ($\text{C}_{15}\text{H}_{24}\text{O}$), 69.3—80.0%; esters as santalyl acetate, 2.3—6.5%; acid value, 2.9—5.0. The alcohols present are isomeric with the two santalols present in East Indian oil and have been termed α - and β -fusanols. These fusanols yield hydrogen phthalates and phenylurethanes. The fact that they react much more slowly than the santalols with phthalic anhydride indicates that they are probably secondary, not primary, alcohols. From their molecular refractions it is probable that both the fusanols are bicyclic compounds containing two olefine linkages. α -Fusanol, $\text{C}_{15}\text{H}_{24}\text{O}$, has b. p. 146—149°/5 mm., d_{15}^{15} 0.9775, n_D^{25} 1.5060, $[\alpha]_D^{25}$ +5.7°. β -Fusanol has b. p. 153—155°/5 mm., d_{15}^{15} 0.9753, n_D^{25} 1.5100, $[\alpha]_D^{25}$ +26°.

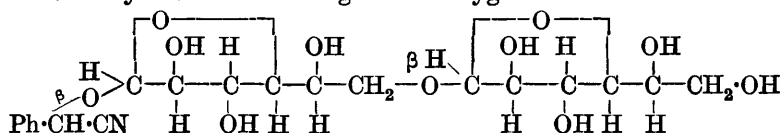
H. C. R.

β -Amyrin from Manilla Elemi Resin. II. ALEXANDER ROLLETT and KLOTHILDE BRATKE (*Monatsh.*, 1923, 43, 685—688; cf. this vol., i, 476).—Potassium persulphate converts β -amyrin, in acetic acid solution, in presence of sulphuric acid, into *oxy- β -amyrin acetate*, leaflets, m. p. 291—292°, soluble in concentrated sulphuric acid to give a yellow solution with a reddish-violet fluorescence. The acetate, on hydrolysis with methyl-alcoholic sodium hydroxide, gives *oxy- β -amyrin*, $\text{C}_{30}\text{H}_{47}\text{O} \cdot \text{OH}$, prisms, m. p. 200—

201°, behaving like the acetate with sulphuric acid, and giving that substance when treated with sodium acetate and acetic anhydride. Oxy- β -amyrin, on oxidation, in glacial acetic acid solution, with chromic anhydride, gives *oxy- β -amyrone*, $C_{30}H_{46}O_2$, needles, m. p. 216—217° (yellow solution in sulphuric acid; *oxime*, $C_{30}H_{46}O \cdot N \cdot OH$, m. p. 248—251° [decomp.]). E. E. T.

The Glucosides. HENRI HÉRISSEY (*Bull. Soc. chim.*, 1923, [iv], 33, 349—413).—Lectures delivered before the Société chimique de France, January 18th, 20th, 1922. G. F. M.

The Biose of Amygdalin. RICHARD KUHN (*Ber.*, 1923, 56, [B], 857—862).—As a result of their experiments on the methylation of amygdalin, Haworth and Leitch (*T.*, 1922, 121, 1921) have drawn the conclusion that the disaccharide of amygdalin has the structure of maltose, but the available evidence was not sufficient to enable them to decide whether its stereochemical representation should be that of a glucose- α - or - β -glucoside. This point has now been elucidated in favour of the latter conception by observation of the mutarotation of the glucose which is liberated by the rapid enzymatic hydrolysis from the glucoside. The following constitution may therefore be assigned to amygdalin:



The hydrolysis of amygdalin under the influence of emulsin occurs in accordance with the equation $C_{20}H_{27}O_{11}N + 2H_2O = 2C_6H_{12}O_6 + C_6H_5 \cdot CHO + HCN$. Three possibilities of mutarotation for the liberated glucose present themselves, (1) both molecules are liberated in the highly active α -form, thus leading to a strongly diminished rotation; (2) α - and β -glucose are produced in equimolecular proportion due to the recession of the specific rotation from 64.5° to 52.5°, and (3) two molecules of β -glucose are produced, thus leading to a subsequent exaltation of the specific rotation. For the experiments, the aqueous solution of amygdalin is mixed with a suitable phosphate buffer and emulsin; after a suitable interval the reaction is interrupted by poisoning the ferment by mercuric chloride or removing it by adsorption with aluminium hydroxide; the specific rotation of the solution is subsequently found to increase. H. W.

The Constitution of the Glucoside, Sinigrin. FRITZ WREDE, EMIL BANIK, and OTTO BRAUSS (*Z. physiol. Chem.*, 1923, 126, 210—218).—Thioglucose obtained from the glucoside, sinigrin, is not identical with that prepared synthetically (cf. Wrede, A., 1922, i, 525), as shown (a) by the fact that it is levorotatory, whilst that prepared synthetically is dextrorotatory, and (b) by the comparison of their penta-acetyl derivatives. That from sinigrin gives $[\alpha]_D$ about -50° , whilst that prepared synthetically gives $[\alpha]_D +1.6^\circ$ (in ethyl acetate). It is suggested that these are the

α - and β -forms which are presumably more stable than the corresponding forms of glucose. Sinigrin has been obtained in an anhydrous form, $C_{10}H_{16}O_9NS_2K$, compact, white, glistening needles, m. p. 79° , $[\alpha]_D -16.13^\circ$ (in water). This indicates that the decomposition of sinigrin by the enzyme myrosin is a simple hydrolysis, $C_{10}H_{16}O_9NS_2K + H_2O = C_6H_5 \cdot NCS + C_6H_{12}O_6 + KHSO_4$. W. O. K.

Some Additive Compounds of Digitonin. A. WINDAUS and R. WEINHOLD (*Z. physiol. Chem.*, 1923, **126**, 299—307).—The following additive compounds of digitonin with alcohols and phenols are described. *α -Naphtholdigitonin*,

$C_{55}H_{90}O_{29}, C_{10}H_8O, 8H_2O$, very fine needles. *β -Naphthol-digitonin*, $C_{55}H_{90}O_{29}, C_{10}H_8O, 10H_2O$. *p-Bromophenol-digitonin*, $C_{55}H_{90}O_{29}, C_6H_5OBr, 8H_2O$, fine needles. *Phenyl mercaptan-digitonin*, $C_{55}H_{90}O_{29}, C_6H_5S, 6H_2O$. *Carvomenthol-digitonin*, $C_{55}H_{90}O_{29}, C_{10}H_{20}O, 10H_2O$, fine needles. *l- α -Terpineol-digitonin*, $C_{55}H_{90}O_{29}, C_{10}H_{18}O, 6H_2O$, very fine needles. *d- α -Terpineol-digitonin*, $C_{55}H_{90}O_{29}, C_{10}H_{18}O, 8H_2O$. *ac-Tetrahydro- β -naphthol-digitonin*, $C_{55}H_{90}O_{29}, C_{10}H_{12}O, 8H_2O$, fine needles. *Phenylmethylcarbinol-digitonin*. *sec-Octylalcohol-digitonin*. These compounds are decomposed, by distillation either in a vacuum, or in steam.

W. O. K.

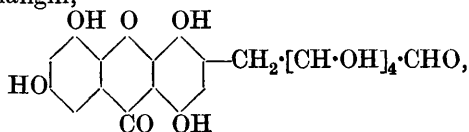
Betulin. K. ALB. VESTERBERG (*Ber.*, 1923, **56**, [B], 845; cf. Vesterberg, A., 1922, i, 825; Schulze and Pieroh, A., 1922, i, 1045; Dischendorfer, this vol., i, 123).—Elementary analysis and, in particular, determination of the saponification number of crystalline betulin diacetate, m. p. $218-218.5^\circ$, lead the author to regard the presence of 30 carbon atoms in the betulin molecule as definitely established. In the formula, $C_{30}H_{48}(OH)_2$, which has also been proposed by Dischendorfer, the uncertainty with regard to the number of hydrogen atoms does not exceed two. H. W.

Betulin. III. IVAN KONSTANTINOVITSCH TRAUBENBERG (*J. Russ. Phys. Chem. Soc.*, 1917, **49**, 381—394; cf. A., 1912, i, 260, 972).—*Betulin dibutyrate*, $C_{24}H_{38}O_2(C_4H_7O_2)_2$, m. p. 107° , has been prepared, thus establishing the hydroxylic nature of the two oxygen atoms of betulin. Betulin, on oxidation with potassium permanganate in acetic acid solution, gives *oxybetulin*, $C_{24}H_{40}O_3$, m. p. $205-206^\circ$, which yields an *acetate*, m. p. $181-182^\circ$; the latter derivative being also obtained by the oxidation of betulin diacetate. Oxybetulin, on oxidation, gives *dehydrodioxybetulin*, $C_{24}H_{38}O_4$, m. p. 256° , which on further oxidation gives a substance not melting below 310° , and containing inorganic matter. As final products of oxidation were obtained *betulinic acid*, $C_{14}H_{22}O_3$, m. p. 277° , and a *lactone*, $C_{15}H_{22}O_3$, m. p. 303° . Betulinamic acid, $C_{22}H_{32}O_{10}N_2$, is shown to contain one nitro- and one nitrile group. From the above and preceding articles, it is concluded that betulin is a substance of the sterol type, and contains one primary and one secondary hydroxyl group, four saturated rings, and one double linking, situated on the chain joining the rings. One of the hydroxyl groups must be in the β - or γ -position to this double linking.

R. T.

The Parent Substance of Indian Yellow. WILHELM WIECHOWSKI (*Arch. expt. Path. Pharm.*, 1923, 97, 462—488).—If mangin, which has been extracted from mango leaves, is fed to rabbits, euxanthic acid (Indian yellow) is excreted in the urine. It thus appears that mangin is the parent substance of Indian yellow.

Mangin, $C_{16}H_{18}O_{11}$, m. p. 273° , $[\alpha]_D -46^{\circ}$ in alcohol, is only slightly soluble in the usual neutral organic solvents. It crystallises from alcoholic solution in needles, from water in prisms. It is not hydrolysed by emulsin, invertase, or other ferments, and it forms an *octa-acetyl* derivative, an *octabenzoyl* derivative, and a *lead salt*, $C_{19}H_{14}O_{11}Pb_2$. When heated for a long time with hydrochloric acid, it yields lævulic acid and tetrahydroxyxanthone, which was isolated as the *lead salt*. The following formula is assigned to mangin,



the position of the hydroxy-groups being uncertain.

Euxanthic acid, $C_{19}H_{18}O_{11}$, has the following constants: m. p. $156\text{--}158^{\circ}$ (decomp.), $[\alpha]_D -79.43^{\circ}$, -81.45° in alcohol.

W. O. K.

Preparation of Melanin from Benzene. OSCAR ADLER (*Biochem. Z.*, 1923, 137, 201—205).—By treatment of benzene with successive portions of 3% hydrogen peroxide in presence of 10% aqueous ferric chloride solution, a 2.7% yield of *benzene-melanin acid* is formed, soluble in dilute alkalis and alcohols. When heated at 270° it is converted into *benzenemelanin*, a black, amorphous powder insoluble in alkalis or organic solvents.

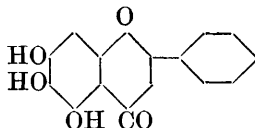
H. K.

Synthesis of Dicyanine-A. S. PALKIN (*Ind. Eng. Chem.*, 1923, 15, 379—381).—The conditions affecting the synthesis of dicyanine-A from 6-ethoxy-2:4-dimethylquinoline ethiodide were studied and variations tried in the kind of solvent used, concentration of hydroxyl-ion, type of alkali, catalysts, water, oxygen, time, and temperature. No solvent was found superior to ethyl alcohol, but excellent results were obtained with sodium sulphide as the alkali salt in 95% alcohol. Chloroform acts as a catalyst in the presence of sodium ethoxide, the yield of dye obtained being about twelve times that obtained by Mikeska, Haller, and Adams. The optimum conditions were, 1.5 c.c. of chloroform per 1 g. of intermediate, 25 g. of sodium sulphide ($Na_2S \cdot 9H_2O$) in 100 c.c. of 95% alcohol, 1 g. of intermediate to 25 c.c. of alcohol and a temperature of 50° for thirty minutes. The dye produced was tested by the Bureau of Standards and found to be an efficient sensitiser.

H. C. R.

Baicalin, a New Flavone-Glycuronic Acid Compound from the Roots of *Scutellaria baicalensis*. KEITA SHIBATA, SHÔJIRO IWATA, and MAKOTO NAKAMURA (*Acta Phytochim.*, 1923, 1, 105—139).—The name *scutellarin* was applied by Takahashi to a crystalline compound from *Scutellaria baicalensis*, to which he ascribed

the formula $C_{10}H_8O_3$ (A., 1890, 64). The same name has, however, been accepted for a flavone-glycuronic acid compound found by Molisch and Goldschmiedt (A., 1902, i, 48) in other species of *Scutellaria*, and it is proposed to call Takahashi's compound *wogonin* (from "wogon," the Japanese term for the root). A new compound, *baicalin*, closely allied to scutellarin, occurs in the roots of *S. baicalensis*, and can be extracted from the roots by boiling 50% alcohol, the yield being 12.5% of the weight of dry root. It is a bright yellow, crystalline substance, $C_{21}H_{18}O_{11}$, m. p. 223°. When hydrolysed with concentrated sulphuric acid, it is decomposed into glycuronic acid and a flavone derivative, *baicalein*, $C_{15}H_{10}O_5$, yellow prisms, m. p. 264—265° (decomp.). A great deal of evidence indicates that baicalein is a trihydroxyflavone, an hydroxychrysin with all three hydroxy-groups in the one phenyl ring. By alkaline hydrolysis, baicalin gives acetophenone, and when fused with potassium hydroxide both baicalin and baicalein give benzoic acid. Baicalein appears to be identical with the 5:6:7-trihydroxy-



flavone (annexed formula) prepared synthetically by Bargellini (A., 1919, i, 545). Evidence that condensation with glycuronic acid to form baicalin takes place at the 6-hydroxy-group is furnished by the observation that baicalin is not oxidised by chloropentaminecobaltichloride, which gives a strong colour reaction with *o*-dihydroxy-compounds but not with corresponding meta-compounds. Scutellarin likewise fails to give a reaction with this reagent, and must therefore be constituted similarly to baicalin.

Pentabenzoylscutellarin forms a white, microcrystalline powder, m. p. 237—238° (decomp.).

Baicalin gives with ferric chloride in alcoholic solution a dark green colour, and with lead acetate an orange-red precipitate. It dissolves in alkalis with a yellow colour, and reduces ammoniacal silver nitrate in the cold. It is difficult to alkylate, but forms with diazomethane in acetone solution a *monomethyl* derivative, m. p. 211—212° (decomp.); this contains a free carboxy-group. *Dibromobaicalin* softens above 270°. Baicalin is laevorotatory, $[\alpha]_D^{25} -144.9^\circ$. *Tetracetylbaicalin* forms microscopic prisms containing $1H_2O$, m. p. 256—257°. The fact that only a tetra-acetyl derivative is formed indicates that the glycuronic acid is in the lactone form. A small quantity of what appeared to be a *penta-acetylbaicalin*, m. p. 212—213° (decomp.), was also obtained. *Tetrabenzoylbaicalin* forms a grey, microcrystalline powder, m. p. 229—230°.

Tribenzoylbaicalein forms small prisms, m. p. 199.5°. Triacetylbaicalein agrees in properties with Bargellini's triacetyl derivative of 5:6:7-trihydroxyflavone (*loc. cit.*). Free baicalein is present with baicalin in the roots of the plant.

Further investigation of wogonin shows that the substance as analysed by Takahashi contained water of crystallisation. The correct formula is $C_{16}H_{12}O_4$, and it contains a methoxy-group. *Acetylwogonin*, $C_{18}H_{14}O_5$, forms long, white needles, m. p. 152—

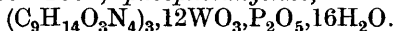
153°; *benzoylwogonin* forms yellowish-white needles, m. p. 170°; methylwogonin, $C_{16}H_{11}O_3 \cdot OMe, H_2O$, forms yellowish-white needles, m. p. 180—181°.

Baicolein and scutellarein, like other hydroxyflavones (cf. this vol., ii, 360) show two absorption bands in the ultra-violet, the bands showing shifts such as would be expected from the constitutions of the compounds. In baicalin, the first band disappears, only a broad band at 3500 remaining, but in scutellarin both bands persist, perhaps through the influence of the 4'-hydroxy-group. Wogonin has an unusual spectrum with only one band, at 3500, but acetylwogonin, like triacetylbaicalein, shows the true flavone spectrum.

The green parts of *S. baicalensis* are found to contain scutellarin. The relation between the scutellarin of the leaves and the baicalin of the roots is a question of great biochemical interest.

E. H. R.

The Extractive Substances of Muscle. Carnosine and its Derivatives. IVAN A. SMORODINCEV (*J. Russ. Physiol.*, 1919, 2, 298).—The author reviews the literature of the subject and describes the following new salts of the dipeptide: *Sulphate*, m. p. 238—240°; *orthophosphate*, m. p. 205—207°; *metaphosphate*, m. p. 200—203°; *iodate*, m. p. 188—190°; *oxalate*, m. p. 216—218°; *tartrate*, m. p. 195—200°; *phosphotungstate*,



The *phenylcarbamido*-derivative, m. p. 178—180°, has also been prepared. Carnosine is hydrolysed by erepsin.

E. S.

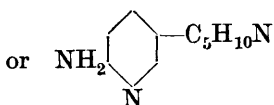
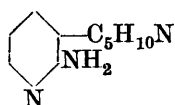
The Alkaloids of *Corydalis cava*. ERNST SPÄTH, ERICH MOSETTIG, and OTHMAR TRÖTHANDL (*Ber.*, 1923, 56, [B], 875—879).—During the course of preparation of corydaline from *Corydalis cava*, two new alkaloids, *d*-tetrahydropalmatine and *d*-corypalmine, have been isolated; in the latter, one of the four methoxy-groups of *d*-tetrahydropalmatine is replaced by hydroxyl.

The alkaloids from *Corydalis cava* are dissolved in ether and agitated with sodium hydroxide solution to remove phenolic substances. The fully alkylated compounds are dissolved in hydrochloric acid and, from this solution, *d*-tetrahydropalmatine hydrochloride separates in the course of a few days. *d*-Tetrahydropalmatine, $C_{21}H_{25}O_4N$, forms colourless crystals which exhibit distinct triboluminescence when crushed. It has m. p. 142°, $[\alpha]_D^{25} +292.5^\circ$ in alcoholic solution. The constitution of the alkaloid is established by its dehydrogenation with iodine and ethyl alcohol and treatment of the product with magnesium methyl iodide which yields a compound identical with that obtained previously by Späth and Lang (A., 1922, i, 166) from palmatine and magnesium methyl iodide. The conception that the dehydro-compound is palmatine is confirmed by direct comparison of the quaternary iodides and of the corresponding tetrahydro-derivatives.

The bulk of the bulbocapnine is removed from the phenolic alkaloids; fractional extraction of the solution of the remainder in chloroform with very dilute hydrochloric acid gives corybulbine

and corypalmine. The former has been considered by Dobbie, Lander, and Paliatsens (T., 1901, 79, 89) as corydaline in which one methoxy-group has suffered demethylation. This conception is confirmed by its conversion into dehydrocorybulbine, methylation of the latter, and reduction to the tetrahydro-compound, which is found to be identical with *r*-corydaline, m. p. 135°. The latter is also obtained by the methylation of corybulbine with diazomethane. *Corypalmine* forms small, colourless crystals, m. p. 236—237°, $[\alpha]_D^{25} +280^\circ$ when dissolved in chloroform; it gives *d*-tetrahydro-palmatine when methylated. H. W.

2-(or 6-)Aminonicotine. A. E. TSCHITSCHIBABIN and L. A. BUCHHOLZ (*J. Russ. Phys. Chem. Soc.*, 1920, 50, 548—552).—The action of sodamide on nicotine in the presence of an indifferent solvent such as vaseline or toluene leads to the formation of an amino-derivative in a manner similar to that observed with other derivatives of pyridine (see A., 1915, i, 590). The new substance



may be the 2- or the 6-amino-compound (annexed formulæ) and is obtained in a yield of about 10%.

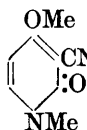
After crystallisation from light petroleum it melts at 124—125° and forms biaxial leaflets or plates, probably of the monoclinic system; the *dipicrate* forms long, thin yellow needles, m. p. 223—225°; the *chloroplatinate*, red prisms, contains 2H₂O, m. p. 244—245°. The action of nitrous acid in the presence of sulphuric acid on aminonicotine leads to 2-(or 6-)hydroxynicotine, crystals, m. p. 121—123°; the *dipicrate* forms large, lustrous needles, m. p. 196—198°, and the *chloroplatinate*, small orange crystals, m. p. 246—248°, also occurring in the form of red prisms containing 3H₂O. G. A. R. K.

The Morphine Group. I. A Discussion of the Constitutional Problem. JOHN MASSON GULLAND and ROBERT ROBINSON (T., 1923, 123, 980—998).

The Morphine Group. II. Thebainone, Thebainol, and Dihydrothebainone. JOHN MASSON GULLAND and ROBERT ROBINSON (T., 1923, 123, 998—1011).

Yohimbine (Quebrachine). II. apo-Yohimbine and Deoxy-yohimbine. GEORGE BARGER and ELLEN FIELD (T., 1923, 123, 1038—1043).

The Constitution of Ricinine. ERNST SPÄTH and GEORG KOLLER (*Ber.*, 1923, 56, [B], 880—887).—The authors have succeeded in replacing the methoxy-group of ricinine by hydrogen and thereby obtaining a substance which they designate ricinidine. The compound is shown by direct synthesis to be 3-cyano-1-methyl-2-pyridone, so that ricinine must be regarded as 3-cyano-4-methoxy-1-methyl-2-pyridone (annexed formula). The constitutions assigned tentatively to ricinine (Späth and Tschelnitz, A., 1922, i, 571) are therefore withdrawn.



Ricinine is converted by potassium hydroxide into ricinic acid (cf. Böttcher, A., 1918, i, 304), which is transformed by phosphoryl chloride at 100° into 4-chloro-3-cyano-1-methyl-2-pyridone, $C_7H_5ON_2Cl$, m. p. 159°; the latter is reconverted by a solution of sodium in methyl alcohol into a mixture of ricinic acid and ricinine. Hydrogenation of the chloro-compound in the presence of palladised barium sulphate leads to the production of ricinidine [3-cyano-1-methyl-2-pyridone], b. p. 243°/18 mm., m. p. 140°. The latter is hydrolysed successively to the corresponding amide, m. p. 216°, and to the carboxylic acid, $C_7H_7O_3N$, colourless needles, m. p. 184°. The elucidation of the constitution of ricinine depends on the recognition of this acid as 1-methyl-2-pyridone-3-carboxylic acid. For this purpose, the three possible acids, viz. 2-pyridone-1-acetic acid, and 1-methyl-2-pyridone-3- and -6-carboxylic acids, have been synthesised.

2-Pyridone-1-acetic acid, $CH \begin{smallmatrix} \text{CH} \cdot \text{CO} \\ \text{CH} : \text{CH} \end{smallmatrix} > N \cdot CH_2 \cdot CO_2H$, m. p. 220—

223°, is obtained from 2-methoxypyridine and methyl iodoacetate. 1-Methyl-2-pyridone-6-carboxylic acid is prepared with difficulty by the action of methyl iodide on the di-silver salt of 2-hydroxypyridine-6-carboxylic acid; it has m. p. 247—248°. Similar treatment of the di-silver salt of 2-hydroxypyridine-3-carboxylic acid and subsequent hydrolysis of the product leads to the isolation of 1-methyl-2-pyridone-3-carboxylic acid, m. p. 184°, which is identical with the acid obtained from ricinidine; in this instance, also, methylation is a matter of difficulty, and is more conveniently effected by treating the dry di-sodium salt with methyl iodide. 1-Methyl-2-pyridone-3-carboxylic acid is converted by successive treatment with thionyl chloride and ammonia into the amide, m. p. 216—217·5° [identical with that obtained during the hydrolysis of ricinidine (see above)], which is further transformed by thionyl chloride or phosphoryl chloride into ricinidine.

Further proof of the identity of ricinidine with 3-cyano-1-methyl-2-pyridone is deduced from the observation that it is converted by phosphoryl chloride and phosphorus pentachloride at 150° into 2-chloro-3-cyanopyridine, m. p. 103—105°. The synthesis of the latter substance is effected by the successive action of phosphoryl chloride and phosphorus pentachloride and ammonia on 2-hydroxypyridine-3-carboxylic acid whereby 2-hydroxypyridine-3-carboxylamide, m. p. 163—164°, is obtained which is transformed by phosphoric oxide into 2-chloro-3-cyanopyridine. H. W.

The Nitration of 2-Aminopyridine. A. E. TSCHITSCHIBABIN and I. G. BYLINKIN (*J. Russ. Phys. Chem. Soc.*, 1920, 50, 471—483; cf. A., 1922, i, 573).—It has already been shown (cf. A., 1916, i, 224; 1915, i, 591) that the nitration of 2-aminopyridine leads to the formation of two isomeric nitro-derivatives, the main product being 5-nitro-2-aminopyridine, and the other is now shown to be the 3:2-compound. The formation of the latter is favoured by raising the temperature during the isomerisation of the nitroamine to the nitro-compound (cf. above).

When diazotised in the presence of sulphuric acid, the 3:2-compound (m. p. 162°) yields 3-nitro-2-hydroxypyridine, yellow needles, from hot water, m. p. 224°, readily soluble in dilute alkali hydroxides. Diazotisation in hydrochloric acid solution leads to 2-chloro-3-nitropyridine, flattened needles, m. p. 101—102°, insoluble in alkali hydroxides, but feebly basic. All attempts to reduce the 3:2-compound to the corresponding diamine failed.

2-Chloro-5-nitropyridine obtained by the diazotisation of the 5:2-isomeride (cf. A., 1915, i, 591) yields, on reduction with stannous chloride, the corresponding amino-compound identical with that prepared by Mills and Widdows (T., 1908, 93, 1372), m. p. 81—82°. The replacement of the amino-group in this compound by bromine by the Sandmeyer reaction leads to 2-chloro-5-bromopyridine, white plates, m. p. 71°, possessing a strong and characteristic odour. The amino-group in the compound, m. p. 81—82°, like that of 3-aminopyridine, is readily diazotisable, and the diazonium compounds prepared in hydrochloric acid solution couple with α - and β -naphthol in alkaline solution, giving red substantive cotton dyes which gradually change to brownish-red and orange, respectively; only the latter is fairly stable to acids.

5-Nitro-2-hydroxypyridine (cf. A., 1915, i, 591) is converted through the silver salt into 5-nitro-2-ethoxypyridine, white plates, m. p. 72°. The reduction of this compound with stannous chloride gives a very unstable, oily amine, which is converted by acetic anhydride into 5-acetamido-2-ethoxypyridine, flattened needles, m. p. 122°. G. A. R. K.

The Bromination of 2-Aminopyridine. A. E. TSCHITSCHIBABIN and (MLLE) V. S. TIASHELOVA (*J. Russ. Phys. Chem. Soc.*, 1920, 50, 483—492).—The nuclear hydrogen atoms of 2-aminopyridine, unlike those of pyridine itself, appear to be readily substituted (cf. A., 1915, i, 591; 1916, i, 224) and bromination proceeds easily, best of all in the presence of one molecular proportion of sulphuric acid. The products are 5-bromo-2-aminopyridine, flattened prisms, m. p. 137° (*picrate*, yellow needles, m. p. 257°), and 3:5-dibromo-2-aminopyridine, white needles, m. p. 105°. The two compounds are separated by means of light petroleum in which the monobromo-compound is sparingly soluble. The dibromo-compound is identical with that described by Fischer and Chur (A., 1916, i, 741) and gives on treatment with nitrous acid the corresponding dibromohydroxy-compound, m. p. 207—208°, previously prepared by Koenigs and Geigy (A., 1884, 1195, 1368).

Diazotisation of the monobromo-compound in the presence of sulphuric acid (cf. preceding abstract) leads to 5-bromo-2-hydroxypyridine, large, sparkling prisms, m. p. 177—178°. Diazotisation in hydrochloric acid solution gives 2-chloro-5-bromopyridine, colourless scales, m. p. 71°, with an odour reminiscent of dibromobenzene, volatile in steam, identical with the substance obtained by Tschitschibabin and Bylinkin (preceding abstract). On treatment with sodamide and amyl nitrite (Tschitschibabin and Riasancev, A.,

1916, i, 224) an unstable substance is obtained which shows the reactions of an *isodiazoxide*, giving a red dye with β -naphthol and yielding with hydrochloric acid the chlorobromo-compound mentioned above and with hydrobromic acid 2 : 5-*dibromopyridine*, flattened needles, m. p. 94—95°, which sublimes. Nitration of the monobromo-compound dissolved in concentrated sulphuric acid leads to the *nitroamine*, microscopic needles, m. p. 181° (decomp.), which when heated with sulphuric acid isomerises to 5-bromo-3-nitro-2-aminopyridine, large yellow needles from alcohol, or short needles or prisms from benzene, m. p. 205°. G. A. R. K.

The Bromination of Nitro-2-aminopyridines. A. E. TSCHITSCHIBABIN (*J. Russ. Phys. Chem. Soc.*, 1920, 50, 492—494).—It has been shown (preceding abstract) that the bromination of 2-aminopyridine leads to 3- and 5-bromo-compounds. The two nitroaminopyridines should therefore yield two different monobromo-derivatives, one of which should be identical with the nitration product of 5-bromo-2-aminopyridine. This is found to be the case. 5-Nitro-2-aminopyridine, m. p. 188° (cf. A., 1915, i, 591), gives on bromination in the presence of dilute sulphuric acid (20 per cent.) a good yield of 3-bromo-5-nitro-2-aminopyridine, yellow needles, m. p. about 215° (decomp.); the compound is slowly decomposed by light. 3-Nitro-2-aminopyridine, m. p. 162°, gives, when brominated under similar conditions, 5-bromo-3-nitro-2-aminopyridine, m. p. 205°, identical with that obtained by Tschitschibabin and Tiasheleva (preceding abstract), thus confirming the constitution previously assigned to the compound melting at 162°. G. A. R. K.

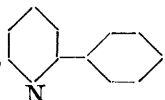
The Sulphonation of 2-Aminopyridine. A. E. TSCHITSCHIBABIN and (MILLE) L. S. TIASHELOVA (*J. Russ. Phys. Chem. Soc.*, 1920, 50, 495—497).—Whilst pyridine is sulphonated with considerable difficulty, 2-aminopyridine undergoes sulphonation almost as readily as aniline. When it is heated with fuming sulphuric acid (10% SO_3) at 180° for four to five hours, a *sulphonic acid*, nodular aggregates of white crystals, m. p. 326—327° (decomp.), is produced. The salts of this acid with metals of the alkali group are very soluble in water, those of calcium, strontium, and barium less so. The sulphonic acid dissolves with difficulty in dilute acids. The orientation of the sulphonic acid is not yet certain, but it is probably the 2 : 5-aminosulphonic acid. On treatment with nitrous acid, it passes into the corresponding 2-hydroxysulphonic acid which is isolated in the form of its hydrated sodium salt, $\text{OH} \cdot \text{C}_5\text{H}_3 \cdot \text{SO}_3\text{Na} \cdot 1\frac{1}{2}\text{H}_2\text{O}$, which loses its water of crystallisation at 125°. Aqueous solutions of the salt give crystalline precipitates with barium and calcium chlorides. G. A. R. K.

The Phenylation of 2-Aminopyridine by Ullmann's Method. A. E. TSCHITSCHIBABIN (*J. Russ. Phys. Chem. Soc.*, 1920, 50, 497—502).—2-Aminopyridine readily reacts with bromo- or iodo-benzene in the presence of potassium carbonate and metallic copper, the
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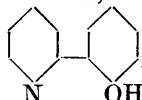
reaction product being separated into the constituents by distillation at atmospheric pressure. The fraction up to 240° contains unchanged starting material, whilst the oil boiling between 240° and 345° consists mainly of 2-anilinopyridine, m. p. 108° (Fischer, A., 1903, i, 52; 1899, i, 635), short, thick prisms; the *picrate* forms prisms, m. p. 222° . 2-Diphenylaminopyridine constitutes the highest fraction, b. p. $345\text{--}370^{\circ}$, and forms plates, m. p. 104° . The *picrate*, prepared in alcoholic solution, melts at 174° , and forms plates or long needles; it is more soluble in alcohol and acetone than 2-anilinopyridine *picrate*. G. A. R. K.

The Diazotisation and Diazo-reactions of 2-Aminopyridine.

A. E. TSCHITSCHIBABIN (*J. Russ. Phys. Chem. Soc.*, 1920, 50, 502—511).—Attempts made to introduce the pyridine nucleus into organic compounds by the Grignard reaction on 2-bromo- and 2-iodo-pyridine failed; the preparation of these substances from sodium 2-pyridineisodiazoxide (A., 1916, i, 224) has been improved and is described. Successful results are, however, obtained by the interaction of the latter substance with phenol. After removing phenol, etc., three substances are obtained, one of which may be readily separated owing to its insolubility in alkali hydroxides. This consists of 2-phenoxypyridine, b. p. $277\text{--}277.5^{\circ}$, m. p. $46\text{--}48^{\circ}$, possessing an odour reminiscent of diphenyl ether, the orange *chloroplatinate*, small prisms, m. p. $175\text{--}177^{\circ}$, and the *picrate* were also prepared. The two compounds soluble in alkali are isomeric pyridylphenols, and may be separated by crystallisation from benzene. The less soluble compound separates in white leaflets or thick, lustrous, hexagonal plates containing a molecule of benzene of crystallisation; after removing the latter it melts at $159\text{--}160^{\circ}$ and is readily soluble both in dilute acids and alkalis, being precipitated from the latter by carbon dioxide. It is probably

p-2-pyridylphenol, . The *hydrochloride* forms long,

slender needles, m. p. $215\text{--}218^{\circ}$; the *chloroplatinate*, large, orange-yellow, flattened needles, m. p. $210\text{--}211.5^{\circ}$ (decomp.), whilst the sparingly soluble *picrate* is obtained in nodular, crystalline aggregates, m. p. $202\text{--}203^{\circ}$. The second, more soluble pyridylphenol

is probably o-2-pyridylphenol, , and is obtained in large,

greenish-yellow prisms, m. p. 56° ; it is less soluble in alcohol than the preceding compound and its phenolic properties are less marked; the yellow colour may perhaps be due to a quinonoid structure. The *hydrochloride* is obtained in a hydrated form, colourless prisms, m. p. 56° , which lose water in a desiccator, the anhydrous substance melting at $167\text{--}170^{\circ}$. The *chloroplatinate*, microscopic needles, softens at $227\text{--}228^{\circ}$. The *picrate* forms slender, long, yellow needles, m. p. 174° . G. A. R. K.

Di-2-pyridylamine. A. E. TSCHITSCHIBABIN and M. A. VOROBIEV (*J. Russ. Phys. Chem. Soc.*, 1920, **50**, 519—522).—Di-2-pyridylamine was originally obtained by Tschitschibabin and Zeide (A., 1915, i, 590), and also by Steinhäuser and Diepolder (A., 1916, i, 739), by heating 2-chloropyridine with 2-aminopyridine in the presence of zinc chloride or barium oxide. It is now shown that the best method of preparing this substance consists in heating 2-aminopyridine with its hydrochloride; a yield of 40% of the theoretical is obtained if the reaction mixture is heated in sealed tubes at 240—250° for twenty to thirty hours. The *hydrochloride* of 2-aminopyridine is prepared by the usual methods, and is obtained in the form of an extremely deliquescent solid, melting at about 86°, and, after drying in a desiccator, containing 2H₂O, which it loses at 105°. Di-2-pyridylamine forms slender, colourless needles, m. p. 95°. The specimen previously described (cf. above) melted at 84°, but on cooling solidified and melted at 95°; the substance thus appears to be polymorphous. The *hydrochloride* forms lustrous prisms, m. p. 115—116°, containing 3H₂O (cf. however, A., 1916, i, 739), which are slowly lost on drying. The *picrate* of the base forms needles, m. p. 225°. The *sulphate* forms hair-like needles, m. p. 248°. G. A. R. K.

The Investigation of 2 : 6-Diaminopyridine. A. E. TSCHITSCHIBABIN and O. A. ZEIDE (*J. Russ. Phys. Chem. Soc.*, 1920, **50**, 522—533).—2 : 6-Diaminopyridine, prepared as before (A., 1915, i, 590), is shown to be a mono-acid base; like 2 : 6-dihydroxypyridine (Gattermann and Skita, A., 1916, i, 419), it couples with aromatic diazo-compounds. The action of nitrous acid on the diamine does not lead to the formation of a colouring matter corresponding with Bismarck brown, but to a 3-nitroso-compound.

The *hydrochloride* of the base is obtained in the form of very unstable white needles. The *sulphate*, (C₅H₇N₃)₂.H₂SO₄.H₂O, forms yellow prisms. The *picrate* forms long, dark-yellow needles, m. p. 240°.

A *monoacetyl* derivative could not be obtained; the *diacetyl* compound, readily formed by the action of acetic anhydride on the base in benzene or glacial acetic acid, forms white, lustrous plates, m. p. 203°. The direct nitration of 2 : 6-diaminopyridine gives a very poor yield of the nitro-derivative, but the diacetyl compound is readily nitrated in the presence of concentrated sulphuric acid, giving a 70% yield of 3-nitro-2 : 6-diacetamidopyridine, light yellow needles, m. p. 192—193°; it appears to form salts with hydrochloric and sulphuric acids. The compound is readily deacetylated by hydrochloric acid, giving 3-nitro-2 : 6-diaminopyridine, lustrous yellow plates, m. p. 230° (blackens). The action of nitrous acid on 2 : 6-diaminopyridine under a variety of conditions, but best of all in the presence of acetic acid, leads to 3-nitroso-2 : 6-diaminopyridine, which crystallises in lustrous, ruby-red needles; it blackens and decomposes without melting when heated; it forms yellow salts with acids, and does not give Liebermann's nitroso-reaction. The mother-liquors from the preparation of this compound readily assume a green or blue coloration, probably due to the presence of readily oxidisable

hydroxypyridines. The nitroso-compound, on oxidation with hydrogen peroxide in ammoniacal solution, yields the nitro-compound described above. The reduction of the nitroso-compound with sodium hyposulphite or zinc dust does not lead to the desired triaminopyridine, owing to the extreme readiness with which the reduction product is oxidised to black colouring matters.

Benzenediazonium chloride couples with 2:6-diaminopyridine, yielding the compound $C_{11}H_{11}N_5$, orange-yellow needles, m. p. 137°, soluble in water with an orange colour, and in sulphuric or hydrochloric acid with a red colour. The solution in hydrochloric acid is decolorised by zinc dust, but rapidly assumes a green colour when exposed to the air.

With diazotised benzidine, a red compound, $C_{22}H_{10}N_{10}$, is produced which crystallises in lustrous, bronze-coloured plates and yields bluish-black, sparingly soluble salts with acids; it dissolves in sulphuric acid with an intense blue colour. G. A. R. K.

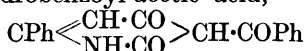
6-Amino-2-methylpyridine. O. A. ZEIDE (*J. Russ. Phys. Chem. Soc.*, 1920, 50, 534—543).—The preparation of 6-amino-2-methylpyridine, first obtained by Tschitschibabin and Zeide (A., 1915, i, 590) has been improved in details and is described. The compound is a mono-acid base the reactions of which are shown to be analogous to those of 2-aminopyridine (compare preceding abstracts). The pure base is a snow-white, crystalline mass, m. p. 40°, which is deliquescent. The following salts were prepared: the *hydrochloride* forms white needles; the *hydrobromide*, long, white prisms, m. p. 149—150°; the *hydriodide*, yellow prisms, m. p. 162°; the *sulphate*, hard, colourless prisms; the *nitrate*, white needles, m. p. 168°; the *picrate*, small, yellow needles, m. p. 202°; *chloroplatinate*, flat, orange, rhombic prisms, m. p. 209°.

The *acetyl* compound, prepared by means of acetic anhydride in benzene solution, forms elongated, white prisms, m. p. 90°, readily soluble in water, alcohol, ether, or chloroform, sparingly soluble in cold petroleum. The *benzoyl* compound, prepared by the Schotten-Baumann method, forms hard, colourless prisms, m. p. 90°, from a mixture of benzene and petroleum; it is sparingly soluble in water and petroleum, and readily soluble in alcohol, benzene, chloroform, or ether.

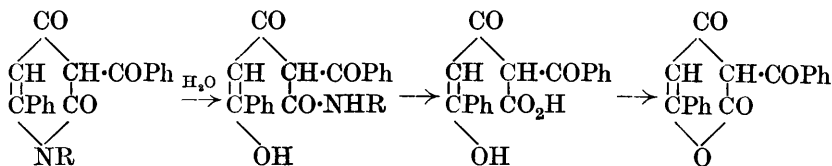
The action of nitrous acid on 6-amino-2-methylpyridine in hydrochloric acid solution leads to the formation, in 50% yield, of 6-*chloro-2-methylpyridine*, a colourless, mobile liquid with a sweet odour, readily miscible with organic solvents, b. p. 183.5—184°/749 mm. (*chloroplatinate*, red prisms insoluble in alcohol, blackens above 208°, decomposes above 290°). 6-Hydroxy-2-methylaminopyridine is formed as a by-product in this reaction, and is separated from the chloro-compound owing to its solubility in alkalis; or it can be obtained by the action of nitrous acid on the amino-compound in the presence of sulphuric acid. It crystallises from a mixture of benzene and light petroleum in groups of needles, m. p. 159° (*picrate*, m. p. 149.5—150°, light yellow needles from water, alcohol, or ethyl acetate; very soluble in acetone); the hydroxy-compound is identical with that prepared by Errera (A., 1901, i, 43).

The nitration of the amine under the usual conditions leads to a 90% yield of 6-nitroamino-2-methylpyridine, slightly yellow needles from hot water or colourless crystals from alcohol, decomp. about 94°. The nitroamine is readily isomerised under the conditions previously employed (see preceding abstracts) to two isomeric nitro-compounds. The isomeride which is volatile in steam is assumed to be 5-nitro-6-amino-2-methylpyridine and forms delicate, light yellow needles, m. p. 141°. The isomeride which is not volatile in steam is taken to be 3-nitro-6-amino-2-methylpyridine; this compound is formed in greater amount than the 5-nitro-compound and is less soluble; it forms yellow leaflets, m. p. 188°. Both isomerides form colourless solutions in strong acids, and these solutions turn yellow on dilution; they are soluble in dilute alkalis but not in dilute acids. G. A. R. K.

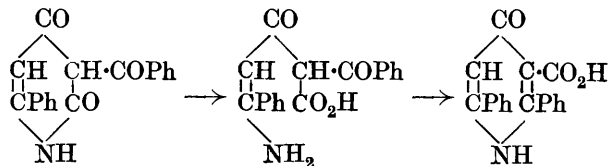
The Lactam Derivatives of Dehydrobenzoylacetic Acid.
P. PETRENKO-KRITSCHENKO (*J. Russ. Phys. Chem. Soc.*, 1917, 49, 251—259; cf. *ibid.*, 1915, 47, 645).—The reactions of some lactam derivatives of dehydrobenzoyl-acetic acid,



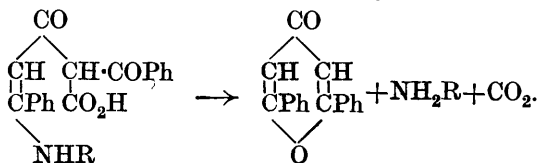
and its *N*-methyl derivative, with acids and strong and weak alkalis are explained as follows. With weak alkali both these substances are hydrolysed to an α -pyrone derivative, as follows, where R may be H or CH₃:



With strong alkalis, the free lactam forms 2:6-diphenylpyridone-3-carboxylic acid, as follows:



In the case of the *N*-methyl derivative, the methyl group is removed by hydrolysis, and the same product is then obtained as from the unsubstituted lactam. With strong acids, the reaction is as follows, where -R may be -H or -CH₃:



R. T.

The Methylation of Pyrrol Ketones. B. V. TRONOV (*J. Russ. Phys. Chem. Soc.*, 1917, **49**, 272—282).—1-Methyl-2-pyrrole methyl ketone, b. p. 199—201°/739 mm., d_4^{15} 1.0445, n_D^{15} 1.5403, is obtained in 56% yield by heating the sodium salt of 2-pyrrol methyl ketone with methyl iodide in a sealed tube, whereas Ciamician and Dennstedt (A., 1885, 378) obtained only an 18% yield by acting on 1-methylpyrrole with acetic anhydride. 1-Methyl-2-pyrrole phenyl ketone, b. p. 299—301°/747 mm., d_4^{15} 1.1312, n_D^{15} 1.6225, is prepared in 70% yield by the action of dimethyl oxalate on the sodium salt of 2-pyrrole methyl ketone. *Di-1-methyl-2-pyrrol ketone*, b. p. 305—307°/755 mm., d_4^{15} 1.1444, n_D^{15} 1.6347, is prepared in the same way in 65% yield. At the same time, some *di-2-methyl-5-pyrrol ketone*, m. p. 192—197°, is produced. Other methods tried for the preparation of the di-1-methylpyrrol ketone did not give the desired product. The action of magnesium methyl iodide on 1-methyl-2-pyrrol phenyl ketone yields α -methylpyrrol- α -phenyl Δ^{β} -allene, $\text{CHMe}\cdot\text{CPh}\cdot\text{C}_4\text{H}_3\text{NMe}$, b. p. 281—283°/750 mm., d_4^{16} 1.0228, n_D^{16} 1.5967. R. T.

Relation between Absorption and Structure. V. The N-Phenylpyridinium Salts. V. A. IZMAILSKI (*J. Russ. Phys. Chem. Soc.*, 1918, **50**, 190—205; cf. König, A., 1906, i, 109; 1911, i, 485).—Various 1-phenylpyridinium salts are reinvestigated and described. These are as follows: 1-Phenylpyridinium bromide, yellow needles, m. p. 155°, iodide, red crystals, m. p. 207°, chloride (H_2O), white needles, m. p. 104—105°, chlorate, white plates with blue fluorescence, m. p. 214°. *o*-Iodophenylpyridinium bromide, yellow crystals, m. p. above 260°, iodide, yellow plates, m. p. 255°, chlorate, white crystals, m. p. 162°. *p*-Iodophenylpyridinium chloride, colourless crystals, m. p. above 260°, chlorate, colourless crystals, m. p. 213°. *m*-Iodophenylpyridinium bromide, colourless crystals, m. p. 189°, iodide, yellow crystals, m. p. 196—197°, chlorate, white plates, m. p. 146°. Tribromo-*m*-iodophenylpyridinium bromide, white crystals, m. p. above 260°. 5-Iodo-*o*-tolylpyridinium bromide, yellow crystals, with 1 molecule of water, m. p. 137—140°, iodide, orange-brown prisms, m. p. above 260°. 2-Hydroxy-1-phenylpyridinium chloride, yellow crystals, m. p. 210°, iodide, yellow crystals, m. p. 162°, chlorate, white needles, m. p. 154°, bromide, white needles, m. p. 128°. β -Hydroxy-*p*-iodophenylpyridinium chloride, white crystals, m. p. 200°, acid sulphate, yellow leaves, m. p. 147°. 1-*o*-Anisylpyridinium bromide, white crystals, m. p. 150°, iodide, yellow crystals, m. p. 153°, chloride (H_2O), yellow crystals, m. p. 137.5°, chlorate, white crystals, m. p. 132°, hydrogen sulphate (H_2O), yellow needles, m. p. 168°. *p*-Anisylpyridinium bromide, yellow crystals containing 1 molecule of alcohol of crystallisation, m. p. 123.5°, iodide, yellow crystals, m. p. 160°, chloride, white crystals, m. p. 100°, chlorate, white plates, m. p. 154°. *m*-Methoxyphenylpyridinium iodide, yellow needles, m. p. 122—123°, chlorate, white, faintly fluorescent needles, m. p. 113—114°. β -Naphthylpyridinium bromide, needles, m. p. 189°, iodide, yellow crystals, m. p. 201°, chloride, white crystals,

containing 1 molecule of alcohol of crystallisation, m. p. 100—103°, chlorate, colourless leaves, m. p. 192—193°. *o*-Phenetidylpyridinium bromide, needles, m. p. 195—196°, iodide, yellow needles, m. p. 186°. R. T.

Derivatives of Indole. SAJURO KURODA (*J. Pharm. Soc. Japan*, 1923, 131—142).—Applying Fischer's method for the synthesis of indole to many phenylhydrazones of ketones, the author has isolated the corresponding indole derivatives; except the product from menthone, these give a red coloration to a pine shaving moistened with hydrochloric acid. The process in general consists in heating a mixture of equal quantities of the hydrazone and zinc chloride at a suitable temperature.

3-Benzyl-2-methylindole prepared from benzylacetonephenylhydrazone, m. p. 59°, and zinc chloride by heating on the water-bath, forms long plates, m. p. 116°. *2-Methyl-3-propylindole*, prepared from methyl-butyl-ketonephenylhydrazone and zinc chloride, is a light, brownish-red oil, b. p. 195°/40 mm. *2-Methyl-3-isopropylindole*, prepared from methylisobutyl-ketonephenylhydrazone and zinc chloride, is a light yellow, viscous oil, b. p. 173°/15 mm. *2-Methyl-3-n-octylindole*, prepared from methyl-n-nonyl-ketonephenylhydrazone and zinc chloride at 100°, is a yellow oil, b. p. 230—235°/35 mm. *3-Benzyl-1:2-dimethylindole*, prepared from benzylacetonephenylmethylhydrazone (a reddish-brown oil) and zinc chloride at 150°, is a light yellow, viscous oil, b. p. 235°/35 mm., having slight green fluorescence. *1:2-Dimethyl-3-propylindole*, prepared from methyl-butyl-ketonephenylmethylhydrazone and zinc chloride at 100°, is a light reddish-brown oil, b. p. 187°/35 mm. *1:2-Dimethyl-3-n-octylindole*, an oil, b. p. 225—230°/36 mm., was prepared from methyl-nonyl-ketonephenylmethylhydrazone, and zinc chloride at 100°. Camphorphenylhydrazone, prepared by Balbiano's method (A., 1886, 72, 808), boils at 210°/17 mm., and yields a hydrochloride, m. p. 151°, when hydrogen chloride is passed into its ethereal solution, without formation of aniline and camphorenonitrile (cf. Balbiano, *loc. cit.*). Its bromine compound, $C_{16}H_{22}N_2Br_2$, forms white needles, m. p. 186°. *Camphorindole* forms colourless plates, m. p. 94°, b. p. 210—215°/25 mm., and is prepared by heating a mixture of the hydrazone and zinc chloride at 150—180°. As a by-product, an *isomeride* of camphorphenylhydrazone, $C_{16}H_{22}N_2$, white plates, m. p. 201°, was isolated from the acid solution; it is not identical with the polycamphorphenylhydrazone of Cazeneuve (*Bull. Soc. chim.*, 1889, [iii], 1, 241). *Menthoneindole*, $C_{16}H_{21}N$, prepared from menthonephenylhydrazone and zinc chloride at 100°, forms colourless plates, m. p. 106°, b. p. 213°/20 mm. In the reaction there were also formed: aniline, and a *base*, $C_{16}H_{23}N$, a light yellow oil, b. p. 181°/18 mm.; it gives a *N-benzoyl* derivative, colourless prisms, m. p. 163°. K. K.

The Action of Sodamide on Quinoline. A. E. TSCHITSCHIBABIN and (MLLE) E. V. ZACEPINA (*J. Russ. Phys. Chem. Soc.*, 1920, 50, 553—557).—The preparation of 2-aminoquinoline by the

action of sodamide on quinoline (A., 1915, i, 591) has been reinvestigated in an endeavour to improve the yield of amino-compound, but without success. The main products of the reaction are *diquinoline*, $C_{18}H_{14}N_2$, and *diquinolyl*, $C_{18}H_{12}N_2$, the former being extremely readily oxidised to the latter, which is identical with the known 2 : 3-compound (Weidel, A., 1882, 69).

The following compounds are described: 2-*Aminoquinoline*, purified by repeated crystallisation from water or regeneration from the picrate, melts at 129° ; the fractions of lower melting point which are obtained contain a little 4-aminoquinoline (hydrated form, m. p. $69-70^\circ$; anhydrous form, m. p. $153-154^\circ$). The *picrate*, sparingly soluble needles, m. p. $255-256^\circ$, and the *hydrochloride*, needles, m. p. $225-227^\circ$, were prepared. *Diquinoline* is isolated in the form of its *hydrochloride*, red needles, from hot water, readily oxidising in the air; the base obtained from it forms yellow leaflets, m. p. 185° . Thus it is not identical, but isomeric with the compound described by Claus (A., 1882, 215). Its salts with mineral acids have a bright red colour and are sparingly soluble; they are extremely readily oxidised to the colourless, readily soluble, salts of 2 : 3-diquinolyl which forms leaflets, m. p. 175° . G. A. R. K.

The Action of Sodamide on *iso*Quinoline. A. E. TSCHITSCHIBABIN and (MLLE) M. P. OPARINA (*J. Russ. Phys. Chem. Soc.*, 1920, 50, 543-548).—*iso*Quinoline reacts with sodamide in the presence of neutral solvents in the same way as pyridine and quinoline, an *aminoisoquinoline* being produced; the position taken up by the entering group is between the nitrogen and the benzene nucleus. The new compound, like those previously described, is a mono-acid base; by the action of nitrous acid, it is converted into the known *isocarbostyryl*, thus proving the constitution assigned to it.

1-*Aminoisoquinoline* is obtained in a yield amounting to 38% and forms silvery plates, m. p. 123° . The *picrate* has m. p. $290-291^\circ$. The *hydrochloride* forms needles, m. p. $233-233.5^\circ$. The *chloroplatinate*, thin, orange needles, does not melt below 300° and crystallises with $1H_2O$.

Diazotisation in presence of sulphuric acid leads to the formation of *isocarbostyryl*, almost white needles, m. p. $206.5-207^\circ$ (cf. Fernau, A., 1893, i, 417); in the presence of hydrochloric acid some 1-chloro*isoquinoline* appears to be produced. G. A. R. K.

Dihydroisoquinoline Derivatives. M. HARTMANN and H. KAGI (U.S. Pat. 1437802).—Methyl α -benzamido- β -3 : 4-dimethoxyphenylpropionate, fine needles, m. p. $104-105^\circ$, obtained by the hydrogenation of methyl veratrylidenehippurate in methyl-alcoholic solution, when condensed at $130-135^\circ$ with phosphorus oxychloride, yields methyl 6 : 7-dimethoxy-1-phenyl-3 : 4-dihydroisoquinoline-3-carboxylate, m. p. 122.5° after recrystallisation from methyl alcohol (*hydrochloride* and *hydrobromide*, yellow crystals). The free ester reacts with methyl iodide to give a 2-methiodide, which is converted by silver chloride into a 2-methochloride. Hydrogenation of methyl piperonylidenehippurate produces methyl

α -benzamido- β -piperonylpropionate, brilliant needles, m. p. 126—127°, which on condensation gives *methyl 6:7-methylenedioxy-1-phenyl-3:4-dihydroisoquinoline-3-carboxylate*, colourless needles, m. p. 140.5°. Methyl α -piperonylamino- β -piperonylpropionate, glassy needles, m. p. 139—140°, yields on condensation *methyl 6:7-methylenedioxy-1-mp-methylenedioxyphenyl-3:4-dihydroisoquinoline-3-carboxylate*, m. p. 140—141° (hydrochloride, partly decomposed by water). Methyl 6:7-methylenedioxy-1-phenetyl-3:4-dihydroisoquinoline-3-carboxylate, prisms, m. p. 111°, is obtained by condensation of *methyl α -(β -phenylpropionylamido)- β -piperonylpropionate*, m. p. 127°, formed by the hydrogenation of *methyl α -cinnamylamino- β -3:4-methylenedioxyphenylacrylate*, m. p. 192°. This compound is prepared by heating together equimolecular proportions of piperonal, cinnamylglycine, and sodium acetate and three molecular proportions of acetic anhydride and boiling the product with methyl alcohol and soda. The above compounds have therapeutic properties.

CHEMICAL ABSTRACTS.

Vapour Pressure of Carbazole. C. F. SENSEMAN and O. A. NELSON (*Ind. Eng. Chem.*, 1923, **15**, 382—383).—A table of the vapour pressures of carbazole between 250° and 355° is given. The determinations were made on carefully purified samples (m. p. 244.8°) (A., 1922, i, 245). Carbazole has b. p. 354.76°, and not 351.5°, as stated in the literature. Interpolation formulæ are derived for the vapour pressures and latent heats of vaporisation: $\log p = 24.2313 - 4570.3/T - 5.0288 \log T$ and $L = 22799 - 13.0T$, respectively. The values given for p are in good agreement with the observed values. H. C. R.

The Aldehyde Derivatives of the Rhodanines and their Fission Products. II. LEON GENDELMAN (*Monatsh.*, 1923, **43**, 537—543; cf. Andreasch, A., 1919, i, 96).—A continuation of previous work by Andreasch. Various substituted rhodanines have been prepared and their hydrolysis products examined and described: 5-cuminyldenerhodanine, $\begin{array}{c} \text{CS} - \text{S} \\ | \quad \diagup \\ \text{NH} \cdot \text{CO} \end{array} > \text{C} : \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{CHMe}_2$,

from cuminaldehyde and rhodanine, when hydrolysed by sodium amyl oxide in boiling amyl alcohol gave α -thiol- p -isopropylcinnamic acid, $\text{C}_6\text{H}_4\text{Pr}^i \cdot \text{CH} : \text{C}(\text{SH}) \cdot \text{CO}_2\text{H}$, fine yellow needles, which are oxidised by alcoholic iodine to the disulphide, yellow needles, m. p. 190°.

3-Phenyl-5- p -chlorobenzylidenerhodanine, $\begin{array}{c} \text{CS} - \text{S} \\ | \quad \diagup \\ \text{NPh} \cdot \text{CO} \end{array} > \text{C} : \text{CH} \cdot \text{C}_6\text{H}_4\text{Cl}$,

from phenylrhodanine and p -chlorobenzaldehyde, forms yellow needles, m. p. 148°. When hydrolysed by barium hydroxide it yields p -chloro- α -thiolcinnamic acid, $\text{C}_6\text{H}_4\text{Cl} \cdot \text{CH} : \text{C}(\text{SH}) \cdot \text{CO}_2\text{H}$, yellowish-white needles, m. p. 157°. 5- p -Chlorobenzylidenethiohydantoin, $\begin{array}{c} \text{C}(\text{NH}) \cdot \text{S} \\ | \quad \diagup \\ \text{NH} - \text{CO} \end{array} > \text{C} : \text{CH} \cdot \text{C}_6\text{H}_4\text{Cl}$, from thiohydantoin and p -chlorobenzaldehyde in acetic acid, forms yellow crystals which blacken at 230° without melting. 3-Phenyl-5- p -tolylidenerhodanine, from p -tolualdehyde and phenylrhodanine, crystallises in yellow

needles, m. p. 136°, and is hydrolysed by barium hydroxide to α -thiol-*p*-methylcinnamic acid, $C_6H_4Me \cdot CH : C(SH) \cdot CO_2H$, yellow needles, m. p. 159°. It is oxidised by alcoholic iodine to the disulphide, yellow needles, m. p. 212°. When treated with alkali hydroxide and benzyl chloride, the thiol-acid yields α -benzylthiol-*p*-methylcinnamic acid, $C_6H_4Me \cdot CH : C(S \cdot CH_2Ph) \cdot CO_2H$, yellow needles, m. p. 134°. 5-mp-Dihydroxybenzylidenerhodanine, $CS-S > C : CH \cdot C_6H_3(OH)_2$, from rhodanine and protocatechualdehyde, is a yellowish-brown powder, m. p. above 270°; its solutions are turned reddish-violet by alkalis and yellow by acids. Attempts to hydrolyse it by means of barium hydroxide or sodium amyloxide were unsuccessful. 3-Camphylrhodanine, $C_{10}H_7 \cdot N \cdot CO > CS-S > CH_2$, is prepared by condensing camphylamine with carbon disulphide by means of aqueous alkali hydroxide to camphylthiocarbamate, $C_{10}H_{17} \cdot NH \cdot CS_2Na$, which is then condensed with chloroacetic ester to give 3-camphylrhodanine as a viscid, yellowish-red oil; this condenses with benzaldehyde to form 5-benzylidene-3-camphylrhodanine, $C_{10}H_7 \cdot N \cdot CO > CS-S > C : CH \cdot C_6H_5$, yellow needles, m. p. 49—50°. 5-*p*-Dimethylaminobenzylidene-3-camphylrhodanine, prepared in a similar manner from dimethyl-*p*-aminobenzaldehyde, forms orange-yellow needles, m. p. 129°. 5-*m*-Nitrobenzylidene-3-camphylrhodanine, from *m*-nitrobenzaldehyde, forms yellow needles, m. p. 126°. Camphylrhodanine condenses with isatin in acetic acid to form camphylrhodanine-2-indoleindigo [2-indoxylidene-3-camphylrhodanine], $C_{10}H_7 \cdot N \cdot CO > CS-S > C : C < \begin{smallmatrix} CO \\ NH \end{smallmatrix} > C_6H_4$, brilliant deep red needles, m. p. 205—206°. F. A. M.

Substitution in the Pyrazole Series. Halogen Derivatives of 3 : 5-Dimethylpyrazole. GILBERT T. MORGAN and ISIDORE ACKERMAN (T., 1923, 123, 1308—1318).

The Oxime of Mesoxamide (isoNitrosomalsonamide) and some Allied Compounds. III. Ring Formation in the Tetra-substituted Series. EDITH HILDA USHERWOOD and MARTHA ANNIE WHITELEY (T., 1923, 123, 1069—1089).

The Action of Reducing Agents on some Polynitrodiphenylamines. NICHOLAS MICHAEL CULLINANE and THOMAS CAMPBELL JAMES (*Aberystwyth Studies*, 1922, 4, 209—212).—Reduction of 2 : 4 : 6-trinitrodiphenylamine (picrylaniline) with alcoholic ammonium sulphide gives the known 1 : 3-dinitro-5 : 10-dihydrophenazine. It forms a *diacetyl* derivative, $C_{16}H_{12}O_6N_4$, yellow prisms, m. p. above 320°, and a *dibenzoyl* derivative, $C_{26}H_{16}O_6N_4$, yellow plates, m. p. 230° (decomp.). As an intermediate compound in the reduction, 2 : 4-dinitro-6-aminodiphenylamine was obtained, yellow leaflets, m. p. 176°. Reduction of picrylaniline with stannous chloride gives a black powder dissolving in concentrated sulphuric

acid with a violet colour. By reduction of picryl-*p*-toluidine with alcoholic ammonium sulphide, 6 : 8-*dinitro-2-methyl-5 : 10-dihydro-phenazine* was obtained, bright yellow needles, m. p. above 340°. The constitution of this substance was confirmed by preparing it from picryltolylene-diamine (T., 1920, 117, 1273) by heating until nitrous fumes were no longer evolved. Reduction of picryl-*m*-toluidine with alcoholic ammonium sulphide appears also to give a dihydrophenazine derivative. E. H. R.

Micro-sublimation of Indigo. KARL PIRSCHLE (*Biochem. Z.*, 1923, 136, 403—410).—The appearances obtained on micro-sublimation of a variety of indigo-containing materials, natural and synthetic, are described. Indirubin and indigotin both sublime in characteristic crystals and also crystallise from liquid paraffin in characteristic crystals. H. K.

isoIndigotin and Indine. A. WAHL and W. HANSEN (*Compt. rend.*, 1923, 176, 1070—1072).—The identity of *isoindigotin* (A., 1909, i, 330, 735) with the indine first obtained by Laurent (*Ann. Chim. Phys.*, 1840, [iii], 3, 471) by the action of potassium hydroxide on disulphoisatide has been established by a comparison of the properties of the substances obtained by the two methods, and of their derivatives. The molecular formula of Laurent's product is definitely $C_{16}H_{10}O_2N_2$, the same as *isoindigotin*. Both substances give a brown compound with potassium hydroxide, and the original substance is in each case generated on dilution with water. Both furnished disulphonic acids, giving anhydrous barium salts, and silver, potassium, and sodium salts crystallising with $2H_2O$. The indinedisulphonic acid described by Schlieper (*Annalen*, 1861, 120, 24) is apparently erroneously so described, and was not obtained in the present research. On reduction with zinc dust and acetic acid, a leuco-compound having the formula $C_{16}H_{12}O_2N_2$, and forming white or pink crystals, m. p. 265°, was produced in each case, and its solution in alkali hydroxides rapidly reoxidised by air to *isoindigotin*. G. F. M.

Action of Sulphur Monochloride on Mercaptans. GOPÂL CHANDRA CHAKRAVARTI (T., 1923, 123, 964—968).

Ring Closure of Hydrazine-dithio- and -monothio-dicarbon-amides with Acetic Anhydride. PRAPHULLA CHANDRA GUHA (*J. Amer. Chem. Soc.*, 1923, 45, 1036—1042).—Acetic anhydride converts hydrazinedicarbothionamide into a diacetyl derivative of 2 : 5-di-imino-2 : 3 : 4 : 5-tetrahydro-1 : 3 : 4-thiodiazole, from which it is easy to remove the acetyl groups; the reaction is also applicable to all alkyl and aryl hydrazinedicarbothionamides. Hydrazine-dicarbomonothionamide, however, behaves differently; instead of losing either hydrogen sulphide or water and forming a di-imino-thiodiazole or -oxydiazole, it loses ammonia and gives a ketoimino-thiodiazole.

The action of boiling acetic anhydride on hydrazinedicarbothionamide leads to 2 : 5-di-imino-3 : 4-diacetyl-2 : 3 : 4 : 5-tetrahydro-1 : 3 : 4-thiodiazole, white needles, m. p. above 315°, which is

hydrolysed by means of concentrated hydrochloric acid to the *hydrochloride*, white needles, m. p. 241°, of 2 : 5-*di-imino*-2 : 3 : 4 : 5-*tetrahydro*-1 : 3 : 4-*thiodiazole*, m. p. 210—211°, yellow *picrate*, of high melting point. The following derivatives of the corresponding *dimethylamide* are described: *diacetyl* compound, white needles, m. p. 219°, free *base*, m. p. 180°, *hydrochloride*, m. p. 235°, *nitroso*-derivative, golden-yellow, m. p. 151°, yellow, crystalline *picrate*, m. p. 205°. The following derivatives of the *diallylamide* have been prepared: *acetyl* derivative, m. p. 113°, *hydrochloride*, and free *base*, m. p. 151°, also the following derivatives of the corresponding *dianilide*: *acetyl* derivative, m. p. 224°, free *base*, m. p. 247°. Similarly, the following derivatives of the di-*p*-toluidide are obtained: *diacetyl* compound, m. p. 235°, free *base*, m. p. 249—250°, and of the *monoanilide*: free *base*, dull, yellow leaflets, m. p. 215°, *hydrochloride*, m. p. 144°, yellow *picrate*, m. p. 226°, *diacetyl* derivative, m. p. 144°. *p*-*Bromophenylhydrazinedicarbothionamide*, m. p. 213°, is prepared by boiling for three to four hours a mixture of one molecular proportion of hydrazine sulphate dissolved in the minimum amount of warm water, and one molecular proportion of sodium carbonate and two molecular proportions of *p*-bromophenylthiocarbimide. It gives the following derivatives of the *mono-p-bromoanilide*: free *base*, m. p. 241°, *diacetyl* derivative, m. p. 229°. *m*-*Chlorophenylhydrazinedicarbothionamide*, m. p. 170°, is prepared in a similar manner, and gives the impure *diacetyl* derivative from which the free *base*, m. p. 186—187°, is obtained. α -*Naphthylhydrazinedicarbothionamide*, m. p. 265°, gives, in the same way, the free *base*, m. p. 275—276°, and the *diacetyl*-derivative, m. p. 270°. The action of boiling acetic anhydride on hydrazinemonothiodi-carbonamide leads to the *diacetyl* derivative, m. p. 295°, of 5-*imino*-2-*keto*-2 : 3 : 4 : 5-*tetrahydro*-1 : 3 : 4-*thiodiazole*, m. p. 240°, *hydrochloride*, m. p. 107—108°.†

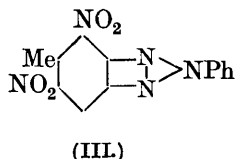
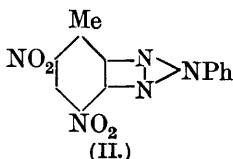
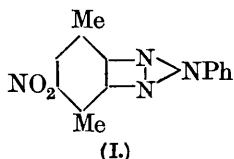
W. S. N.

Benzbisthiazoles. III. STEPHEN RATHBONE HOLDEN EDGE (T., 1923, 123, 1011—1014).

Dyes of the Aurin Type. I. HARRY BAINES and JOHN EDMUND DRIVER (T., 1923, 123, 1214—1218).

Certain *o*-Nitrohydrazo-compounds. MICHELE GIUA and MARIO GIUA (*Gazzetta*, 1923, 53, i, 165—174).—It has been found previously (A., 1918, i, 552) that the action of gaseous hydrogen chloride on methyl- or ethyl-alcoholic solutions of certain *o*-nitrohydrazo-compounds yields intense wine-red or carmine colorations. It is now found that this reaction may be extended and employed for the identification of products formed by the action of phenylhydrazine on aromatic nitro-compounds containing labile groupings such as halogens, alkyloxy-, or nitro-groups, etc. The ortho-position to the labile group being usually occupied by a nitro-group, the primary product of this reaction is the *o*-nitrohydrazo-compound, but under certain conditions derivatives of 2 : 1 : 3-benzotriazole or phenyl- ψ -aziminobenzene are obtained (cf. Kehrman and Messinger, A., 1892, 889). The compound, described as 3 : 5-

dinitroso-2-benzeneazo-*p*-xylene, m. p. 185° (A., 1920, i, 98), must, indeed, be regarded as the 2:1:3-benztriazole derivative of formula I and that described as 6-nitro-2:4-dinitroso-3-benzene-azotoluene, as the dinitro-2-phenylmethyl-2:1:3-benztriazole of formula II or III:



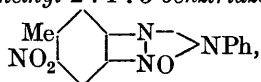
The products formed by the action of gaseous hydrogen chloride on some *o*-nitrohydrazo-derivatives in alcoholic solutions must be considered as azimino-oxides or azonitroso-derivatives, containing,

not the grouping $\text{NO} \cdot \dot{\text{C}} \cdot \dot{\text{C}} \cdot \text{N} \cdot \text{NR}$, but either $\begin{array}{c} \cdot \text{N} \cdot \cdot \\ \cdot \text{N} \cdot \cdot \\ \cdot \text{NO} \end{array} > \text{N} \cdot$ or $\begin{array}{c} \cdot \text{N} \cdot \cdot \\ \cdot \text{O} \cdot \cdot \\ \cdot \text{N} \cdot \cdot \end{array} > \text{N} \cdot$.

When, however, the action of phenylhydrazine or one of its derivatives with substituents in the nucleus on a nitro-compound with a labile group yields, not an *o*-nitrohydrazo-compound, but a derivative of phenyl-2:1:3-benztriazole, no red coloration is given by the gaseous hydrogen chloride reaction. In some cases, gaseous hydrogen chloride in ethyl- or methyl-alcoholic solution is not a suitable agent for the formation of azonitroso-compounds, as it acts on these in a somewhat complicated manner, especially when its action is prolonged and the temperature is not duly regulated.

As regards the cause of the red coloration formed by the nitro-hydrazo-compounds with the gaseous hydrogen chloride, two suggestions are made. It may be due to the formation of an additive compound of the acid with the intermediate nitrosoazo-compound, $\cdot \text{N} \cdot \text{N} \cdot \dot{\text{C}} \cdot \dot{\text{C}} \cdot \text{NO}$, or of a more complex compound (cf. Jacobson, Bartsch, Loeb, and Steinbreck, A., 1909, i, 681). The second suggestion, which is supported by Jacobson's results (1892—1909; also A., 1922, i, 589), is that part of the hydrazo-compound reacts with the gaseous hydrogen chloride, giving rise to the corresponding azo-compound, the two hydrogen atoms thus eliminated causing fission of another molecule of the hydrazo-compound with formation of two molecules of primary amine. A similar reaction was observed by Andreae (A., 1880, 466).

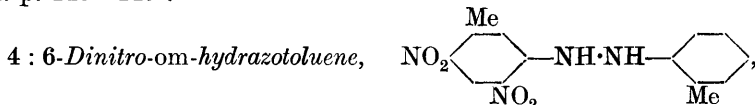
5-Nitro-2-phenyl-6-methyl-2:1:3-benztriazole 3-oxide,



prepared by treating 2:4-dinitro-5-methylhydrazobenzene (A., 1918, i, 552), either in hot alcoholic solution with a few drops of 15% sodium hydroxide solution, or in a reflux apparatus with glacial acetic acid, or in alcoholic solution with gaseous hydrogen chloride solution, forms pale yellow, flat, silky needles, m. p. 155—156°.

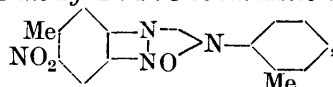
4 : 6-Benzeneazo-4 : 6-dinitro-*m*-toluene, $C_6H_2Me(NO_2)_2 \cdot N:NPh$, obtained by oxidising benzenehydrazo-2 : 6-dinitro-*m*-toluene in alcoholic solution by means of freshly precipitated mercuric oxide, crystallises in brick-red lamellæ, m. p. 117—118°.

Benzeneazo-2 : 4-dinitro-*m*-toluene forms reddish-yellow lamellæ, m. p. 148—149°.

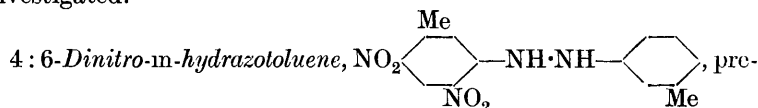


prepared by the interaction of γ -trinitrotoluene and *o*-tolylhydrazine, crystallises in lustrous, orange-red lamellæ, m. p. 151—152° (decomp.), dissolves in concentrated sulphuric acid giving a red solution, and in alcoholic solution yields a dark red coloration with alkali.

6-Nitro-2-*o*-tolyl-5-methyl-2 : 1 : 3-benztriazole N-oxide,

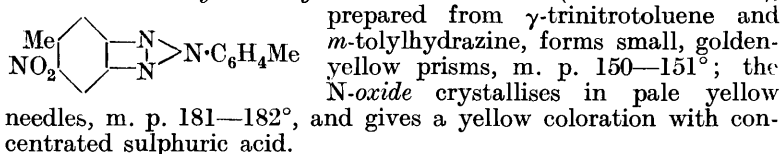


obtained from the preceding compound by means of either 25% potassium hydroxide solution or gaseous hydrogen chloride, forms yellow needles, m. p. 142—143°, and dissolves slowly in cold, concentrated sulphuric acid to a yellow solution. When prepared by means of hydrogen chloride, it is accompanied by a garnet-red, halogenated compound, m. p. above 220°, which has not been investigated.



pared from γ -trinitrotoluene and *m*-tolylhydrazine, crystallises in orange-yellow needles, m. p. 165—166° (decomp.), forms a dark red solution in concentrated sulphuric acid, and gives a red coloration with alkali in alcoholic solution.

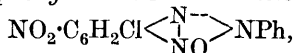
6-Nitro-2-*m*-tolyl-5-methyl-2 : 1 : 3-benztriazole (annexed formula),



6-Nitro-2-*p*-tolyl-5-methyl-2 : 1 : 3-benztriazole N-oxide,

$C_{14}H_{12}O_3N_4$, crystallises in lustrous, yellow lamellæ with a greenish-yellow reflection, m. p. 186—187°.

6-Chloro-5-nitro-2-phenyl-2 : 1 : 3-benztriazole N-oxide,



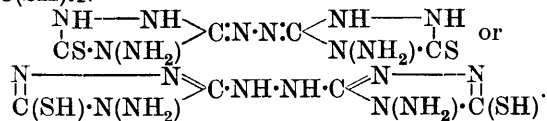
prepared from 5-chloro-2 : 4-dinitrohydrazobenzene, either by boiling it with glacial acetic acid or by saturating its alcoholic

solution with gaseous hydrogen chloride, forms golden-yellow needles, m. p. 195—196°. When reduced by means of hydrazine hydrate, this compound yields a product with the same melting point as Zincke and Scharff's phenyl- ψ -aziminonitrochlorobenzene (A., 1910, i, 140), namely, 196°. T. H. P.

Action of Diazomethane on Xanthosine. P. A. LEVENE (*J. Biol. Chem.*, 1923, 55, 437—442).—The velocity of hydrolysis of the hydrogenated pyrimidine nucleoside indicates that the pentose radicle is attached to a nitrogen atom of the base. Assuming that the same mode of attachment exists in all nucleosides, the structure of those containing a pyrimidine base follows immediately. In the case of the purine nucleosides, however, alternative positions of attachment are possible. It is now shown that, in xanthosine, the ribose molecule is attached to the nitrogen atom in position 7 of the base. Thus, methylation of xanthosine with diazomethane yielded an amorphous *dimethyl* derivative, $[\alpha]_D^{20} -28^\circ$, together with caffeine, and, when the methylation was continued for eight hours, tetramethyluric acid. The production of the last two compounds is attributed to the hydrolytic and oxidising actions of diazomethane. When hydrolysed by dilute acid, dimethyl-xanthosine gave theophylline; hence the 1- and 3-positions of the purine base are free in the nucleoside, thus leaving only position 7 as the point of attachment of the pentose. The yield of theophylline was small owing to considerable formation of melanin. E. S.

Ring Closure with Hydrazinedicarboxamides containing Sulphur. III. The Action of Hydrazine on Hydrazinedicarbonthioamide. F. ARNDT and FRANZISKA BIELICH (*Ber.*, 1923, 56, [B], 809—817; cf. Arndt and Milde, A., 1921, i, 813; Arndt and Tschenschner, A., 1922, i, 375).—The action of hydrazine on hydrazinedicarbonthioamide has been described by Purgotti and Vigano (A., 1902, i, 322), who have isolated a product which they regard as dithio-*p*-urazine, $S:C \begin{smallmatrix} \text{NH}\cdot\text{NH} \\ \text{NH}\cdot\text{NH} \end{smallmatrix} CS$. Since

the constitution ascribed to this compound seems doubtful to the authors, they have re-examined the reaction with different results and have isolated the amphoteric 4-amino-3-iminothiourazole, $NH_2\cdot N \begin{smallmatrix} \text{C}(\text{NH})\cdot\text{NH} \\ \text{CS} \text{---} \text{NH} \end{smallmatrix}$, 4-aminodithiourazole, $NH_2\cdot N \begin{smallmatrix} \text{CS}\cdot\text{NH} \\ \text{CS}\cdot\text{NH} \end{smallmatrix}$ or $NH_2\cdot N \begin{smallmatrix} \text{C}(\text{SH})\cdot\text{N} \\ \text{C}(\text{SH})\cdot\text{N} \end{smallmatrix}$, and (probably) 4 : 4-diaminohydrazothiourazole,



4-Aminoiminothiourazole crystallises in irregular leaflets, m. p. 240—242° (decomp.). It is soluble in alkalis, ammonia, and mineral acids, but not in acetic acid. It gives a colourless *nitrate*, m. p. 153° (decomp.), and a *methyl* ether. It reacts with benzaldehyde in hydrochloric acid solution to give the *benzylidene* compound,

$\text{CHPh} \cdot \text{N} \cdot \text{N} < \begin{array}{c} \text{C}(\text{NH}) \cdot \text{NH} \\ \text{CS} \text{---} \text{NH} \end{array}$, lustrous, pale yellow prisms, m. p. 274°

after previous darkening (the corresponding *S*-methyl ethyl has m. p. 242° after softening at 235°).

4-Aminodithiourazole crystallises in small, colourless needles, m. p. 228° (decomp.) after softening at 225° . It is oxidised by ferric chloride in hydrochloric acid solution to the corresponding disulphide, $(\text{C}_2\text{H}_2\text{N}_4\text{S}_2)_x$, a pale yellow precipitate, m. p. (indefinite) 214° (decomp.). It gives a silver salt, $\text{C}_2\text{H}_2\text{N}_4\text{S}_2\text{Ag}_2$, and a barium salt, $(\text{C}_2\text{H}_3\text{N}_4\text{S}_2)_2\text{Ba} \cdot 4\text{H}_2\text{O}$. The benzylidene derivative forms pale yellow crystals, m. p. 136° after previous softening. The amino-compound is converted by benzyl chloride and alcoholic potassium hydroxide solution into the corresponding dibenzyl ether,

$\text{NH}_2 \cdot \text{N} < \begin{array}{c} \text{C}(\text{S} \cdot \text{C}_6\text{H}_7) \cdot \text{N} \\ \text{C}(\text{S} \cdot \text{C}_6\text{H}_7) \cdot \text{N} \end{array}$, matted needles, m. p. 147° .

4 : 4'-Diaminohydrazothiouazole (?) crystallises in long, colourless, or pale-yellow needles. It has m. p. $207\text{--}225^\circ$ after previous softening, the indefiniteness appearing to be due to tautomeric or stereochemical change, and not to the presence of impurity in the material. It is a powerful reducing agent, but its smooth conversion into a disulphide could not be effected by means of ferric chloride or iodine solution. It gives an unstable silver salt. The benzylidene compound crystallises in small needles, m. p. 215° (decomp.). The benzyl ether, leaflets, m.p. 214° (decomp.), yields salts with the mineral acids of which the nitrate, m. p. 132° , is the most sparingly soluble. The benzylidene derivative of the benzyl ether forms small needles, m. p. $136\text{--}137^\circ$; it yields a hydrochloride, m. p. 181° .
H. W.

Action of Hydroxylamine and of Dihydroxyammonia on certain Nitroso-derivatives. A. ANGELI and ANTONIO PIERONI (*Atti R. Accad. Lincei*, 1923, [v], 32, i, 151—153).—From the analogies in behaviour shown by two groups when directly united and when occupying ortho- or para-positions in an aromatic nucleus (A., 1917, i, 452; 1920, i, 665), it is to be expected that aromatic compounds of the form $\text{NHR} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$, $\text{NHR} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}$, or $\text{NR} \cdot \text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{OH}$ would, in some reactions, behave similarly to the hydrazines or diazo-hydrates. When treated with nitrous acid, amines of the first of the above forms give, not the corresponding diazonium salts, but compounds of the probable formula $\text{NR} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2$ (cf. Ikuta, A., 1888, 467), which may be regarded also as derivatives of diazoiminoquinone, $\text{NR} \cdot \text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{N}$. Further, since diazonium hydroxides are converted by the action of hydroxylamine into the corresponding azides, $\text{R} \cdot \text{N}_2 \cdot \text{OH} + \text{NH}_2 \cdot \text{OH} = \text{R} \cdot \text{N} \cdot \text{N} \cdot \text{N} + 2\text{H}_2\text{O}$, the action of this reagent on nitroso-derivatives of the type $\text{NHR} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}$ should furnish either diazoiminoquinone or a very simple derivative of it. This is actually found to be the case.

The action of hydroxylamine on *p*-nitrosodiphenylamine in alkaline solution yields a compound, $\text{C}_{12}\text{H}_{10}\text{N}_4$, which forms large, pale brown crystals, m. p. 71° , and on reduction with tin and

hydrochloric acid gives the amine, $\text{NHPh}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$. The formula $\text{NH}\cdot\text{NPh}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}$ being unlikely, this compound has probably the structure $\text{NHPh}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}\cdot\text{N}$ or $\text{NPh}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}\cdot\text{NH}$, the diazo-compound, $\text{NPh}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}$, first formed undergoing reaction with a second molecule of the hydroxylamine.

Similarly, the action of hydroxylamine on the nitroso-compound, $\text{NHMe}\cdot\text{C}_6\text{H}_4\cdot\text{NO}$, yields a crystalline compound, m. p. 52° . Both these compounds, for which the name *photo-azides* is suggested, exhibit sensitiveness towards light resembling that of silver salts. Paper moistened with a dilute benzene solution of the phenyl derivative and exposed to light rapidly turns violet and then black; with the methyl derivative first a red and afterwards a violet coloration is obtained.

Dihydroxyammonia, obtained from benzosulphohydroxamic acid and an alkali, acts readily on *p*-nitrosodiphenylamine in alkaline solution, yielding an acid compound, which forms deep yellow crystals, m. p. 74° , and undergoes rapid alteration when either heated or exposed to light.

T. H. P.

Certain Polypyrroles. ANTONIO PIERONI and ALDO MOGGO (*Gazzetta*, 1923, **53**, i, 120—135).—Part of the work here described has been already published (A., 1922, i, 766). Besides *p*-bromobenzeneazoxycarboxylamide, naphthalene- β -azoxycarboxylamide may serve as a reagent for the pyrrole nucleus, with which it forms pyrrolineazo- β -naphthalene and pyrrolinebisazo- β -naphthalene (cf. Fischer and Hepp, A., 1886, 1041). The action of *p*-bromophenyldiazonium chloride on iodole or on heptaiododipyrrol (A., 1922, i, 763) yields bis-2 : 5-*p*-bromobenzeneazodi-iodopyrrole.

Naphthalene- β -azoxycarboxylamide, $\text{C}_{10}\text{H}_7\cdot\text{NO}\cdot\text{N}\cdot\text{CO}\cdot\text{NH}_2$, prepared in the ordinary way from β -naphthylamine, crystallises in orange-yellow, silky needles, m. p. 178° , and with β -naphthol and a few drops of potassium hydroxide gives a violet solution which, when heated, becomes red and yields a red precipitate of β -naphthylazo- β -naphthol.

Bis-2 : 5-*p*-bromobenzeneazodi-iodopyrrole, $\left\{ \begin{array}{l} \text{Cl}\cdot\text{C}(\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_4\text{Br}) \\ \text{Cl}\cdot\text{C}(\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_4\text{Br}) \end{array} \right\} > \text{NH}$,

forms red crystals and decomposes, with liberation of iodine, at 259° .

T. H. P.

Azo-dyes of the 2-Pyridine Series. A. E. TSCHITSCHIBABIN (*J. Russ. Phys. Chem. Soc.*, 1920, **50**, 512—519).—Sodium pyridine isodiazoxide (A., 1916, i, 224, and this vol., i, 597, 598) reacts in alcoholic solution with certain phenols and aromatic amines, giving true azo-dyes. The coupling proceeds very slowly, but is greatly accelerated by passing a slow stream of carbon dioxide through the liquid; indeed, no condensation takes place with amines if the presence of carbon dioxide is excluded. Curiously enough, no condensation product could be obtained with the sodium salt of *G* acid (sodium β -naphthol-6 : 8-disulphonate). The attempts to condense α -aminopyridine with nitrosonaphthol and nitrosodimethylaniline were also unsuccessful. Azo-dyes containing a

pyridine nucleus as first component are much deeper in colour than the corresponding benzene derivatives; whilst as a second component the pyridine nucleus has little effect on the colour. The simple dyes obtained do not appear to be very stable.

The following compounds are described: *2-Pyridineazo-β-naphthol*, orange-red needles, m. p. 137° , obtained in 40% yield in addition to some 2-ethoxypyridine; insoluble in water and cold alkalis, soluble in dilute acids, dissolves in concentrated sulphuric acid with a dark purple colour; the *hydrochloride* forms red needles. *2-Pyridineazo-α-naphthol* appears to exist in two isomeric forms, one consisting of red needles with a green reflex, giving a dirty violet solution in sulphuric acid, and another which forms dark needles giving orange-red solutions in acids or alkalis. *2-Pyridine-azoresorcinol* is obtained partly in the form of its *mono-sodium* salt, an orange powder containing one molecule of water of crystallisation, and partly as its *hydrochloride*, which is also obtained by treating the sodium salt with hydrochloric acid, red, flattened needles containing $2\text{H}_2\text{O}$. The *base* can be liberated from the sodium salt by means of carbon dioxide and forms an orange, crystalline powder (prisms) which swells and blackens at $186\text{--}188^{\circ}$ and gives orange solutions in acids or alkalis. *2-Pyridine-3-azo-2:6-diaminopyridine* forms brownish-red crystals containing alcohol of crystallisation which is readily lost on keeping, the substance then melting at 167° . It dissolves sparingly in sulphuric acid, giving a greenish-yellow solution. G. A. R. K.

Action of Iodine on some α -Substituted Semicarbazides and its Application to their Estimation. A. DOUCET (*J. Pharm. Chim.*, 1923, [vii], 27, 361–365).—Iodine reacts with α -phenylsemicarbazide otherwise than with semicarbazide itself; no nitrogen is liberated, but two hydrogen atoms are eliminated as hydrogen iodide and phenylazocarboxylamide, $\text{Ph}\cdot\text{N}\cdot\text{N}\cdot\text{CO}\cdot\text{NH}_2$, melting at 114° , is formed. The latter forms, with an excess of iodine, an unstable additive compound which separates in small, bronze needles, but is readily dissociated by solvents and loses its iodine when treated with sodium thiosulphate. The estimation of 1-phenylsemicarbazide may be carried out by adding 50 c.c. of *N*/10-iodine to a solution of 0.2 g. of the substance in 10 c.c. of alcohol containing 1 g. of sodium acetate. After keeping the mixture for ten minutes 50 c.c. of *N*/10-sodium thiosulphate are run in and the excess is titrated back with *N*/10-iodine, using starch as indicator. Every 2 atoms of the original iodine used correspond with 1 mol. of phenylsemicarbazide. *m*-Benzamidosemicarbazide behaves exactly as the above, giving *m*-benzamidoazocarboxylamide, $\text{NH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}\cdot\text{CO}\cdot\text{NH}_2$, which differs from phenylazocarboxylamide in being insoluble in ether, chloroform, or benzene. The *azo-derivative* is a stable compound, melting at 186° and giving an unstable additive compound with iodine. W. T. K. B.

Cataphoresis of Proteins. THE. SVEDBERG and ERIC R. JETTE (*J. Amer. Chem. Soc.*, 1923, 45, 954–957).—A method is described by which the rate of migration of a protein particle under

the influence of an electric field may be experimentally determined. The method depends on the fact that under the illumination of ultra-violet light, proteins fluoresce. This fluorescence may be readily photographed and the position of the boundaries of the protein sol measured on the photographic plate. Photographs are included in the paper showing qualitatively the effect of changing the hydrogen-ion concentration of a 0.3% egg-albumin sol on its rate of migration.

J. F. S.

The Decomposition of Proteins. II. N. TROENSEGAARD (*Z. physiol. Chem.*, 1923, **127**, 137—185).—Proteins, gelatin, gliadin, and casein are acetylated when heated with acetyl chloride in acetic acid solution. The acetyl proteins are reduced with sodium and amyl alcohol and the products fractionated. The chief products appear to be heterocyclic compounds, probably pyrrole derivatives. Aliphatic amines and amino-alcohols appear to be absent.

W. O. K.

Comparative Value of the Dialysis Reaction (Abderhalden) and the Reaction with *Bacterium coli* for the Detection of Proteolysis. E. WOLLMAN and (MME) E. WOLLMAN (*Bull. Soc. Chim. biol.*, 1923, **5**, 253—257).—The authors' method (*Compt. rend. Soc. Biol.*, 1919, **82**, 1263), in which the tryptophan present in the peptones produced by proteolysis is converted into indole (detected by Ehrlich's reagent) by the action of *B. coli*, gives more regular results and is more sensitive than Abderhalden's dialysis method.

E. S.

Investigation of Formaldehyde-protein. A Case of Divergence from the Usual Characteristics of a Transition. Mechanism of Gel Formation. L. REINER and A. MARTON (*Kolloid Z.*, 1923, **32**, 273—279).—Formaldehyde-protein has been prepared from the sera of rabbits, horses, cows, and guinea-pigs and the physical properties of the product have been examined. The results show that the change in properties which generally indicate increased or decreased stability of the product do not all point in the same direction. The stability towards heat, and the reduction of the tendency to coagulate on the addition of albumin indicate an increased stability, whilst the increased sensitiveness towards salts, the more pronounced Tyndall cone, and the decreased electrical conductivity indicate a coagulation or at least a decreased stability of the complex compound over that of the original protein.

J. F. S.

The Action of Proteins and Blood-serum on Colloidal Gold Solution and its Quantitative Interpretation. PAUL REZNIKOFF (*J. Lab. Clin. Med.*, 1922, **8**, 92—103).—Serum-albumin, euglobulin, and pseudoglobulin, tested against colloidal gold solution, gave characteristic curves dependent on the concentration. Contrary to Fischer, the author finds that serum-albumin has a distinct precipitating effect on colloidal gold in certain concentration. Howe's method for isolating the globulins was found not to be accurate.

CHEMICAL ABSTRACTS.

Sensitisation of Salts by Globulin as the Cause of the Coagulation of Gold [Sols] by Globulin Solutions. G. HEINRICH FISCHER and A. FODOR (*Kolloid Z.*, 1923, **32**, 279—284).—The precipitation of gold sols by alkaline globulin solutions and by similar solutions containing 0.4% of sodium chloride has been investigated for various hydrogen-ion concentrations. The experiments indicate that with increasing hydration of the globulin the coagulation is retarded. But it is remarkable that coagulation is not entirely absent in solutions of hydrogen-ion concentration of the order 10^{-12} when treated with globulin free from or poor in sodium chloride, whereas with albumin solutions in which the albumin is present as enhydrones (A., 1922, i, 691) and is strongly hydrated there is no increase in the size of the gold particles.

J. F. S.

Colloid Chemistry of Yeast Proteins. HEINRICH LÜERS and KARL SCHUSTER (*Kolloid Z.*, 1923, **32**, 334—337).—The yeast proteins, zymocasein and cerevesin, have been separated from yeast, the former by treating the liquor from compressed yeast with 20% acetic acid until the filtrate shows no further precipitation. This occurs at $p_H=4.0-4.5$. The precipitate is pressed, washed with faintly acidified water, and dialysed under toluene against water until the acid reaction disappears. The filtrate from the zymocasein is treated with sodium acetate and the cerevesin salted out with ammonium sulphate. The two proteins have been investigated with respect to their chief colloidal properties. The isoelectric point of cerevesin is found to be 2.6×10^{-5} from measurements of its coagulation by alcohol, and by heat, its surface tension, and its cataphoresis. The values of these constants show that this vegetable protein is to be grouped with the known animal and plant proteins. The tendency of zymocasein to swell in acid and acidified solutions of neutral salts has been investigated, and a far-reaching analogy with animal casein found. Zymocasein therefore belongs to the group of phosphorus-containing proteins (casein and vitellin).

J. F. S.

Collargol. A. F. GERASIMOV (*J. Russ. Phys. Chem. Soc.*, 1917—1918, **49**, 604—607; cf. A., 1917, i, 98; this vol., i, 492).—The addition of sodium chloride to a solution of collargol in quantities insufficient to precipitate the latter causes the gradual formation of a deposit of silver chloride in a colloidal form; the reaction is $2Ag + 2NaCl + O + H_2O = 2AgCl + 2NaOH$. This reaction is responsible for the deterioration of samples of solid collargol when these are not kept protected from air and moisture. Potassium iodide produces an analogous result, colloidal silver iodide being deposited. Silver chloride is shown to have a peptising action on collargol.

G. A. R. K.

The Influence of Electrolytes on the Coagulation of Collargol by Acetic Acid. ALEXEI FEDOROVITSCH GERASIMOV (*J. Russ. Phys. Chem. Soc.*, 1917, **49**, 442—448).—Various inorganic salts are added singly and in pairs, in various quantities and pro-

portions, to solutions of colloidal silver, and acetic acid is then added until coagulation occurs. The amount of acid which needs to be added depends, not only on the quantity of the salts present, but also on the nature of the component salts of each pair. When the mixtures are added in small quantity, their mutual influence is negligible, whilst with large quantities, the activity of each salt may be neutralised. When intermediate quantities of mixtures are added, the effect is largely the sum of the effects of the components.

R. T.

The Proteic Acids of Urine. II. Antoxyproteic Acid. S. EDLBACHER (*Z. physiol. Chem.*, 1923, **127**, 186—189; cf. A., 1922, i, 692, 883).—Antoxyproteic acid contains only a small quantity of nitrogen titratable by formol (3·69%, excluding that which can be distilled as ammonia), but on hydrolysis yields a relatively high percentage of mono-amino-acids (37·10%), and also contains histidine, arginine, and lysine. It therefore appears to be of the nature of a polypeptide.

W. O. K.

Precipitation Forms of Casein. FRITZ LOEBENSTEIN (*Kolloid Z.*, 1923, **32**, 264—272).—The significance of the various forms in which casein is precipitated in connexion with digestion is discussed. The conditions under which the various forms are produced have been investigated in the case of calcium caseinate solutions. Precipitation has been effected in the presence of hydrochloric acid of physiological concentrations and also in the presence of carbohydrates (lactose, maltose, sucrose, and dextrin), salts (sodium chloride and hydrogen carbonate, potassium chloride, citrate, phosphate, and sulphate, calcium citrate and phosphate and magnesium phosphate), albumin and ferments (pepsin and rennin), and the forms produced have been investigated. Hydrochloric acid is shown to have a marked effect on the solution of the casein. Calcium caseinate solutions give no precipitate in the presence of 0·2—0·3% hydrochloric acid; lower and higher concentrations of hydrochloric acid produce increasingly large precipitates, which differ considerably in their nature and in the time required for their formation. The addition of sugars prevents the precipitation over the whole concentration range of hydrochloric acid from 0·35 to 0·55%. Albumin has much the same action as the sugars, that is, it hinders precipitation and aids solution. The salts mentioned above, when present in physiological quantities, increase the precipitation over the whole range of hydrochloric acid concentrations. Pepsin does not affect the precipitation by hydrochloric acid, whilst rennin accelerates both the precipitation and the solution of casein.

J. F. S.

The Combination between Oxygen and Hæmoglobin, and the Criteria of Adsorption. N. K. ADAM (*Nature*, 1923, **111**, 496—497).—The question is discussed whether the attraction of hæmoglobin for oxygen, which appears to be a localised property of the hæmoglobin particles, is correctly regarded as an adsorption phenomenon, even although the amount of oxygen taken up at

different pressures can be fairly accurately represented by the "adsorption isotherm." The author prefers to regard a process as being rightly classified as adsorption only if the substance taken up by the surface continues to be taken up until the whole surface is uniformly covered. Probably only a very small part of the surface of the hæmoglobin particles can be actually covered by oxygen when combination ceases at the stage of oxy-hæmoglobin. All cases of adsorption, from a gaseous phase, or from solution, on plane or nearly plane interfaces are compatible with the definition, whilst it is also probably applicable to those of adsorption on colloidal surfaces.

A. A. E.

Adsorption and Hæmoglobin. (SIR) W. M. BAYLISS (*Nature*, 1923, **111**, 666—667; cf. Adam, preceding abstract).—The fact that when hæmoglobin is fully saturated with oxygen, the oxygen is taken up in the proportion of one molecule to each atom of iron in the hæmoglobin molecule does not exclude the possibility of adsorption at local foci, nor does an explanation based on true chemical combination account also, for example, for the greater affinity of hæmoglobin for carbon monoxide than for oxygen. It is pointed out that hæmoglobin under most conditions exists in the form of colloidal aggregates, so that the possibility of the intervention of surface phenomena must be considered. Adam's (*loc. cit.*) criterion of adsorption is briefly criticised, in that it appears to neglect cases in which two or more substances are adsorbed simultaneously.

A. A. E.

The Triphosphonucleic Acid of Thannhauser and Dorf-müller. R. FEULGEN and H. ROSSENBECK (*Z. physiol. Chem.*, 1923, **127**, 67—79).—It is concluded that the triphosphonucleic acid described by Thannhauser and co-workers (*A.*, 1914, **i**, 1015; 1916, **i**, 522; 1918, **i**, 47, 316; 1920, **i**, 895; 1921, **i**, 201) does not exist.

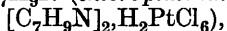
W. O. K.

The Structure and Properties of Chondrin and of Hydrogen Chondroitin Sulphate (a New Method for the Preparation of Hydrogen Chondroitin Sulphate). M. RAKUZIN and (MLLE) EK. BRAUDO (*J. Russ. Phys. Chem. Soc.*, 1917, **49**, 200—207).—A solution of chondrin in water is decomposed by 2% aluminium hydroxide into hydrogen chondroitin sulphate, which remains in solution, whilst the chondrin residue is adsorbed in the colloid. When 5% of the latter is present in the solution, the reaction proceeds in two stages; first, the amphoteric radicles which give the Ostromisslenski and the xanthoproteic reactions are hydrolysed off, and then the hydrogen chondroitin sulphate. Using 1% of colloid, the chondrin is adsorbed as a whole, without decomposition. The optical rotation of some hydrogen chondroitin sulphate prepared in the above way is $[\alpha]_D -46.59^\circ$, whence $[\alpha]_D$ for the chondrin residue is calculated to be -386.85° .

R. T.

Chondroitinsulphuric Acid. W. SAVIALOV (*Z. physiol. Chem.*, 1923, **126**, 219—249).—*Chondran*, $C_{32}H_{36}O_{16}N$, isolated as its tetrabenzoate, $C_{60}H_{52}O_{20}N$, is obtained from chondroitinsulphuric

acid on hydrolysis with acid, along with *chondroitine tribenzoate*, isolated as its *hydrochloride*, $C_{40}H_{32}O_{12}N, HCl$. This corresponds with a formula $C_{19}H_{20}O_9N$ for chondroitine. Chondrosine, $C_{14}H_{18}O_8N$, has been isolated as the *osazone*, $C_{26}H_{28}O_6N_5$, light yellow, tufted crystals, m. p. 154° (corr.). The amorphous base, $C_{14}H_{16}O_8N, 5H_2O$, has also been obtained, and the *sulphate*. Chondrosine, when heated with baryta water yields chitonic acid, $C_6H_{10}O_6$, and a base, C_7H_9N (*chloroplatinate*, white flocks,



and when oxidised, *isosaccharic acid*, m. p. 208° , is obtained. If chondrosine sulphate is warmed with an excess of copper hydroxide, a *compound*, $(C_5H_8O_4N)_2Cu$, giving a red biuret reaction, is obtained.

W. O. K.

Keratin. IV. A. HEIDUSCHKA and E. KOMM (*Z. physiol. Chem.*, 1923, 126, 261—276).—The proteoses obtained from the partial hydrolysis of horn (cf. A., 1922, i, 967) have been fractionated and the solubilities and reactions of the various heterokeratoses, protokeratoses, and deuterokeratoses investigated. W. O. K.

The Preparation and the Properties of Ovokeratin. M. A. RAKUZIN (*J. Russ. Phys. Chem. Soc.*, 1917, 49, 159—164).—A quantity of ovokeratin was prepared from the membranes of eggs, by Ladenburg's method. The sodium proteinate from the alkali washing of the membranes gave Adamkiewicz's, Molisch's, Pettenkofer's, and Ostromisslenski's reactions for albumins, and appears to be a hitherto unknown albuminate, $[\alpha]_D -4.87^\circ$. The subsequent acetic acid washing removed from the membranes amino-acids, which gave only Ostromisslenski's reaction with picramic acid, and had $[\alpha]_D -27.82^\circ$. Ammonium and potassium ovokeratinate were prepared, $[\alpha]_D$ being -36.79° , and -38.96° , respectively. Ovokeratin gives the biuret and the xanthoproteic reactions, and also Millon's and the above-mentioned four reactions. Its phosphorus content is very small, whilst 2.3% of sulphur is found. This is much lower than the value obtained by Lindval, who found 4.25% of sulphur in ovokeratin. R. T.

Influence of Carnosine and of Different Ions on the Digestion of Proteins by Pepsin. IVAN ANDREEVITSCH SMORODINCEV (*J. Russ. Physiol.*, 1922, 4, 279—280).—The activity of pepsin is not influenced by glycerol; extracts of the enzyme in this solvent maintain their activity for years.

The action of pepsin on edestin and casein is inhibited by the following substances in the concentrations (expressed as normality) stated: carnosine (1/160); sodium and potassium hydroxides (1/320—1/640); sodium, potassium, and lithium carbonates (1/160—1/320); sodium, potassium, and lithium hydrogen carbonates (1/20—1/40); ammonia (1/80); disodium hydrogen phosphate (1/8). The inhibitory effect is attributed to the hydroxyl-ions. No such action is shown by carnosine hydrochloride and nitrate (1/10), or by sodium, potassium, and ammonium chlorides and nitrates (1/10). The digestion of edestin by pepsin is inhibited by

1/4*N*-solutions of the chlorides and 1/8*N*-solutions of the nitrates of sodium, potassium, and ammonium, but that of casein is not influenced by normal solutions of these salts. The inhibitory action of salts is due to the anions.
E. S.

Adsorption of Saccharase by Alumina. H. VON EULER and K. MYRBÄCK (*Z. physiol. Chem.*, 1923, 127, 115—124).—The adsorption of saccharase by alumina is maximum at p_H 6.0—6.5, using acetic acid and ammonium as a buffer, although with other buffers, particularly phosphates, irregular results are obtained. The addition of acetone to the solution of the enzyme increases the adsorption, but it also destroys the saccharase. Hence, only alcohol should be used to increase the adsorption of the enzyme.

W. O. K.

Inactivation of Saccharase by Halogens. H. VON EULER and K. JOSEPHSON (*Z. physiol. Chem.*, 1923, 127, 99—114).—The degree of inactivation of saccharase by iodine increases with the time. In the case of bromine the degree is independent of the time. In both cases, it is independent of the concentration of the enzyme, and in the case of iodine, at least, it is independent of the p_H . Iodine appears to be more efficient than other poisons in inhibiting the activity of highly purified saccharase, whilst the bromine equivalent (the amount of saccharase inactivated by one molecule of bromine) agrees with that of silver as already determined.

W. O. K.

Existence of Two Amylotic Ferments in Malt Diastase. E. OHLSSON (*Compt. rend. Soc. Biol.*, 1922, 87, 1183—1184; from *Physiol. Abstr.*, 1923, 8, 9).—In malt extract, two enzymes are present, one converting starch into dextrin, the other responsible for the conversion of starch or dextrin into maltose. These may be differentiated by keeping the enzymes at certain temperatures and at certain hydrogen-ion concentrations. At 5° and p_H 4, the dextrin-forming enzyme disappears rapidly, whilst the maltose-forming enzyme remains practically unaltered. Kept at p_H 6 and at 70° for twenty minutes, the extract rapidly loses its property of forming maltose, while retaining its dextrin-forming capacity.

W. O. K.

Investigations on the Starch-liquefying Function of Malt Diastase. W. WINDISCH, W. DIETRICH, and ARTUR BEYER (*Woch. Brau.*, 1923, 40, 49—50, 55—56, 61—63, 67—70).—The experimental results given indicate that the liquefaction of starch by diastase probably depends on increase in the degree of dispersion of the starch or amylopectin. The liquefying action proceeds best when p_H has the value 5.03, the reaction being thus similar to the optimum reaction for saccharification of starch by diastase.

The method suggested for determining the liquefying power of malt diastase consists in treating amylopectin made from wheat starch with an aqueous extract of the malt in presence of a buffer mixture of sodium acetate and acetic acid, the filtered liquid being

afterwards hydrolysed by means of hydrochloric acid and the dextrose thus formed estimated iodometrically. The amount of starch liquefied by the diastase present in 1 g. of malt is taken as a measure of the liquefying power. Kjeldahl's law of proportionality is found to hold for the liquefying, as well as for the saccharifying, power, but the liquefying powers bear no constant relation to the saccharifying powers with different malts.

T. H. P.

An Investigation of the Chemical Nature of Two Typical Enzymes : Pancreatic and Malt Amylases. H. C. SHERMAN (*Proc. Nat. Acad. Sci.*, 1923, 9, 81—86).—A summary of work on enzyme hydrolysis (cf. A., 1922, i, 283). Preparations of pancreatic and malt amylases have been made, precautions being taken to reduce the hydrolysis of the enzyme. The pancreatic amylase showed marked enzymic activity at a dilution of 1 : 100,000,000, whereas the usual protein tests are 1,000 times less sensitive. Both the amylase preparations were submitted to quantitative analysis by the Van Slyke method, which showed that they yielded all the typical products of hydrolysis of proteins. The amylases were very much more sensitive to antiseptics which precipitate proteins than to those of the lipid dissolving type. The activity of the amylases decreases when suspended in pure water at a greater rate than when in the presence of substances which are the product of protein hydrolysis. The addition of amino-acids checks the deterioration of the enzyme as measured by the change in its saccharogenic power and amylolytic activity. Arginine, histidine, lysine, tryptophan, and cystine were studied in this connexion. Arginine and cystine increase the activity of the amylases, but the other acids only exert a favourable influence on the saccharogenic power. The results show that the amylolytic and saccharogenic activity are to some extent different properties of the amylase. The first products of the amylase are those amino-acids which tend to prevent the initial hydrolytic stages, and acids like lysine and tryptophan are produced in subsequent stages. This is in accord with the view that the amylolytic occurs before the saccharogenic stage of enzyme action. The optimum activity of the two enzymes is shown at quite different hydrogen-ion concentrations, that of pancreatic amylase at p_H 6.9 and of malt amylase at p_H 4.4. The activity of the former is fully twice that of the latter.

W. E. G.

Kinetics of Ester Hydrolysis by Liver Lipase. E. KNAFFLENZ (*Arch. exp. Path. Pharm.*, 1923, 97, 242—261).—The hydrolysis of alkyl esters by the enzymes of the liver proceeds as a reaction of the first order, equal quantities being hydrolysed in equal times. The activity of the enzymes ceases at any $p_H < 5.2$, which is also the lowest p_H at which fats are hydrolysed. The optimum p_H for the hydrolysis of alkyl esters is 7.8—8.8, whilst in the case of fats, the optimum p_H is higher. In the hydrolysis of fats, if the reaction coefficient of the first order be calculated, it is found to decrease as the reaction proceeds.

W. O. K.

Urease. STURE LÖVGREN (*Biochem. Z.*, 1923, **137**, 206—257).—In continuation of the author's observations (A., 1922, i, 185) on urease, an investigation has been made of the influence on the position of the optimal p_H , of the phosphate concentration, the enzyme concentration, and the concentration of the reaction products. The empirical modification of the unimolecular equation given in the previous paper is not found to be generally applicable over the whole range of conditions studied. A new equation, developed from an equation of the type $F(x, y, \dots, z) = \text{const.}$ is described containing five coefficients. For details of the evaluation of these constants the original should be consulted. H. K.

Influence of Glycine on the Fermentative Action of a Soja-bean Urease. NAOSABURO KATÔ (*Biochem. Z.*, 1923, **136**, 498—529).—A long series of experiments is detailed on the influence of glycine on the action of urease. The salient points are the following. Using a single urease preparation, for a given quantity of urease, there is an optimal carbamide concentration which is termed the "equivalent carbamide concentration" (*E.C.C.*) which is uninfluenced by dilution or temperature changes. It follows that the ratio of the ammonia formed at a given carbamide concentration to that formed at the equivalent carbamide concentration is a variable quantity and is called the "gradation" of the urease action for this particular carbamide concentration. The gradation is subject to temperature influences and such changes are called the "quality" of the gradation. The magnitude of the *E.C.C.* increases with increase of the quantity of urease used. The quantity of ammonia evolved at the *E.C.C.* is a constant for the urease preparation. Addition of glycine influences these three "constants" in such a way that more ammonia is evolved. If the experiment is repeated with more glycine, then the proportion of ammonia below the *E.C.C.* is unchanged, but above the *E.C.C.* there is more evolved than in the former experiment. In urease preparations, two constituents are postulated to account for the great variations possible in the experimental results. H. K.

Analogies between Methylene-blue and Oxydases. P. A. ASCHMARIN (*J. Russ. Physiol.*, 1922, **4**, 283—284).—Methylene-blue accelerates considerably the indophenol and *p*-phenylenediamine reactions. In the former case, the velocity is augmented five to ten times, and in the latter five to twenty times, according to the concentrations of the reagents and the temperature. The last-named factors exert a similar influence in the presence of methylene-blue as in the presence of oxydases (cf. Vernon, A., 1911, ii, 750; Battelli and Stern, A., 1913, i, 139, 140). Methylene-blue may be considered as a substance analogous to the oxydases. E. S.

The Interaction of Hydrogen Sulphide, Thiocyanogen, and Thiocyanic Acid with Unsaturated Compounds. FREDERICK CHALLENGER, ALAN LAWRENCE SMITH, and FREDERIC JAMES PATON (*T.*, 1923, **123**, 1046—1055).

Organo-derivatives of Thallium. VI. Compounds of the Type R_2TlX . ARCHIBALD EDWIN GODDARD (T., 1923, **123**, 1161—1172).

Physiological Chemistry.

The Immediate Effect of Heavy Exercise (Stair-running) on some Phases of Circulation and Respiration in Normal Individuals. II. Oxygen and Carbon Dioxide Content of Blood Drawn from a Cubital Vein at Different Intervals after Exercise. CHRISTEN LUNDGAARD and EGGERT MÖLLER (*J. Biol. Chem.*, 1923, 55, 477—485).—The oxygen content of blood from the cubital vein, which has a low value immediately after heavy leg exercise (this vol., i, 502), increases to a value almost equal to that of arterial blood in two to four minutes and returns to the normal in five to eight minutes after the cessation of such exercise. Simultaneously with the increase in oxygen content, the carbon dioxide content decreases markedly (5 to 10 vol. %); this is probably due to accumulation of lactic acid in the muscles.
E. S.

Physiology of Muscular Exercise. I. Changes in Acid-base Equilibrium following Short Periods of Vigorous Muscular Exercise. DAVID P. BARR, HAROLD E. HIMWICH, and ROBERT P. GREEN (*J. Biol. Chem.*, 1923, 55, 495—523).—Short periods of vigorous leg exercise are followed by a large diminution in the carbon dioxide capacity, a reduction in the alkalinity, and an increase in the lactic acid content of both arterial and venous blood (drawn from the arm). In the case of arterial blood, there is also a diminution in the carbon dioxide tension; venous blood has not yielded consistent results in this respect. No quantitative relationship has been observed between the reduction in carbon dioxide capacity and the increased concentration of lactic acid. The above changes vary in magnitude according to the vigour of the work; they are scarcely detectable after light exercise.
E. S.

Physiology of Muscular Exercise. II. Comparison of Arterial and Venous Blood following Vigorous Exercise. DAVID P. BARR and HAROLD E. HIMWICH (*J. Biol. Chem.*, 1923, 55, 525—537).—The diminution in the carbon dioxide capacity of blood drawn from the arm shortly after vigorous leg exercise (cf. preceding abstract) is smaller in venous than in arterial blood. This is due to the removal of lactic acid from the blood during its circulation through the tissues of the arm. In the region of the active tissues, however, the venous capacity is equal to, or less than, the arterial. Apparently, lactic acid passes from the active muscles into the blood, from which it is again removed by

the less active tissues. There is no appreciable difference between the reaction of arterial and of venous blood following exercise.

E. S.

Physiology of Muscular Exercise. III. Development and Duration of Changes in Acid-Base Equilibrium. DAVID P. BARR and HAROLD E. HIMWICH (*J. Biol. Chem.*, 1923, 55, 539—555).—The carbon dioxide tension of arterial blood increases during the first two minutes of vigorous exercise and thereafter diminishes progressively; the return to the normal takes place slowly and commences several minutes after exercise has ceased. With venous blood, the increase continues during a longer period. The remaining changes in the blood (cf. preceding abstracts) are continuous from the commencement of exercise, reach a maximum either during exercise, if this is continued for about seven and a half minutes, or after exercise, if it is of shorter duration; the return to the normal then takes place slowly. The direction of the changes at any particular time is apparently conditioned by the difference in the rates at which lactic acid is being absorbed by, and removed from, the blood.

E. S.

Seasonal Tide of Blood Phosphates in Infants. A. F. HESS and M. A. LUNDAGEN (*J. Amer. Med. Assoc.*, 1922, 79, 2210—2212).—The seasonal tide of blood phosphates with a diet of raw milk showed a decline from about 4 mg. % in December to 3.5 mg. % in March, after which the blood phosphates quite steadily rose to 4.5 mg. % in June. The low level of phosphates in March would have been lower but for the fact that whenever the phosphates fell to 3.75 mg. % the child was given either sun treatment or irradiation from an artificial source. Ultra-violet light can also raise to normal a subnormal amount of calcium in the blood. In some experiments, 7 mg. % have been raised to 10 by irradiations during two or three weeks with the carbon arc light. The seasonal variation indicates that the chemical constitution of human blood is not constant for all periods of the year. This probably is true for other tissues. Marked fluctuations are observed only in young children. Seasonal changes in the composition of the blood appear to be correlated with certain seasonal diseases.

CHEMICAL ABSTRACTS.

Blood Lipoids. I. The Relation of Cholesterol and Protein Deficiency to Basal Metabolism. A. A. EPSTEIN and HERMAN LANDE (*Arch. Intern. Med.*, 1922, 30, 563—577).—A low blood cholesterol value was found associated with high basal metabolism and a high blood cholesterol value with a low basal metabolism. Thus, a low blood cholesterol value was observed in hyperthyroidism and a low basal metabolism in nephrosis.

CHEMICAL ABSTRACTS.

Variation in the Lipoid Content of the Plasma after Injection of Peptone. Comparison with Anaphylactic Shock. (MME) PAULETTE JUNG and RENÉ WOLFF (*Bull. Soc. Chim. biol.*, 1923, 5, 200—206).—Intravenous injection of Witte's peptone into

dogs produced large variations in the lipid content of the plasma. The fatty acid content increased consistently, the increase in one case amounting to 87% (calculated on the dry weight of the plasma); the variations in cholesterol and lipid phosphorus were, however, irregular. Values approaching the normal were again obtained when the coagulability of the plasma returned. Preliminary experiments indicate that there is also a disturbance in the lipid content of the plasma during anaphylactic shock. E. S.

Is Pyruvic Acid the Forerunner of Acetaldehyde in Human Blood? The Presence of Carboxylase in Human Blood. WILHELM STEPP and BEHREND BEHRENS (*Z. physiol. Chem.*, 1923, 127, 80—92).—By the use of the "silver" method of Stepp and Fricke (A., 1922, ii, 236) for the estimation of acetaldehyde, estimations have been made of the amount produced from pyruvic acid in the presence of blood. It is concluded that a carboxylase is present in small quantities in the blood. W. O. K.

Comparative Concentration of Urea in the Blood and Saliva in a Series of Pathological Cases. H. W. SCHMITZ (*J. Lab. Clin. Med.*, 1922, 8, 78—82).—The urea content of saliva was about 89.4% of that of the blood; salivary urea estimations may replace those of blood urea in determinations of the functional activity of the kidneys. CHEMICAL ABSTRACTS.

Decomposition of Glycogen by Blood-serum. DIONYS FUCHS and GEZA HETÉNYI (*Biochem. Z.*, 1923, 136, 469—470).—The change of rotation of the blood-serum of diabetics and of non-diabetics when mixed with 1% glycogen solution was observed in eighty cases. In thirty-three cases the total mean change of rotation in diabetics was -0.053° , in non-diabetics -0.036° , and in forty-seven cases (different observer) for diabetics -0.070° , and for non-diabetics -0.063° . The conclusion is drawn that the diabetic blood-serum has a greater power of breaking down glycogen than that of the non-diabetic. H. K.

Nature of Antiferments (Antitrypsin). BORIS I. SLOVITZOV and W. JA. XENOPHONTOVA (*J. Russ. Physiol.*, 1919, 2, 267).—Evidence is advanced supporting Jobling's view that antitrypsin is a lipoid. Thus, serum, when extracted with chloroform, loses its antitryptic power, whilst the soap obtained by saponification of the extract has the same antitryptic power as the serum. Sodium oleate in minimal concentrations (0.003%) has also been observed to exert a marked antitryptic action. Glycerol does not show this effect. E. S.

Digestion. I. The Digestive Enzymes of Coelenterates. II. Digestion in Elasmobranchs and Teleosts. M. BODANSKY and W. C. ROSE (*Amer. J. Physiol.*, 1922, 62, 473—481; 482—487). I. The following enzymes are present in the jelly fish, *Stomolophus meleagris*, and in the Portuguese man-of-war, *Physalia arethusa*: pepsin, trypsin, rennin, amylase, maltase, and lipase. Invertase is present in negligible amount. Inulinase and lactase are absent.

Proteins naturally used as food (fish) are more readily hydrolysed than are proteins foreign to the customary diet (egg-albumin, beef fibrin and casein), suggesting a specific adaptation of the enzymes to the individual proteins on which they customarily act.

II. A peptic enzyme, having a maximum activity at a p_H of about 3.0, was demonstrated in the gastric mucosa of the elasmobranchs *Squalus acanthias* (dogfish), *Pristis pectinatus* (sawfish), *Torpedo galvani* (torpedo ray) and in the teleosts *Lutjanus aya* (red snapper), *Paralichthys lethostigma* (flounder), *Lactophrys tricornis* (cowfish) and *Mycteroperca bonaci* (black grouper). Fish pepsin effectively digests a larger variety of proteins than does the pepsin of either jellyfish or of Portuguese man-of-war. Rennin is present in the stomach of the torpedo ray, red snapper, flounder, and catfish; but absent from that of the dogfish, sawfish, cowfish, and mullet. The pyloric caeca of the red snapper contain trypsin, pepsin, rennin, amylase, and lipase; inulinase, maltase, and lactase are absent. The secretions of the pyloric appendages of the red snapper contain most of the enzymes which are usually found in the pancreatic juice of higher vertebrates.

CHEMICAL ABSTRACTS.

The Structure of the Alimentary Canal and its Enzymes in the Bee (*Apis mellifera*, L.). E. N. PAVLOVSKI and E. J. ZARIN (*Quart. J. Microsc. Sci.*, 1922, **66**, 509—556).—The stomach (mid intestine) of the worker and drone contained catalase, amylase, invertase, lipase, pepsin, trypsin, and rennin. Inulase, lactase, and emulsin were absent. Catalase was found in the rectum, but was subject to seasonal variation. From triturated stomachs, catalase decreased in the extracts on keeping, whilst from whole stomachs it increased. Glycerol had a repressive influence on invertase. Methods for the preparation of extracts and for testing their activity are given.

CHEMICAL ABSTRACTS.

Uric Acid Metabolism. III. The Influence of Fats and Carbohydrates on the Endogenous Uric Acid Elimination. HOWARD B. LEWIS and RALPH C. CORLEY (*J. Biol. Chem.*, 1923, **55**, 373—384).—The experimental conditions were similar to those employed in the case of proteins and protein derivatives (A., 1918, i, 277). No increased excretion of uric acid was observed after the ingestion of cream (135 g.), lactose (100 g.), sucrose (100 g.), or dextrose (100 g.). Increases were, however, produced by glycerol (50 g.), honey (200 g.), and commercial glucose syrup (200 g.), the effect being most marked in the case of glycerol. When these and the previous results are regarded from a quantitative point of view, the stimulating action of the substances on uric acid excretion is found to run roughly parallel with the specific dynamic action. It is considered that these results are in harmony with the view previously advanced that a rise in uric acid excretion following the ingestion of food is due, at least in part, to a stimulation of cellular metabolism.

E. S.

Histochemistry of Spermatogenesis. H. STEUDEL and K. SUZUKI (*Z. physiol. Chem.*, 1923, **127**, 1—13).—Fish testicles were

shaken with water, filtered, and the filtrate evaporated to a syrup. When kept, a sediment separated, which consisted of inorganic salts and gave reactions for tryptophan, creatinine, and cystine, and from which leucine was isolated. In the filtrate from the deposit, the presence of alanine, leucine, lysine, creatinine, agmatine, and histamine was determined. W. O. K.

Some Physico-chemical Properties of the Constituents of the Egg of *Paracentrotus lividus*, Lk. FRED VLÈS, (MLLE) G. ACHARD, and DJ. PRIKELMAIER (*Compt. rend.*, 1923, **176**, 1179—1181).—Portions of the unfertilised eggs of *Paracentrotus lividus* were made into an emulsion with acidified sea-water having p_H 5·8 equal to that of the interior, and the emulsion was subjected to cataphoresis in sea-water of p_H 3, 4·1, 5·0, 5·8, and 9. A distinct transport to the cathode was observed in p_H 3, 4·1, and 5·0, and to the anode in p_H 9. In p_H 5·8, the direction was uncertain, but with a slight tendency towards the anode. The isoelectric point of one of the principal constituents of the ovular complex corresponds therefore with a p_H between 5·0 and 5·8. Experiments with an emulsion of p_H 8 gave less regular results, and it appears that the complex shows a maximum coherence in the neighbourhood of the isoelectric point, and any variation in the p_H of the interior of the egg produces a corresponding change in the viscosity, conductivity, osmotic pressure, etc., and will explain the observations previously made on the effect of change of p_H on fecundation, division of the egg, etc. G. F. M.

Distribution of Nitrogen between the Body of the Mature Chick, the Yellow of the Egg, and the Waste [Shell, Amnion]. N. W. ROMENSKI (*J. Russ. Physiol.*, 1919, **2**, 284).—The body of the new-born chick contains 54·12—65·82%, the yellow of the egg 27·63—37·01%, and the waste 6·42—12·68% of the total nitrogen of the egg. If the chick is left without food for thirty-six hours after birth, there is practically no diminution in the nitrogen it contains. E. S.

Chemical Composition of the Grey Substance of the Human Brain in Relation to the Function of the Brain. A. K. LENZ (*J. Russ. Physiol.*, 1919, **2**, 168—169).—The essential differences between the composition of the grey matter of the cortex and that of the ganglia are a greater proportion of water and proteins in the former and of lipoids in the latter. The proteins in the two portions are of similar type. These results indicate the important rôle of the proteins in the function of the brain. E. S.

Chemical Composition of the Grey and White Matter of the Human Brain. B. I. SLOVTZOV and A. M. GEORGIEVSKAIA (*J. Russ. Physiol.*, 1922, **4**, 277).—Analyses have been made of the grey and white matter of the brain. The former is richer in proteins and extractives, and the latter in lipoids. The composition of rabbit's brain is distinctly modified, especially in the lipid fraction, by methyl-alcoholic poisoning. E. S.

Autolysis of the Grey Matter of the Brain. A. M. GEORGIEVSKAIA (*J. Russ. Physiol.*, 1922, 4, 277).—During autolysis of the brain both the proteins and lipoids dissolve. After some time, however, the insoluble fractions of these substances may increase owing to the formation of less soluble products. There is a considerable increase in amino-nitrogen during autolysis of the brain.

E. S.

The Nucleic Acids of the Pancreas. H. STEUDEL and SATOSU NAKAGAWA (*Z. physiol. Chem.*, 1923, 126, 250—256).—In the pancreas, guanine and adenine are present in equimolecular proportions. Apparently about 5 g. of nucleic acid are contained in 100 g. of the dry residue, obtained after extraction of the glands by alcohol and ether.

W. O. K.

Pancreatic Rennin. A. EPSTEIN (*Proc. Soc. Exp. Biol. Med.*, 1921, 19, 3—6).—By suitable treatment (detailed in the original communication) of pancreatic extract, a substance which conceals the presence of rennin can be removed. Rennin is so far inseparable from trypsin, and combined they constitute about 1—2% of dry pancreatic extract as an acidic substance of protein nature, hygroscopic, coagulating at 82—85°, not removed by ordinary precipitants, and active only in the presence of calcium-ions.

CHEMICAL ABSTRACTS.

The Effect of Pancreatic Rennin on Blood Coagulation. A. EPSTEIN and NATHAN ROSENTHAL (*Proc. Soc. Exp. Biol. Med.*, 1921, 19, 79—84).—Pancreatic rennin-trypsin (cf. preceding abstract) together with calcium chloride reduce the coagulation time of normal blood from 11—12 minutes to 0.25—0.5 minute. The coagulation time varies inversely with the amount of enzyme.

CHEMICAL ABSTRACTS.

The Question of the Cadaverine Content in Aqueous Extracts of Autolysed Pancreatic Glands. (MLLE) V. A. SEMENOVITSCH (*J. Russ. Phys. Chem. Soc.*, 1917—1918, 49, 608—612).—A sterile extract made from 12 kilos. of pancreatic glands derived from freshly killed cattle was tested for the presence of cadaverine (pentamethylenediamine), using Werigo's method (A., 1892, 1368). The mixed picrates of the bases present proved to contain a compound having the melting point of arginine picrate, but no cadaverine could be found (cf. Kutscher and Lohmann, A., 1904, ii, 425; 1905, ii, 466).

G. A. R. K.

Nervous Control of the Kidney in Relation to Diuresis and Urinary Secretion. VI. The Effect of Unilateral Section of the Splanchnic Nerve on the Elimination of certain Substances by the Kidney. E. K. MARSHALL, jun., and M. M. CRANE (*Amer. J. Physiol.*, 1922, 62, 330—340).—Increased blood flow through the kidney, brought about by section of the splanchnic nerve, increases markedly the elimination of water, chlorides, and carbonates, to a less extent that of urea, phosphates, and sulphates, whilst the elimination of creatinine, ammonia, and phenol-

sulphonephthalein is unchanged. The results are thought to support the theory of filtration through the glomeruli and reabsorption and secretion by the tubules.

CHEMICAL ABSTRACTS.

Hippuric Acid Synthesis as a Test of Renal Function.

SERGIUS MORGULIS, G. P. PRATT, and H. M. JAHR (*Arch. Intern. Med.*, 1923, **31**, 116—144).—In normal persons, 2 g. of benzoic acid, administered as such or as the sodium salt, is completely synthesised to hippuric acid and the kidney is stimulated to enhanced activity. In nephritic and cardiorenal patients the synthesis is never complete but, even in severe nephritis, from 53 to 95% of the ingested benzoic acid may be recovered as hippuric acid and from 59 to 100% as total benzoic acid in the twenty-four hours following the administration of benzoic acid.

CHEMICAL ABSTRACTS.

Relation of Lipoids to Suprarenal Physiology. I. The Cholesterol and Lipoid Phosphorus Contents of the Blood of Rabbits Before and After Suprarenalectomy. EMIL J. BAUMANN and O. M. HOLLY (*J. Biol. Chem.*, 1923, **55**, 457—475).—A rise in the blood lipid phosphorus was observed in every case after removal of both glands and occasionally after removal of one, but no significant changes occurred in the cholesterol content. During the few days preceding the death of the animals, both the cholesterol and the lipid phosphorus content of the blood rose; these changes, however, were probably due to blood concentration. The results thus offer no support for the hypothesis that cholesterol is either formed or stored in the suprarenal glands. E. S.

The Active Principles of the Pituitary Gland. HAROLD WARD DUDLEY (*J. Pharm. Expt. Ther.*, 1923, **21**, 103—122).—Further unsuccessful attempts have been made to isolate the uterine stimulant from extracts of powdered pituitary glands. The greater part of the active principle was found to be concentrated in the alcohol-soluble portion of the butyl alcohol extract previously described (A., 1920, i, 344). From this, creatinine was isolated in the form of its double picrate with potassium. The mother-liquors from the crystallisation of this salt gave a preparation of high activity, which was further separated into two fractions by means of acetone. The insoluble fraction consisted of a dry powder with an activity on the isolated uterus about twelve times as great as that of histamine; when tested on the blood pressure, it gave a pure pressor effect. The soluble fraction was a deliquescent resin with a much smaller uterine activity; its pressor action was preceded by a depressor effect. The author concludes, in opposition to the view of Abel and Rouiller (*J. Pharm. Expt. Ther.*, 1922, **20**, 65), that at least three active principles are present in pituitary extracts. E. S.

Substances Extractable from Human Muscle. I. A.

SMORODINCEV (*J. Russ. Phys. Chem. Soc.*, 1917, **49**, 263—266).—An extract was made of fresh human muscle, and was analysed for bases in the usual way. The muscle thus extracted contained

0.45% of nitrogen, and the following bases were isolated: Purine bases, 0.036%, carnosine, 0.164%, methylguanidine, 0.041%, carnitine, 0.031%, creatinine, traces. The same substances exist in similar proportions in the muscles of domestic animals.

R. T.

Creatinine and Creatine in Muscle Extracts. IV. Concerning the Formation of Creatine from Methylguanidine in Muscle. FREDERICK S. HAMMETT (*J. Biol. Chem.*, 1923, **55**, 323).—Incubation of extracts of muscle tissue with methylguanidine under various conditions led to no increase in total creatine. This supports the results of Baumann and Hines (A., 1918, i, 417) and is against the view that methylguanidine is the precursor of creatine.

E. S.

The Rate of Deposition and Paths of Absorption of Strontium in the Rat. ETHEL MAY KINNEY and E. V. MCCOLLUM (*J. Pharm. Expt. Ther.*, 1923, **21**, 165—176).—When fed to rats in the form of carbonate, strontium is rapidly deposited in the bones, even although adequate amounts of calcium are present in the diet. The rate of deposition is greater with young than with mature animals. Strontium may also enter the body through the placenta and the milk of the mother.

E. S.

The Zinc Content of the Body and certain Organs of Invertebrates. GABRIEL BERTRAND and R. VLADESCO (*Bull. Soc. chim.*, 1923, [iv], **33**, 341—345).—The zinc content of the whole bodies, and also of certain specific organs of numerous molluscs, was determined by the method previously described (*ibid.*, 1921, **29**, 53), and quite exceptionally large amounts were found in oysters (*Ostrea edulis*), ranging up to 27 mg. per 100 g. of the fresh material, and 152 mg. per 100 g. of dry material. Still larger quantities of from 50—131 mg. per 100 g. of fresh material were found in Portuguese oysters (*Gryphea angulata*). The average content of other shell fish such as mussels, cockles, etc., was 2—5 mg. per 100 g. The distribution of the zinc in the various organs was very uneven, being in general lowest in the muscular portions. The metal appears to play an important part in the phenomenon of fecundation.

G. F. M.

Growth of Caterpillars. EMIL ABDERHALDEN (*Z. physiol. Chem.*, 1923, **127**, 93—98).—Determinations have been made of the weight and of the nitrogen content of caterpillars at various periods in their development.

W. O. K.

The Transformation of Proteins. P. A. GLAGOLEV and M. N. VISCHNIAKOV (*J. Russ. Physiol.*, 1917, **1**, 25).—No appreciable difference has been observed in the composition of silk obtained from silkworms fed on the leaves of *Maclura aurantiaca* and on mulberry leaves (*Morus var. Tatarica*). The percentages of sericin and of fibroin, and the amino-acid composition of the latter, were practically identical in the silk from the two sources. The cocoons from the worms on the first diet, however, had a larger fat content.

E. S.

The Effect of Heat on the Calcium Salts and Rennin Coagulability of Cow's Milk. L. S. PALMER (*Proc. Soc. Exp. Biol. Med.*, 1921, **19**, 137—142).—The fact that a colloidal suspension of calcium hydrogen phosphate is largely precipitated by heating at 63° for thirty minutes explains the loss of the salt when milk is pasteurised. Dialysed milk is not coagulated by rennin in several hours, but the further addition of a small quantity of calcium chloride or hydrogen chloride causes instant clotting. Experiments show that a solution of colloidal calcium hydrogen phosphate and gelatin does not affect coagulation by rennin.

CHEMICAL ABSTRACTS.

The Presence of Formic Acid in the Urine of Infants and Older Children. M. McNEAL and CH. J. ELDRIDGE (*Amer. J. Diseases Children*, 1922, **23**, 419—422).—Examination of the urine of children by a modification of Autenrieth's method demonstrates the presence of formic acid.

CHEMICAL ABSTRACTS.

Ingested Fat and Body Fat as Precursors of the Acetone Substances. ROGER S. HUBBARD (*J. Biol. Chem.*, 1923, **55**, 357—363).—On diets moderately low in antiketogenic material, the amounts of acetone compounds excreted are the same whether they are derived from ingested or from tissue fat. E. S.

The Relation between Creatine Excretion and Acidosis. ALEXANDER PALLADIN (*Biochem. Z.*, 1923, **136**, 359—365).—The total nitrogen, creatinine, creatine, and acetone content of the urine of fasting dogs which received a daily injection of phloridzin was followed daily. Regarding the acetone substances in the urine as a measure of the acidosis, it is found that creatine excretion is apparently independent of the acidosis. Such dogs given small quantities of protein show diminished acetone products but unchanged creatine excretion. Fats increase the acetonuria without influencing the creatine excretion. The acidic or basic character of the foodstuffs is likewise without influence on the creatine.

H. K.

Influence of Cooling on the Excretion of Creatine. ALEXANDER PALLADIN (*Biochem. Z.*, 1923, **136**, 353—358).—Rabbits cooled until the rectal temperature fell to 30° excrete creatine in the urine as well as dextrose. If, however, the diet contains copious carbohydrate, no creatine appears.

H. K.

Secretion of Bile Acids in Cystinuria. HANS EPPINGER (*Arch. exp. Path. Pharm.*, 1923, **97**, 51—53).—An analysis has been made of the contents of the gall-bladder in a case of cystinuria. Sodium taurocholate appears to be decreased, as compared with the normal.

W. O. K.

The Natural Porphyrins. O. SCHUMM (*Z. physiol. Chem.*, 1923, **126**, 169—202).—The porphyrin in the urine of normal and of diseased subjects, and more particularly in cases of lead poisoning, has been investigated. The blood in some cases of congenital hæmatoporphyrinuria has been examined and the serum found to

contain porphyrin and hæmatin, besides a small quantity of oxyhæmoglobin and sometimes much bilirubin. W. O. K.

Theory of Narcosis by Inhalation Anæsthetics. II. Narcosis by Indifferent Gases under Pressure. KURT H. MEYER and HEINR. HOPFF (*Z. physiol. Chem.*, 1923, 126, 281—298).—It is found that with indifferent gaseous or volatile substances of very different types, narcosis sets in when the pressure of the vapour is such that the concentration of the substance in the cell lipid has reached a certain approximately constant value, 0·05—0·18 mol. per litre, according to the type of animal employed.

W. O. K.

Production of Muconic Acid from Benzene in the Animal Organism. HANNS NEUMAERKER (*Z. physiol. Chem.*, 1923, 126, 203—209).—If muconic acid be injected subcutaneously into a rabbit, about 60% may be recovered from the urine. On the other hand, after the injection of benzene in quantities of 1—3 g., no muconic acid could be detected in the urine. This indicates that if muconic acid is formed from benzene in the body, the amount produced is small.

W. O. K.

Synthesis of Amino-acids in the Animal Organism. II. The Synthesis of Ornithine in the Body of the Fowl. JAMES H. CROWDLE and CARL P. SHERWIN (*J. Biol. Chem.*, 1923, 55, 365—371).—When fed to fowls on a nitrogen-free diet, benzoic acid was excreted partly unchanged and partly as ornithuric acid. Simultaneously, there was a slight increase in the amount of uric acid excreted, but the percentage, calculated on the total nitrogen eliminated, showed a considerable decrease. Apparently, ornithine can be synthesised from waste uric acid nitrogen. No increased production of ornithuric acid was observed when histidine and proline were fed simultaneously with the benzoic acid; arginine, however, produced this effect.

E. S.

The Pharmacological Effect of the Three Stereoisomerides of Camphor, and of some Camphor Derivatives, on Smooth Muscle. MAX DOHRN (*Arch. exp. Path. Pharm.*, 1923, 97, 38—50).—*l*-Camphor has a greater paralysing effect on smooth muscle than the racemic form, and this again a greater effect than *d*-camphor. Other camphor derivatives, including *i*-aminocamphor, dihydrocamphenepyzazine, dihydrocamphenepiperazine, camphorquinone, methylcamphorylcarbinol, oxymethylenecamphor, camphorylcarbamide, camphoryl- ψ -carbamide, camphoryl- ψ -semi-carbazide, and dicamphorylcarbamide have also been investigated as to their pharmacological effects.

W. O. K.

Chemistry of Vegetable Physiology and Agriculture.

Formation of Fats and Lipoids. I. Influence of the Nature of the Carbohydrate Food on the Fat Content of the Tubercle Bacillus, and the Characters of these Fats. ÉMILE F. TERROINE and J. E. LOBSTEIN (*Bull. Soc. Chim. biol.*, 1923, 5, 182—199).—The influence of the composition of the culture medium on the lipid content of the tubercle bacillus has been investigated. With a medium otherwise identical, but containing dextrose in place of glycerol, the fat content of the bacilli diminished by about 60%; at the same time there was an increase in the protein content. The tubercle bacillus contains minimal quantities of cholesterol. E. S.

The Effect of Reaction on the Fixation of Nitrogen by *Azotobacter*. H. W. JOHNSON and C. B. LIPMAN (*Univ. California Pub. Agr. Sci.*, 1922, 4, 397—405).—A vigorous strain of *Azotobacter chroococcum* was grown in solutions of which the reactions were definitely determined by the hydrogen electrode. The nitrogen fixed in the solution of each reaction was estimated and the changes in reaction during incubation were measured. The reaction of the solution below p_H 8.0 changed very little, because below p_H 6.0 no growth occurred, and between 6.0 and 8.0 the solution was highly buffered. Above p_H 8.0, the reaction changed greatly, possibly because of incomplete reaction of the alkali at the time of titration, but more probably because of absorption of carbon dioxide by the strong alkali. The amount of nitrogen fixed was not greatly affected by reactions between p_H values of 6.2 and 8.8, although reactions around p_H 7.0 and 8.0 seemed to be most favourable. Slight changes outside of these values caused an abrupt decrease in fixation. CHEMICAL ABSTRACTS.

The Coagulative Enzyme of the Yeast-cell. A. M. NASTUKOV and N. S. PIATNICKI (*J. Russ. Phys. Chem. Soc.*, 1917, 49, 183—186).—An enzyme extracted from macerated yeast-cells is found to retain its power of coagulating so-called nutritive yolk-of-egg solution after heating in an autoclave at a pressure of 1.25 atmospheres. The product of coagulation, after filtering and extracting with alcohol, ether, or chloroform, gave on analysis, C 48.06%, H 7.06%, N 11.53%, S 0.98%, and P 5.46%. This shows that it cannot be vitellin or ψ -nuclein, formed by the action of pepsin, or of endotryptase, contained in yeast-cells, on yolk of egg. Yeast cells, therefore, must contain two enzymes, endotryptase, and a coagulative enzyme. R. T.

The Fermentation of Glyceric and Pyruvic Acids. A. N. LEBEDEV and A. N. POLONSKI (*J. Russ. Phys. Chem. Soc.*, 1917, 49, 93—94).—A short résumé of the work on the subject. Both acids are fermented by yeast to carbon dioxide and acetaldehyde, but whilst sugar solutions are completely fermented under com-

parable conditions, pyruvic acid gives only a 40% yield of decomposition products (other than carbon dioxide); the yield from glyceric acid is somewhat more favourable.

It is suggested that the experimental facts do not support the view that pyruvic acid is an intermediate compound in the alcoholic fermentation of sugar and that glyceric acid could equally well be such an intermediate product.

G. A. R. K.

The Fermentation of Pyruvic Acid in the Presence of Sugar.

A. N. LEBEDEV and A. N. POLONSKI (*J. Russ. Phys. Chem. Soc.*, 1917, 49, 328—344).—Solutions containing pyruvic acid and sucrose in various proportions were fermented by yeast. The quantity of carbon dioxide produced from such mixtures is greater than when each alone is fermented, whilst the yields of alcohol and acetaldehyde are diminished. This is probably due to the differential actions of zymase and carboxylase. Curves are drawn showing the velocities of fermentation of sucrose and pyruvic acid, separately and together, and at various concentrations. These show that fermentation proceeds more slowly in the mixture than for the separate components. If the solution be neutralised or made alkaline, the yields of acetaldehyde diminish, showing that carboxylase is less active in such conditions. Both the latter enzyme and zymase at first act rapidly and then very slowly, contrary to the views of Palladin, Gromov, and Monteverde (*A.*, 1914, i, 604). Less acetaldehyde is reduced to alcohol as the proportion of sugar in the mixture increases.

R. T.

The Fermentation of Glyceric and Pyruvic Acids. A. N. LEBEDEV and A. N. POLONSKI (*J. Russ. Phys. Chem. Soc.*, 1917, 49, 344—357).—Glyceric acid was fermented by yeast, and the quantity of carbon dioxide, acetaldehyde, and acetic acid produced were measured. The values thus obtained show that the reaction cannot consist only of the elimination of carbon dioxide from the acid, but may also involve more complete oxidation. Similar measurements were made for pyruvic acid, in acid, neutral, and weakly alkaline solutions. The amount of carbon dioxide produced is greatest with acid solutions, whilst with neutral or alkaline solutions the amount produced corresponds with the reaction $\text{CH}_3\cdot\text{CO}\cdot\text{CO}_2\text{H} \rightarrow \text{CO}_2 + \text{CH}_3\cdot\text{CHO}$. The acetaldehyde thus produced is converted partly into alcohol and acetic acid by the Cannizzaro reaction, and partly into alcohol by reduction, 2.5 times as much of the latter being formed as of the acid. More carbon dioxide and alcohol are produced from pyruvic than from glyceric acid, and less acetaldehyde and acetic acid. Not more than 40% of pyruvic acid is used in the production of the latter two substances and of alcohol, showing that it cannot be an intermediate product in the formation of alcohol by the fermentation of sugars.

R. T.

Action of Ultra-violet Rays on Alcoholic Fermentation by *Botrytis cinerea*. ROMOLO DE FAZI (*Atti R. Accad. Lincei*, 1923, [v], 32, 235—236).—Fermentation of must from grapes infected with *Botrytis cinerea* is accelerated by exposure of the must to the light from a quartz mercury vapour lamp.

T. H. P.

Iron and Manganese Content of certain Species of Seeds. J. S. MCHARGUE (*J. Agric. Res.*, 1923, 23, 395—399).—Analysis of a large number of seeds showed that in grasses and cereals the manganese content was roughly equal to that of iron; but in leguminous plants the amount of iron was considerably greater than that of manganese. A. G. P.

Influence of Potassium on the Development of Plants and their Morphological and Anatomical Structure (with Special Consideration of Farm Crops). H. WEISZMANN (*Z. Pflanzen. Düngung*, 1923, 2, 1—79).—A large number of pot and sand culture experiments are described in which the effects of potash starvation, and of fertilisation at different periods of the plant's growth, on the development of individual plant organs is studied. Unlike nitrogen- and phosphate-starvation, a deficiency of potassium does not markedly affect the plant structure in the early stages, but the wilting and death of the plant soon occurs. The plant loses its power of synthesis (particularly in the case of sugar beet) and the reserve storing organs (fruits, seeds, tubers, etc.) show little development at all. The latter effects are those most noticeably remedied when potassium is afterwards supplied to the starved plant.

Potassium affects the development of individual organs only so long as its total-yield increasing action proceeds. Flowering and fruiting are increased by potassium feeding, but to a lesser extent than in the case of phosphates. With cereals, potassium manuring increases the weight and size of individual grains, but does not often increase the actual number of grains, as does phosphatic manuring. Potassium increases the size and quantity of potato tubers, and the size of root crops. The enlarged top growth (stems and leaves) produced by supplying potassium to a previously starved plot results mainly from longer leaves and stems and not from a greater number of them. Deficiency of potassium frequently causes deformity in leaves, notably curling and spotting, and may also affect the colouring of leaf, stem, and grain. The mechanical properties of cereal straws are improved by potassium manuring; with non-cereals, the length of side shoots and their internodal spacing is increased, but the actual number of shoots is but little altered. The action of potassium on plants in general is not so uniform as that of nitrogen and phosphates. Consistent effects of potassium on the anatomical structure of plants can only be traced in a few instances, and then only with difficulty.

A. G. P.

A New Method for the Separate Extraction of Vacuole and Protoplasmic Material from Leaf-cells. ALBERT CHARLES CHIBNALL (*J. Biol. Chem.*, 1923, 55, 333—342).—The method depends on the fact that, after plasmolysis by immersion in an organic solvent such as ether or butyl alcohol, the greater part of the vacuole content may be expressed without rupturing the leaf-cells. The remainder may be extracted by repeatedly treating the residues with very dilute hydrochloric acid (0.002 *N*) and again

expressing; dilute acid is used in place of water since the latter would dissolve some of the protoplasmic protein. The residue from the hydrochloric acid extract contains the protoplasmic material, which may be extracted by grinding with water. The method has been applied to spinach leaves. E. S.

The Role of Vitamins in Cell Chemistry. W. R. HESS (*Z. physiol. Chem.*, 1923, 127, 196—198; cf. A., 1922, i, 399; Abderhalden, *ibid.*, i, 607).—It is claimed that Abderhalden's results do not disprove the author's conclusion that vitamin-B probably acts as a biocatalyst in cell oxidation processes. W. O. K.

Assimilation of Electrolytes by Plants. I. SILVESTR PRÁT (*Biochem. Z.*, 1923, 136, 366—376).—By determination of the electrical conductivity of nutrient solutions, the steady fall of concentration through absorption by growing plants can be followed quantitatively. Resorption of electrolytes depends on the intensity of the growth and is little affected by the transpiration. Using pure solutions (*M*/100) of sodium and potassium chlorides, it is found that the concentration of these salts is unchanged in the absorbed water whilst magnesium and calcium chlorides are taken up in lesser concentrations. H. K.

Synthesis of Acid Amides in Plants through Nourishing with Ammonium Salts. A. I. SMIRNOV (*Biochem. Z.*, 1923, 137, 1—34).—Etiolated plant shoots of barley grains rich in carbohydrates show a pronounced assimilation of nitrogen as ammonia, as is proved by the increased amide nitrogen content (attributed to formation of asparagine). The rate of this assimilation is greatest on the first day and falls off thereafter through the disappearance of carbohydrates. Calcium salts exert a favourable influence. The etiolated shoots of seeds with a low reserve of carbohydrates, such as lupines, take up ammonium salts in the presence of dextrose, but less so than do barley grains in the absence of dextrose. Methods are described for the pure culture of higher plants under sterile conditions. H. K.

Chemical Constituents of Green Plants. XXVII. Succinic Acid. HARTWIG FRANZEN and RUDOLF OSTERTAG (*Biochem. Z.*, 1923, 136, 327—335).—From a critical survey of the literature, it is concluded that out of thirty-three plants in which succinic acid is stated to occur, it occurs certainly in ten and probably in another three. H. K.

Protein Precipitation in Grasses. MARGARET H. O'DWYER (*Proc. Linnæan Soc. New South Wales*, 1922, 47, 513—515; cf. Petrie, *ibid.*, 1908, 33, 837; Chibnall and Schryver, A., 1921, i, 482; Buston and Schryver, A., 1922, i, 182).—Comparison of the precipitation of proteins by Stützer's reagent, tannin-sodium chloride solution, 94% alcohol, and Barnstein's method with Australian grasses appears to support Petrie's statement that Stützer's reagent precipitates some of the non-protein nitrogen.

CHEMICAL ABSTRACTS.

The Chemical Constituents of Green Plants. XXV. The Acids of the Apple (*Pyrus malus*). HARTWIG FRANZEN and FRITZ HELWERT (*Z. physiol. Chem.*, 1923, 127, 14—38).—By the use of the ester-hydrazide method, it is shown that malic acid is the most important acid of the apple, and that there are also present quantities of citric acid besides small amounts of succinic and of lactic acid and traces of oxalic and of unsaturated acids.

W. O. K.

Chemical Constituents of a Chinese Drug "Hsiung-Ch'uang." II. YOSHIHARU MURAYAMA and TAKEYOSHI ITAGAKI (*J. Pharm. Soc. Japan*, 1923, 143—148; cf. A., 1922, i, 310).—In addition to the main constituent cnidiolactone (*loc. cit.*), the volatile oils obtained by distilling the powdered drug with steam contains also a small quantity of sedanonic acid, m. p. 113° (the oxime, needles, has m. p. 128°), and a sesquiterpene, a light yellow oil, b. p. 110—120°/5 mm., which gives a coloration changing from dark green to violet-red with acetic anhydride and concentrated sulphuric acid.

K. K.

The Relationship of Cotton to Water and Steam. A Summary of the Literature. ROBERT GEORGE FARGHER and ALEXANDER MITCHELL WILLIAMS (*J. Text. Inst.*, 1923, 14, T., 77—82).—A review of the literature, divided into the following chapters: (1) removal of the minor constituents of cotton by water, (2) chemical action of water and steam on cellulose, (3) general humidity relations, (4) physical effects of moisture content, (5) effect of steam on the appearance of cotton, (6) other effects. Fifty-eight references are cited.

J. C. W.

A Comparison of the Volatile Products Derived from Cotton by the Action of Water, and of Sodium Hydroxide, and 2·7 Atmos. Pressure. PERCY HERBERT CLIFFORD and ROBERT GEORGE FARGHER (*J. Text. Inst.*, 1923, 14, T., 117—124).—The material employed in the investigation was obtained by condensing the steam issuing from a kier in which raw American cotton was heated under 2·7 atmos. pressure, either with water or 2% sodium hydroxide solution. Several gallons of distillate were collected, the quantity of cotton used being a few tons. The systematic isolation of the products is fully described.

The distillate from sodium hydroxide contained the following compounds. (1) Neutral products: Acetone; methyl alcohol; a trace of a compound, $C_6H_{12}O_2$, giving a p-nitrophenylhydrazone, m. p. 210°; a colourless aldehyde or ketone, $C_{10}H_{20}O$, which rapidly became yellow and formed a semicarbazone, m. p. 116—116·5°; and a compound, $C_{18}H_{30}O$, which had a pleasant, camphor-like odour, and was indifferent to reagents for carbonyl or hydroxyl groups. The last two compounds were obtained together as a small quantity of oil, b. p. 90—140°/2 mm., and were separated by distillation in steam, the indifferent compound being the more volatile. (2) Volatile bases: Ammonia; trimethylamine (the picrate has m. p. 224°, not 216° as usually given); dimethylamine (the hydrogen oxalate, has m. p. 149—150°); and a pyrrolic substance.

The distillate from water alone contained acetaldehyde, but not methyl alcohol, the other neutral products being similar to those obtained from sodium hydroxide. A quantity of the aqueous extract in the kier was evaporated under diminished pressure, extracted with ether and chloroform, and acidified, when a jelly was obtained which yielded methyl alcohol and acetone on distillation with sodium hydroxide. The methyl alcohol appears to come, therefore, from a substance which is removed from the cotton by boiling with water, and not from the residual cotton.

The evidence afforded by the distribution of methyl alcohol and acetone in the distillates therefore strongly supports the view that raw cotton contains pectin, which has hitherto been somewhat doubtful.

A separate small experiment in which cotton was treated with 1% sodium hydroxide showed that 100 g. of cotton yielded 14 mg. of acetone and 4 mg. of methyl alcohol, that is, two molecular proportions of acetone to one of methyl alcohol. J. C. W.

Chemical Investigations of the Fruit of *Evodia Rutaecarpa*. YASUHIKO ASAHINA [with M. ISHIO, K. KASHIWAGI, S. MAYEDA, and A. FUJITA] (*Acta Phytochim.*, 1923, 1, 67—89).—A reprint in German of a series of papers previously published in Japanese (cf. A., 1916, i, 238, 621; 1921, i, 48; 1922, i, 47). Kermack, Perkin, and Robinson (T., 1921, 119, 1615) have criticised the conclusion that the base $C_{10}H_{12}N_2$ from isoevodiamine is 2- β -aminoethylindole, suggesting that it is more probably 3- β -aminoethylindole. Physiological experiments in which the base was compared with 3- β -aminoethylindole show, however, that the two are quite different. E. H. R.

Distribution of Pentosans in the Maize Plant at Various Stages of Growth. JOHN H. VERHULST, W. H. PETERSON, and E. B. FRED (*J. Agric. Res.*, 1923, 23, 655—663).—Chemical examination of maize plants of various ages shows that the amount of pentosans in the plant increases with the total dry matter, being approximately one-sixth of the dry matter. In the early stages of growth, the production of pentosans in the plant-tissue is greater than that of dry matter; its formation from starch, etc., is suggested. The percentage of pentosan in particular organs of the plant increases with the development of that organ. Only traces of methyl pentosans were found, but pentoses were found in small but regular quantities throughout the plant's growth.

The pentosans in green corn tissue are destroyed by *Bacillus flavigina*, and also by *B. coli communis*. A. G. P.

Mannitol from *Orobancha Cumana*. A. KIESEL (*Z. physiol. Chem.*, 1923, 126, 257—260).—The substance, m. p. 165°, obtained from *Orobancha Cumana* by extraction with alcohol is shown to be mannitol. W. O. K.

The Presence of Aucubin and of Mannitol in the Foliated Stems of *Rhinanthus Crista-Galli*, L. (MILLE) MARIE BRAECKE (*Bull. Soc. Chim. biol.*, 1923, 5, 258—262).—Aucubin is present

in the foliated stems as well as in the seed (cf. A., 1922, i, 1225). Mannitol, but not dulcitol, has also been isolated. E. S.

The Chemical Constituents of the Rutaceæ. VII. The White Dittany, *Dictamnus albus*, Linn. H. THOMS (*Ber. Deut. pharm. Ges.*, 1923, 33, 68—83).—A hot 85% alcoholic extract of dittany root deposited a saponin on cooling, and, after concentrating on a water-bath to a syrupy extract, crystals were deposited which after recrystallisation from alcohol melted at 279—280° and had the composition $C_{16}H_{18}O_5$. The substance possessed a lactonic character, and was named *dictamnolactone*. No methoxyl- or acetyl-derivatives, oximes, or semicarbazones could be obtained, and bromine gave a substitution product. The general behaviour of the substance indicated a cyclic structure, probably similar to that of santonin. In the residual extract from which the dictamnolactone had been separated the presence of sucrose, invert-sugar, a pentose, an ethereal oil, a waxy substance, a phenolcarboxylic acid, and an alkaloid was established. The alkaloid *dictamnine*, $C_{12}H_{11}O_2N$, crystallised from absolute alcohol in colourless prisms, m. p. 132—133°. It formed a sparingly soluble chromate, and a *chloroaurate* and *chloroplatinate*, the latter melting at 152°.

G. F. M.

Soil Acidity as Measured by Sugar Inversion, the Truog Test, and the Hydrogen-ion Concentration and its Relation to the Hydrolysis of Ethyl Acetate. F. W. PARKER and O. C. BRYAN (*Soil Sci.*, 1923, 15, 99—107).—The reaction of a number of soils was determined by the above three methods and compared with the acidity developed by shaking soil suspensions with ethyl acetate. A fairly good correlation appeared to exist between the three standard methods, the Truog test and sugar-inversion showing the best parallelism. It was shown that acid silicates catalyse the inversion of sucrose, and probably are the main factor in the sugar inversion by soils. The hydrolysis of ethyl acetate by soil suspensions was not catalysed by acid silicates. A. G. P.

Relations between Calcium Carbonate, certain Fertiliser Chemicals, and the Soil Solutions. FRED. W. MORSE (*Soil Sci.*, 1923, 15, 75—92).—The results of published data are discussed and interpreted mathematically, and analyses of water extracts of soils from limed and fertilised plots given. In soils containing solid calcium carbonate, the quantity actually in solution is dependent solely on the proportion of carbon dioxide in the soil atmosphere. The addition of calcium phosphate and sulphate and of ammonium sulphate tends to decrease the amount of calcium carbonate in the soil solution. Sodium nitrate and potassium chloride have the reverse effect. The p_H value of extracts from unlimed plots is scarcely altered by treatment with superphosphate and potassium chloride. Ammonium sulphate lowers the p_H value of the extracts and sodium nitrate increases it. A. G. P.

The Manganese Content of some Dutch Soils, and some Observations Thereon. D. H. WESTER (*Pharm. Weekblad*, 1923, **60**, 446—451).—Manganese found in the dried soils by the methods previously described (A., 1920, ii, 451) varied from a trace up to 120 mg. per 100 g. of dried soil. The more fertile soils contain more manganese than the less fertile, but no connexion is found between the contents of iron and manganese, although some connexion between manganese and phosphate content in some localities is not unlikely. The manganese content of the ash of leaves and seeds is generally much higher than that of the soils.

S. I. L.

The Quantity and Composition of Colloidal Clay in Soil. VÁCLAV NOVÁK and LAD. ŠMOLÍK (*Kolloid Z.*, 1923, **32**, 338—343).—A number of experiments are described which have been undertaken with the object of ascertaining the quantity of colloidal clay in two specimens of agricultural earth and in one specimen of clay poor in humus derived from a clay-slate. The total quantity of colloidal material, including the humus substances, in agricultural earth, when dispersed in an ammoniacal solution, probably exceeds 8%. The quantity of inorganic colloidal matter, that is, colloidal alumina, is probably somewhat greater than 5%. Three specimens of iron containing colloidal clays have been analysed and found to contain large amounts of alkalis and alkaline earths.

J. F. S.

The Interpretation of Mechanical Analysis of Soils as Affected by Soil Colloids. R. O. E. DAVIS (*J. Amer. Soc. Agron.*, 1922, **14**, 293—298).—The application of a correction, expressing the amount and distribution of soil colloids, to the results of mechanical analysis is essential, especially in the case of the silt and clay groups. These groups of mineral particles are composed in part of colloidal material which may be estimated by absorption of water vapour.

CHEMICAL ABSTRACTS.

Organic Constituents of the Soil. G. S. FRAPS (*Texas Agr. Exp. Sta. Bull.*, 1922, **300**, 1—10).—Estimations are compared of the organic carbon, nitrogen, and pentosans in a number of surface- and sub-soils. The estimation of organic carbon gives little indication of the quality of a soil; the percentage can be judged from that of the nitrogen. The average amount of pentosans increases with the average nitrogen content. The rate of disappearance in soil of pentosans from various sources was found to vary widely. The amount of reducing substance, calculated as sugars, produced by heating soils with dilute sulphuric acid was 0.002—0.215% (average 0.058%). No relation could be found between the permanganate-soluble and -insoluble nitrogen, and the results of pot experiments with nitrogen on soils. An average of 10% of the nitrogen of soils was dissolved by 0.1N-potassium hydroxide solution.

CHEMICAL ABSTRACTS.

Organic Chemistry.

Partial Combustion of Methane. E. BERL and H. FISCHER (*Z. angew. Chem.*, 1923, **36**, 297—302).—The possibility of oxidising methane to methyl alcohol, formaldehyde, formic acid, carbon monoxide, and carbon dioxide by means of oxygen, ozone, sulphur dioxide, and sulphur trioxide, and the effect of temperature on the various reactions occurring are discussed from a theoretical point of view based on the heats of possible reactions. Investigations were made oxidising methane with air between 500° and 900°, gaseous mixtures of various compositions being passed through heated tubes not containing catalysts, and the products collected and analysed. Experiments with sulphur dioxide and sulphur trioxide were carried out between 250° and 800°, using silica as catalyst. Some qualitative experiments were also performed with nitrogen peroxide. Using an equal volume of air at 675°, under the conditions of the experiments 17% of the methane consumed was obtained as formaldehyde, the remainder appeared as carbon monoxide. With sulphur dioxide, most of the methane oxidised formed carbon dioxide, using sulphur trioxide with a large excess of methane at 595°, the small quantity of methane oxidised gave formaldehyde and nothing else. Nitrogen peroxide yields formaldehyde with other products. Experiments on the stabilisation of formaldehyde with ammonia showed that substance to be of little utility. T. S. W.

The Possibility of Using Chlorosulphonic Acid to Absorb Ethylene from Gaseous Mixtures. W. TRAUBE and R. JUSTH (*Brennstoff-Chem.*, 1923, **4**, 150—154).—Although the absorption of ethylene in bromine water or fuming sulphuric acid is satisfactory for analytical purposes, the products formed do not readily yield derivatives of ethylene of technical value. Experiments made with chlorosulphonic acid showed that this substance gives an absorption of ethylene almost as rapid and complete as 25% fuming sulphuric acid, whilst if the chlorosulphonic acid be mixed with an equal or twice its weight of pure sulphuric acid the reagent obtained can replace the fuming sulphuric acid in even the most accurate analyses. Experiments were also carried out on the effect of passing gases containing ethylene through chlorosulphonic acid. It was found that even with rapid currents of gas of the order of 1 litre in one minute nearly 90% of the ethylene is absorbed in one washing from gas containing 7% of ethylene. Only 6% absorption was obtained with concentrated sulphuric acid under the same conditions. The compound formed with the chlorosulphonic acid is its ethyl ester, b. p. 155—160°, which remains uncondensed to a very small extent only; this small amount can be removed from the gas by means of activated charcoal. Only

80% of the theoretical amount of ethylene is absorbed by the pure acid owing to some of the latter reacting with its ethyl ester to form an ethionic acid derivative, $\text{SO}_2\text{Cl}\cdot\text{C}_2\text{H}_4\cdot\text{SO}_3\text{H}$. Ethylchlorosulphonate can yield several products of technical value, e.g., with water it gives alcohol, and with concentrated hydrochloric acid ethyl chloride.

T. S. W.

The Question of Atomic Equilibria in Molecules of Hydrocarbons of the $\text{C}_n\text{H}_{2n-2}$ Series. ALEXEI EUGRATOVITSCH FAVORSKI (*J. Russ. Phys. Chem. Soc.*, 1920, 50, 557—570).—It was shown some years ago that monosubstituted acetylenes isomerise under the influence of alcoholic alkalis (A., 1888, 798); disubstituted acetylenes are produced if the original substituent is a primary group, the intermediate formation of an allene derivative being assumed: $\text{CH}_2\text{R}\cdot\text{C}:\text{CH} \rightarrow \text{CHR}:\text{C}:\text{CH}_2 \rightarrow \text{CR}:\text{C}:\text{CH}_3$. The reaction stops at the allene stage, if the substituent is a secondary group, $\text{CHRR}'\cdot\text{C}:\text{CH} \rightarrow \text{CRR}':\text{C}:\text{CH}_2$, whilst acetylenes carrying a tertiary group as a substituent are not isomerised. Recently, however, it was found that $\delta\delta$ -dimethyl- Δ^{β} -pentinene, $\text{CMe}_3\cdot\text{C}:\text{CMe}$, is not produced by the action of sodium ethoxide on $\alpha\beta$ -dibromo- $\beta\gamma\gamma$ -tetramethylpropane, the product being $\delta\delta$ -dimethyl- $\Delta^{\alpha\beta}$ -pentadiene, $\text{CMe}_3\cdot\text{CH}:\text{C}:\text{CH}_2$. It is now suggested that the above scheme must be extended. When R is a primary group the formation of the disubstituted acetylene proceeds to completion; when R is a tertiary radicle, as in the above example, it is the allene derivative which is alone capable of existence, whilst when R is a secondary radicle both forms possess approximately equal stability.

The formation of the allene derivative appears to be due to the instability of the isomeric dimethylpentinene; this view is confirmed by the attempts to synthesise the latter, the allene being obtained in its place.

[With OLGA ALEXÉEVA.]—Ethyl*tert.*-butylcarbinol was converted into the corresponding bromohydrin, α -bromo- α -*tert.*-butylpropane, and the elements of hydrogen bromide were removed from this compound by means of alcoholic potash. The product consisted of a mixture of two hydrocarbons which were separated by fractionation. The fraction boiling at 84 — 86° , d_4^{20} 0.7414; d_4^{20} 0.7220, gives acetic and $\alpha\alpha$ -dimethylpropionic acids on oxidation, and is therefore $\alpha\alpha$ -dimethyl- Δ^{β} -pentene, $\text{CHMe}:\text{CH}\cdot\text{CMe}_3$, whilst the fraction, b. p. 93 — 95° , consists of $\beta\gamma$ -dimethyl- Δ^{β} -pentene, $\text{CMe}_3\cdot\text{CMeEt}$, d_4^{20} 0.7553, d_4^{20} 0.7363; on oxidation, acetone, methyl ethyl ketone and $\beta\gamma$ -dimethylpentane- $\beta\gamma$ -diol (Meerwein, A., 1913, i, 485) are obtained from it. The hydrocarbon boiling at 84 — 86° was converted by means of bromine in chloroform into the dibromide, b. p. 86 — $88^\circ/15$ mm., d_4^{20} 1.5530, d_4^{20} 1.5303, and this was treated with an excess of alcoholic potassium hydroxide, giving an 89 per cent. yield of $\delta\delta$ -dimethyl- $\Delta^{\alpha\beta}$ -pentadiene (*tert.*-butylallene), b. p. 81 — 82.5° , d_4^{20} 0.7365, d_4^{20} 0.7183, $[\eta]_D$, 33.050. On oxidation with permanganate, it yields formic and $\alpha\alpha$ -dimethylpropionic acids.

The course of the reaction here is as follows: $\text{CMe}_3 \cdot \text{CHBr} \cdot \text{CHBr} \cdot \text{CH}_3 \rightarrow \text{CMe}_3 \cdot \text{CH} \cdot \text{CBr} \cdot \text{CH}_3 \rightarrow [\text{CMe}_3 \cdot \text{C} \cdot \text{C} \cdot \text{CH}_3] \rightarrow \text{CMe}_3 \cdot \text{CH} \cdot \text{C} \cdot \text{CH}_2$, which was confirmed as follows: $\delta\delta$ -dimethyl- Δ^2 -pentinene, obtained from pinacolin, was converted into the *sodium* derivative, and this was heated with an excess of methyl iodide in a sealed tube for eight hours at 120° . The *hydrocarbon* isolated boiled at $81-83^\circ$, d_4^{20} 0.7363, d_4^{20} 0.7182, $[\text{R}_L]_D$ 33.056, and was thus identical with *tert*.-butylallene; its structure was confirmed by oxidation.

G. A. R. K.

The Metallic Derivatives of *tert*.-Butylacetylene [$\delta\delta$ -Dimethyl- Δ^2 -pentinene]. A. E. FAVORSKI and LEONID MOREV (*J. Russ. Phys. Chem. Soc.*, 1920, **50**, 571—581).—The *copper* derivative of the hydrocarbon, $\text{CMe}_3 \cdot \text{C} \cdot \text{CH}$, which was prepared from pinacolin (cf. A., 1888, 798) occurs in two polymeric modifications, red crystals, and a yellow, amorphous powder or plate-like crystals. The yellow form appears to pass into the red on warming at about 80° ; both forms melt at about 140° . A third, orange form may also exist.

Cryoscopic determinations show that the molecular weight of the yellow modification is higher than that of the red, the values for the solution of either form in benzene being lower than those found in ether. On keeping the solutions, the molecular weight gradually falls until it nearly reaches the theoretical value for the unimolecular compound; decomposition appears to set in at that point. Heating also favours the dissociation of these compounds. By crystallising the substance from benzene, it is possible to transform the yellow modification into the red, and the reverse change is brought about by chloroform. On prolonged keeping of the solutions of either modification, gradual decomposition takes place, a gummy solid being deposited consisting of a colloidal form of copper. Such a decomposition can be brought about by heating the dry yellow modification in a tube at 150° , when a copper mirror is formed and a white sublimate of the dimeric form of $\alpha\alpha$ -dimethyl- Δ^2 -pentinene, m. p. $130-131^\circ$, collects on the cool parts of the tube.

On oxidation with alkaline potassium ferricyanide, the copper salt yields the same dimeric compound, m. p. $130-131^\circ$, in addition to some $\beta\beta$ -dimethylbutyric acid, b. p. $176-178^\circ$.

The *silver* compound of dimethylpentinene is colourless, and crystallises from benzene in fine needles. The benzene solutions on keeping deposit a silver mirror.

The constitution of the polymeric forms of the copper compound is discussed, and their formation is attributed to the residual affinity of the trebly-bound carbon atoms and that of the singly-bound copper.

G. A. R. K.

Action of Potassium Acetate on Aliphatic Bromides as a Method of Determining Constitution. I. B. K. MERESHKOWSKY (*Annalen*, 1923, **431**, 231—242).—From existing data and the experimental results indicated below, it is concluded that the action of potassium acetate on aliphatic bromides proceeds according to the following rules. I. Monobromides. Bromine is removed

from primary or secondary carbon with formation of an acetic ester, from tertiary carbon with formation of an unsaturated hydrocarbon, a hydrogen atom being taken from the carbon atom bearing fewest hydrogen atoms. II. Dibromides. (1) Diprimary dibromides give esters of the corresponding glycols. (2) Primary-secondary dibromides give (a) unsaturated monobromides, in which bromine remains on the primary carbon atom, and (b) glycol diacetates. Dissecondary dibromides behave similarly. (3) Primary-tertiary dibromides give exclusively unsaturated monobromides, with bromine on the primary carbon. Secondary-tertiary dibromides react in the same way, bromine remaining on the secondary carbon. (4) Ditertiary dibromides give doubly unsaturated hydrocarbons. If the bromine atoms are attached to neighbouring carbon atoms, the ester of the unsaturated alcohol may be isolated as an intermediate product. III. Tribromides. (1) Diprimary-secondary tribromides lose bromine from a primary carbon atom, giving an unsaturated bromo-ester, $\text{CH}_2\text{:CBr} \dots \text{CH}_2\text{:OAc}$. (2) Diprimary-tertiary tribromides give unsaturated mono-esters, the third bromine atom being left on a primary carbon atom, CHBr:C< . (3) From dissecondary-primary tribromides only unsaturated 1:2-dibromides are formed. (4) Tribromides with two bromine atoms on primary carbon and one on tertiary carbon give unsaturated dibromides, $\text{CBr}_2\text{:C<}$. (5) Tribromides having two bromine atoms on one primary carbon atom and one on secondary carbon give a mixture of unsaturated dibromides, the 1:2-dibromide predominating, CHBr:CBr- , $\text{CBr}_2\text{:CH-}$. IV. Tetrabromides react according to the schemes for dibromides and tribromides. Bromine attached to unsaturated carbon does not react. By the elimination of hydrogen bromide from a 1:2-dibromide the double bond remains next to the remaining bromine atom, e.g., -CBr:C< , and not -CHBr:C=C< . If the halogen atoms in the bromide are removed from one another, each reacts as though it alone were present in the molecule. It is probable that the acetic ester is invariably the initial stage in the formation of an unsaturated product.

β -Bromoisobutane is converted by heating with anhydrous potassium acetate and glacial acetic acid into isobutylene. Dimethylbutene dibromide, $\text{CMe}_2\text{Br.CMe}_2\text{Br}$, gives $\beta\gamma$ -dimethyl- Δ^2 -butadiene, $\text{CH}_2\text{:CMe.CMe:CH}_2$, and the ester, $\text{OAc.CMe}_2\text{:CMe}_2\text{:OAc}$. The observation of Bainbridge (T., 1914, 105, 2291), that $\alpha\beta$ -dibromopropane gives α -bromopropylene is confirmed; the glycol diacetate, $\text{OAc.CHMe.CH}_2\text{:OAc}$, is also formed. $\alpha\beta\gamma$ -Tribromopropane is converted into the triacetate (Wurtz, *Annalen*, 1857, 102, 340), and the ester, $\text{CH}_2\text{:CBr.CH}_2\text{:OAc}$, b. p. $103.5^\circ/100$ mm. or $163\text{--}164^\circ/762$ mm., d_4^{20} 1.48894, d_4^{20} 1.45668, n_D^{20} 1.466572 (cf. Henry, A., 1872, 686), which is also produced by heating $\beta\gamma$ -dibromopropylene with potassium acetate. $\alpha\alpha\beta$ -Tribromopropane (cf. Reboul, A., 1879, 127; Mouneyrat, A., 1899, i, 97), b. p. $89.2^\circ/20$ mm., d_4^{20} 2.39384, d_4^{20} 2.35484, n_a^{20} 1.57016, n_D^{20} 1.573983, n_B^{20} 1.58470, n_γ^{20} 1.593719, gives a small amount of $\alpha\alpha$ -dibromopropylene, CHMe:CBr_2 , b. p. $123\text{--}126^\circ/759$ mm., and, as the chief

product, $\alpha\beta$ -dibromopropylene, $\text{CMeBr}\cdot\text{CHBr}$, b. p. $129-130^\circ/759$ mm., d_4^{20} 2.04558, d_4^{20} 2.00768, n_a^{20} 1.52618, n_D^{20} 1.529992, n_B^{20} 1.53987, n_Y^{20} 1.549323 (cf. Linnemann, *Annalen*, 1865, **136**, 57). $\alpha\beta$ -Dibromopropylene is also formed by the action of potassium acetate on $\alpha\beta\beta$ -tribromopropane, b. p. $80.6^\circ/20$ mm., d_4^{20} 2.33690, d_4^{20} 2.29854, n_a^{20} 1.56247, n_D^{20} 1.566963, n_B^{20} 1.577794, n_Y^{20} 1.585556 (cf. Reboul, *loc. cit.*). Revised physical data are given for the ester, $\text{CBr}_2\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{OAc}$ (this vol., i, 528), derived from $\alpha\alpha\beta\gamma$ -tetrabromoisobutane: d_4^{20} 1.77845, d_4^{20} 1.75001, n_a^{20} 1.513898, n_D^{20} 1.517607, n_B^{20} 1.527015, n_Y^{20} 1.53509, and for the corresponding alcohol, $\text{CBr}_2\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{OH}$, m. p. 31° , d_4^{20} 2.02099, d_4^{20} 1.99193, n_a^{20} 1.556423, n_D^{20} 1.560942, n_B^{20} 1.571956, n_Y^{20} 1.580662. W. S. N.

Bromotrinitromethane. II. ERICH SCHMIDT, RICHARD SCHUMACHER, and RICHARD ASMUS (*Ber.*, 1923, **56**, [B], 1239—1242; cf. A., 1922, i, 826).—During attempts to add the ester of hypobromous acid to the olefinic double linking by means of bromotrinitromethane in alcoholic solution, it has been found that treatment with alkali is unsuitable for compounds containing a labile halogen atom. The difficulty can be overcome by the use of potassium ferrocyanide in acetic acid solution (cf. Chattaway and Harrison, T., 1916, **109**, 171).

Bromotrinitromethane may also be brought into reaction with the olefinic double linking in the presence of acids, particularly formic acid, thus: $\cdot\text{CH}\cdot\text{CH}\cdot + \text{HO}\cdot\text{CHO} + \text{CBr}(\text{NO}_2)_3 \rightarrow \cdot\text{CH}(\text{O}\cdot\text{CHO})\cdot\text{CHBr}\cdot + \text{CH}(\text{NO}_2)_3\cdot$.

Bromomethoxyhydrindene, $\text{C}_9\text{H}_8\text{Br}\cdot\text{OMe}$, a pale yellow liquid, b. p. $98^\circ/2$ mm., is obtained in 71.9% yield by the gradual addition of bromotrinitromethane to an ice-cold solution of freshly distilled indene in methyl alcohol.

The addition of cyclohexene to a solution of carbamide and bromotrinitromethane in formic acid results in the production of 2-bromocyclohexanyl formate, $\text{C}_6\text{H}_{10}\text{Br}\cdot\text{O}\cdot\text{CHO}$, a colourless liquid, b. p. $68-69^\circ/0.5$ mm., the yield being 70% of that theoretically possible. It is converted by methyl alcohol and hydrochloric acid into 2-bromocyclohexane-1-ol, a colourless liquid which gradually darkens when preserved, b. p. $60-61^\circ/\text{about } 1$ mm. In a similar manner, propenylbenzene gives β -bromo- α -formoxypropylbenzene, $\text{CHMeBr}\cdot\text{CHPh}\cdot\text{O}\cdot\text{CHO}$, a colourless liquid, b. p. $104^\circ/1$ mm., in 69.4% yield, whereas camphene gives O-formylcamphenebromohydrin, $\text{C}_{10}\text{H}_{16}\text{Br}\cdot\text{O}\cdot\text{CHO}$, a colourless liquid, b. p. $109-111^\circ/0.6$ mm., the yield being 73.5% of that theoretically possible.

H. W.

Examination and Dehydration of Methyl Alcohol with the Aid of Magnesium. NIELS BJERRUM and LÁSLÓ ZECHMEISTER (*Ber.*, 1923, **56**, [B], 1247; cf. this vol., i, 529).—The molecular conductivity of picric acid dissolved in methyl alcohol which has been dehydrated by means of magnesium is identical with that observed in the solvent which has been treated with calcium.

H. W.

The Purification and some Physical Properties of certain Aliphatic Alcohols. II. ROGER F. BRUNEL (*J. Amer. Chem. Soc.*, 1923, **45**, 1334—1338; cf. A., 1921, i, 299).—The thermometer previously used has been recalibrated, and used to determine the boiling points of various aliphatic alcohols and ketones.

n-Propyl alcohol, obtained by the hydrolysis of pure propyl hydrogen phthalate, has b. p. $97.175 \pm 0.01^\circ/760$ mm., d_4^{25} 0.7998, n_D^{25} 1.3834. *iso*Propyl alcohol has b. p. $82.258 \pm 0.005^\circ/760$ mm., d_4^{25} 0.7808, n_D^{25} 1.3748, and is obtained by the reduction of pure acetone, b. p. $56.085 \pm 0.01^\circ/760$ mm. *sec.*-Butyl alcohol has b. p. $99.529 \pm 0.005^\circ/760$ mm., d_4^{25} 0.8023, n_D^{25} 1.39495, and is prepared by the reduction of pure methyl ethyl ketone, b. p. $79.370 \pm 0.01^\circ/755$ mm. The following data are also given. Methylisobutylcarbinol, b. p. $131.85 \pm 0.01^\circ/760$ mm., d_4^{25} 0.80245, n_D^{25} 1.40895. Methylpropylcarbinol, b. p. $119.275 \pm 0.01^\circ/754$ mm., d_4^{25} 0.80483, n_D^{25} 1.4043. Diethylcarbinol, b. p. $115.40 \pm 0.01^\circ/754$ mm., d_4^{25} 0.8154, n_D^{25} 1.4077. Dipropylcarbinol, b. p. $155.00 \pm 0.04^\circ/750$ mm., d_4^{25} 0.8129, n_D^{25} 1.4178. W. S. N.

Action of Magnesium Halides on the Epibromohydrin of Ethylglycerol. RAYMOND DELABY (*Compt. rend.*, 1923, **176**, 1326—1327; cf. this vol., i, 531).—A study of the action of magnesium chloride and magnesium bromide on the epibromohydrins of ethyl- and butyl-glycerol showed that, in order to bring about the reaction described by Würtz (*Compt. rend.*, 1860, **50**, 1197) with the resultant precipitate of magnesium hydroxide, the materials used should be quite pure. Certain experimental aspects of the reaction are discussed and the optimum conditions are indicated.

H. J. E.

Tetramethylglycerol. J. PASTUREAU and H. BERNARD (*Compt. rend.*, 1923, **176**, 1400—1402; cf. A., 1922, i, 717).—Saponification of the chlorohydrin of tetramethylglycerol affords a better yield than the preparation by means of the acatin. *Tetramethylglycerol* [$\beta\delta$ -dimethylpentane- $\beta\gamma\delta$ -triol], $\text{OH}\cdot\text{CMe}_2\cdot\text{CH}(\text{OH})\cdot\text{CMe}_2\cdot\text{OH}$, was obtained in the form of brilliant needles, m. p. 99° . An attempt to prepare the glycide, $\text{Me}_2\text{C}=\text{CH}\cdot\text{CMe}_2\cdot\text{OH}$, resulted in the formation of a small quantity of colourless liquid which was readily hydrolysed to tetramethylglycerol.

H. J. E.

Solubility of Mannitol in Mixtures of Ethyl Alcohol and Water. HENRY JERMAIN MAUDE CREIGHTON and DAVID S. KLAUDER (*J. Franklin Inst.*, 1923, **195**, 687—691).—Within the temperature range 0 — 60° , the logarithm of the solubility of mannitol in mixtures of ethyl alcohol and water at any temperature is a function of the solubility in pure water, the molar fraction of alcohol present in the solvent, and the absolute temperature; whilst at a particular temperature it is a function of the solubilities in the pure component solvents and the molar fractions of the latter.

E. E. T.

The Influence of Temperature on Two Alternative Modes of Decomposition of Formic Acid. CYRIL NORMAN HINSHELWOOD and HAROLD HARTLEY (T., 1923, 123, 1333—1338).

The Decomposition of Pertrichloroacetic Acid. FR. FICHTER, ALBERT FRITSCH, and PAUL MÜLLER (*Helv. Chim. Acta*, 1923, 6, 502—506).—When a salt of trichloroacetic acid is electrolysed, no ethane derivative is formed, but exclusively the ester, trichloromethyl trichloroacetate. This behaviour resembles that of *cyclo*-propanecarboxylic acid (this vol., i, 677), and should be explainable in a similar way through the formation of trichloromethyl alcohol by the decomposition of pertrichloroacetic acid formed at the anode. To study its decomposition, the latter was prepared by mixing trichloroacetic anhydride and hydrogen peroxide and heating the mixture in such a manner that the gaseous decomposition products could be collected and analysed. The decomposition was found to proceed according to the equation $\text{CCl}_3\cdot\text{CO}_2\cdot\text{OH} = \text{CO}_2 + \text{COCl}_2 + \text{HCl}$, probably through the stages $\text{CCl}_3\cdot\text{CO}_2\cdot\text{OH} = \text{CO}_2 + \text{CCl}_3\cdot\text{OH}$ and $\text{CCl}_3\cdot\text{OH} = \text{COCl}_2 + \text{HCl}$. The formation of trichloromethyl alcohol as an intermediate product in the electrolysis of a trichloroacetate is consequently extremely probable. An attempt to prepare trichloroacetyl peroxide by the action of barium peroxide on trichloroacetic anhydride was unsuccessful; the compound apparently cannot exist. E. H. R.

A New Source of Ceryl Cerotate. ADOLF BAREUTHER (*Chem. Umschau*, 1923, 30, 117—119).—The bottom layers of sunflower oil from a tank which had been used for its storage were found to become cloudy and gelatinous after refining owing to the presence of ceryl cerotate, which was held in solution in the crude oils by the free fatty acids present. The wax was found to originate from the husks of the sunflower seeds, and had gradually concentrated in the bottom layers of oil. 42 G. of the crude wax were isolated from 30 kg. of oil ($=0.14\%$). The wax was purified by recrystallisation from chloroform, and both ceryl alcohol and cerotic acid were prepared from it. H. C. R.

γ -Oxalyl Derivatives of $\beta\beta$ - and $\alpha\beta$ -Dimethylacrylic Acids. LUCY HIGGINBOTHAM and ARTHUR LAPWORTH (T., 1923, 123, 1325—1332).

The Highly Unsaturated Fatty Acids of Fish Oils. J. B. BROWN and G. D. BEAL (*J. Amer. Chem. Soc.*, 1923, 45, 1289—1303).—The mixed fatty acids of menhaden oil undergo an increase in molecular weight, as shown by titration, when heated at 240° in a current of carbon dioxide, but the esters can be distilled almost without decomposition. Menhaden oil is esterified by means of alcoholic hydrogen chloride, and the ester, after distillation, treated with bromine in ethereal solution at -10° to -5° . The percentage yield of bromide (polybromide number) and its bromine content are determined. The methyl ester, b. p. $195\text{--}240^\circ/15$ mm., has polybromide number 38.3, Br 68.31%, calc. for methyl clupanodonate, Br 68.79%; ethyl ester, (1), b. p. $195\text{--}240^\circ/15$ mm., (2) b. p.

240—265°/15 mm., has polybromide number (1) 32·5, 33·8, (2) 85·4 (? 35·4), Br (1) 67·43, 67·48%, (2) 69·49%, calc. for ethyl clupanodonate, Br 67·84%; *n*-butyl ester, b. p. 190—245°/15 mm., has polybromide number 31·5, Br 67·64%, calc. for butyl clupanodonate, Br 65·82%. That substitution does not occur is probable, since the *n*-butyl ester from linseed oil, b. p. 190—240°/15 mm., gives a bromide, m. p. 160° (polybromide number, 51·0), Br 59·30%, evidently *n*-butyl hexabromostearate, for which Br 59·38%. De-bromination of the bromide of the lower boiling ethyl ester of menhaden oil, by means of zinc and alcohol, gives an ester, iodine number 333, from which an acid, iodine number 342, mol. wt. 305, is obtained on hydrolysis. It is therefore evident that a pure ester of clupanodonic acid, $C_{18}H_{28}O_2$, is not obtained in this way (cf. Tsujimoto, A., 1921, i, 78). Analytical data are given to show that the methyl ester of menhaden oil may be partly separated by distillation into fractions, varying in boiling point between 156—166°/15 mm. and 255—260°/15 mm., which are probably derived from acids of the C_{14} , C_{16} , C_{18} , C_{20} , and C_{22} series. Treatment of the lead soaps of menhaden oil by means of ether, and decomposition of the separated portions, give solid and liquid acids, but the methyl esters derived from the latter are also only partly separable by distillation. Separation of the barium soaps by means of benzene containing moist alcohol gives a liquid mixture of acids, of molecular weight varying between 255·2 and 336·7, from which methyl esters are obtained, probably containing methyl arachidonate, methyl docosapentenoate, and perhaps methyl docosahexenoate. The most complete separation is effected by reducing the polybromides by means of zinc and methyl alcohol, and fractionally distilling the product. A fraction is obtained which is believed to be pure methyl clupanodonate, b. p. 215°/15 mm., n_D^{20} 1·4860, iodine number 348·8. The corresponding bromide, methyl octobromostearate, is a white, amorphous solid, m. p. 240°. In other fractions, the presence of methyl arachidonate, methyl eicosapentenoate, methyl docosatetreanoate, methyl docosapentenoate, and methyl docosahexenoate seems probable. Exactly similar results are obtained starting from cod oil or herring oil.

Unsaturated acids are obtained by the hydrolysis of the unsaturated esters derived from the polybromides. These are brominated, giving liquid and solid bromides, which are separately reduced, and again brominated. By suitable analyses, made at each step, it is shown that the liquid bromides contain less bromine than the solid bromides, and that, on reduction, the former give a product having an iodine number lower than that of the original acid, whilst the molecular weight is only slightly less. This product, on rebromination, yields only a small amount of solid bromides. Since the degree of unsaturation decreases, structural change evidently occurs. Probably either a double bond migrates to the $\alpha\beta$ -position in respect to the carboxyl (or ester) group, or a double bond may disappear by ring formation, as from a 1:5-diene grouping.

The following analytical data are recorded. Menhaden oil has saponification number, iodine number, and n_D^{20} , respectively, 191·2,

151·7, 1·4778. Salmon oil has 185·0, 137·2, 1·4768. Cod oil has 186·9, 151·0, 1·4770. Herring oil has 186·5, 139·8, 1·4765. Sardine oil has 187·3, 158·1, 1·4791. W. S. N.

Sludge Formation in Transformer Oils. HANS STÄGER (*Helv. Chim. Acta*, 1923, 6, 386—396).—When the type of oil used for transformers is extracted with acetone, the portion removed consists principally of unsaturated cyclic compounds. The residual oil, however, still gives the normal decomposition products when subjected to prolonged heating in air, namely, acids soluble in oil, and soluble and insoluble sludges containing asphaltic acids and asphalt-like products. The acetone-soluble portion is not, therefore, solely responsible for the sludge formation. [Cf. *J.S.C.I.*, 1923, July.] E. H. R.

Reduction of Ethyl Ethylidenemalonate as Affected by Choice of Reducing Agent. LUCY HIGGINBOTHAM and ARTHUR LAPWORTH (*T.*, 1923, 123, 1618—1624).

[Physical] Properties of Sodium Potassium Tartrate Tetrahydrate Related to the Piezo-electric Effect. JOSEPH VALASEK (*Physical Rev.*, 1922, 20, 639—664; cf. *ibid.*, 1922, 19, 478; 1921, 17, 475).—In an investigation of the nature of the structure underlying piezo-electric phenomena, a study was made of the temperature-variation between -30° and $+30^\circ$ of various physical properties of sodium potassium tartrate tetrahydrate. From results of the measurement of the refractive index, the following are abstracted: for the barium line λ 5536, $n^{21.3} = 1.49170, 1.49348$, and 1.49721 for the α , β , and γ axes, respectively, of the index ellipsoid, these having the same direction as the c , b , and a crystallographic axes. Corresponding values for n^0 are $1.4930, 1.4947$, and 1.4986 , respectively. The variation with temperature is linear, the average coefficient being 59×10^{-6} per 1° . The coefficient of volume expansion was found to be 0.0001428 , and since the substance has d^0 1.766 , d^t $1.766 - 0.0002522t$ between -10° and $+20^\circ$. The specific rotatory power of an aqueous solution changes less than 0.4° between 4° and 40° ; $[\alpha]_D^{25} + 25.9^\circ$. The electrical conductivity depends between -20° and $+30^\circ$ on the direction of the current; above 20° , it increases very rapidly. The following values are abstracted: $-65^\circ, 2.0 \times 10^{-14}$ mhos/cm.³; $0^\circ, +9.0 \times 10^{-14}$ and -5.0×10^{-14} ; $20^\circ, +22.0 \times 10^{-14}$ and -11.0×10^{-14} ; $43^\circ, 5.00 \times 10^{-9}$. Values for the electro-optic constant, e_{41} , were computed; that at 20° is -1.94×10^{-8} , and a real pyro-electric effect was unexpectedly observed. The ultra-red absorption band is computed to be at about 55μ . Rochelle salt appears to be an exception to Neumann's principle of symmetry. A. A. E.

Synthesis of Glycuronic Acid from Dextrose. MAX BERGMANN and W. WALTER WOLFF (*Ber.*, 1923, 56, [B], 1060—1065).—An example is given of the production of a reducing acid of the sugar group by the oxidation of a glucoside.

α -Menthylglycuronic acid, $2C_{16}H_{28}O_7 \cdot H_2O$, flat, prismatic plates, m. p. 130° , to a viscous liquid which decomposes at about 140° , aa^*

$[\alpha]_D^{18} + 51.9^\circ$ in absolute alcohol, is prepared by the action of bromine and aqueous sodium hydroxide on a solution of α -menthylglucoside (Fischer and Bergmann, A., 1917, i, 468) in pyridine at the atmospheric temperature; the *sodium, silver, barium, calcium, and lead* salts are described. The acid or the corresponding β -menthylglycuronic acid is hydrolysed by boiling *N/2* aqueous hydrochloric acid, the liberated menthol is removed with ether and, after addition of sodium acetate, the solution is treated with the requisite nitrogenous base dissolved in ether, and ethyl acetate or similar solvent whereby the following compounds are produced: the phenylbenzylhydrazone of glycurulactone, $C_{19}H_{20}O_5N_2$, microscopic needles, m. p. 155° , decomp. 158° , $[\alpha]_D^{26} - 25.75^\circ$ in methyl-alcoholic solution, which is converted by alkalis into the salts and by alcoholic ammonia into the amide (quadratic leaflets, m. p. 176°) of the corresponding acid; the *phenylhydrazone of glycuronic acid phenylhydrazone*, $C_{18}H_{22}O_5N_4$, m. p. 182° , decomp. 185° ; the *aniline* compound, $(C_{12}H_{14}O_6NNa)_2 \cdot H_2O$, m. p. 212° . (β -Menthylglycuronic acid and aniline give a *compound*, $C_{38}H_{63}O_{14}N$, hexagonal plates, m. p. 182° .)

α -Methylglucoside is converted by barium hydroxide and bromine in aqueous solution at the atmospheric temperature into glyoxylic acid which was identified as the *phenylbenzylhydrazone*, colourless needles, m. p. 172° , and the *phenylmethylhydrazone*, large, colourless leaflets, m. p. 170° .
H. W.

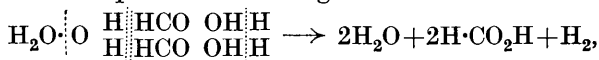
Lysolecithins and Lysocephalins. P. A. LEVENE and IDA P. ROLF (*J. Biol. Chem.*, 1923, **55**, 743—749).—It has been shown that by the action of cobra venom on egg-yolk the unsaturated fatty acid radicles are removed from the lecithin therein contained with the production of a phosphatide to which the name lysocithin has been given (cf. Delezenne and Fourneau, A., 1914, i, 781). A reinvestigation of this action has shown that the cephalin contained in the egg-yolk undergoes a similar transformation. Thus, hydrolysis of the phosphatide fraction from the product of the action of cobra venom on eggs yielded palmitic and stearic acids, choline, and hydroxyethylamine; no unsaturated acids were, however, present. It is proposed to use the names *lysolecithin* and *lysocephalin* for the partly hydrolysed phosphatides produced by the action of cobra venom on lecithin and cephalin, respectively. Since several lecithins, differing in the nature of their saturated fatty acids, are known to occur, it is probable that several lysolecithins also exist. So far, it has been impossible to effect a separation of lysolecithin and lysocephalin by means of their cadmium chloride compounds.

E. S.

The Mechanism of Oxidative Processes. V. Oxidation of Aldehydes. HEINRICH WIELAND and AUGUST WINGLER (*Annalen*, 1923, **431**, 301—322; cf. A., 1921, i, 889).—Formaldehyde reacts in aqueous or ethereal solution with hydrogen peroxide, with formation of *dihydroxymethyl peroxide*, $OH \cdot CH_2 \cdot O \cdot O \cdot CH_2 \cdot OH$, large, glistening prisms, m. p. $62-64^\circ$ (slight decomp.), which is identical with the impure product described by Legler (*Annalen*,

1883, 217, 381) as hexa-oxymethylene-triperoxide. The compound decomposes when warmed, either alone or in solution, with production of two molecules of formic acid and one molecule of hydrogen. The reaction proceeds in non-hydroxylic solvents, but is catalysed by hydroxyl-ions. The hydrogen evolved is non-reactive; iodine is not decolorised when added to the solution containing the decomposing peroxide, and neither methylene-blue nor benzoquinone is reduced. If, however, the reaction is conducted in the presence of palladium black, formaldehyde is produced, because the hydrogen formed is sufficiently activated by the catalyst to react in the sense of the equation: $\text{OH}\cdot\text{CH}_2\cdot\text{O}\cdot\text{O}\cdot\text{CH}_2\cdot\text{OH} \xrightarrow{2\text{H}} 2\text{CH}_2(\text{OH})_2$. On account of the instability of the oxygen-oxygen linking, the peroxide is a somewhat vigorous oxidising (dehydrogenating) agent. Iodine is rapidly liberated from iodides, sulphurous acid is oxidised to sulphuric acid, and quinol to quinone. In each of these reactions, or if the aqueous solution is warmed with zinc dust, formaldehyde is produced. When the dry peroxide decomposes, or when the decomposition takes place in neutral aqueous solution, an excess of formic acid (compared to hydrogen) is obtained, owing to the side-reaction: $\text{OH}\cdot\text{CH}_2\cdot\text{O}\cdot\text{O}\cdot\text{CH}_2\cdot\text{OH} \rightarrow \text{H}\cdot\text{CO}_2\text{H} + \text{H}\cdot\text{CHO} + \text{H}_2\text{O}$, the mechanism suggested being: $\text{OH}\cdot\text{CH}_2\cdot\text{O}\cdot\text{O}\cdot\text{CH}_2\cdot\text{OH} \rightarrow \text{H}\cdot\text{CHO} + \text{OH}\cdot\text{CH}_2\cdot\text{O}\cdot\text{OH}$; $\text{OH}\cdot\text{CH}_2\cdot\text{O}\cdot\text{OH} \rightarrow \text{H}\cdot\text{CO}_2\text{H} + \text{H}_2\text{O}$. The heat of formation of the peroxide (75 Cal.) may be computed from the heat of formation of formic acid from formaldehyde and oxygen (2×61 Cal.), and the heat of decomposition of hydrogen peroxide (-47 Cal.).

The conclusion of Bach and Generosow (this vol., i, 13), that the reaction between hydrogen peroxide and formaldehyde in alkaline solution proceeds according to the scheme :



is severely criticised, particularly in view of the decomposition of dihydroxymethyl peroxide in the absence of water, the a priori unlikelihood that water would undergo fission in the manner suggested, and the inactivity of the hydrogen evolved.

Acetaldehyde also gives a peroxide, but the reaction is reversible, $2\text{Me}\cdot\text{CHO} + \text{H}_2\text{O}_2 \rightleftharpoons \text{OH}\cdot\text{CHMe}\cdot\text{O}\cdot\text{O}\cdot\text{CHMe}\cdot\text{OH}$, since an aqueous solution containing acetaldehyde (2 mols.) and hydrogen peroxide (1 mol.) gives the reactions of both constituents even after standing. *Dihydroxyethyl peroxide* is obtained from the ethereal solution as a colourless oil, having a faint pungent odour, somewhat reminiscent of paracetaldehyde, and possessing properties very similar to those of the lower homologue (cf. Baeyer and Villiger, A., 1900, i, 626). The action of mineral acids causes decomposition into acetaldehyde and hydrogen peroxide. On keeping under reduced pressure, more rapidly on warming, acetaldehyde and water are eliminated, with formation of diethylidene diperoxide, an insoluble, very explosive resin: $\text{OH}\cdot\text{CHMe}\cdot\text{O}\cdot\text{O}\cdot\text{CHMe}\cdot\text{OH} \rightarrow \text{Me}\cdot\text{CHO} + \text{OH}\cdot\text{CHMe}\cdot\text{O}\cdot\text{OH}$; $2\text{OH}\cdot\text{CHMe}\cdot\text{O}\cdot\text{OH} \rightarrow 2\text{H}_2\text{O} + \text{CHMe} \begin{array}{c} \text{O}\cdot\text{O} \\ \diagup \quad \diagdown \\ \text{O}\cdot\text{O} \end{array} \text{CHMe}$. When an

aqueous solution of dihydroxyethyl peroxide is warmed (cf. Heimrod and Levene, A., 1911, i, 13), hydrogen is not evolved, but decomposition occurs in two directions with formation of (1) acetaldehyde (2 mols.) and hydrogen peroxide (1 mol.), or (2) aldehyde, acetic acid, and water. The latter reaction evidently proceeds as follows: $\text{OH}\cdot\text{CHMe}\cdot\text{O}\cdot\text{O}\cdot\text{CHMe}\cdot\text{OH} \rightarrow \text{OH}\cdot\text{CHMe}\cdot\text{O}\cdot\text{OH} + \text{Me}\cdot\text{CHO}$; $\text{OH}\cdot\text{CHMe}\cdot\text{O}\cdot\text{OH} \rightarrow \text{H}_2\text{O} + \text{Me}\cdot\text{CO}_2\text{H}$, and is analogous to the side-reaction in the decomposition of dihydroxymethyl peroxide. In the presence of an excess of concentrated sodium hydroxide the fission into acetaldehyde and hydrogen peroxide is quantitative. The behaviour of this peroxide is thus, in contrast to the lower homologue, similar to that of the chloral derivative, $\text{CCl}_3\cdot\text{CH}(\text{OH})\cdot\text{O}\cdot\text{O}\cdot\text{CH}(\text{OH})\cdot\text{CCl}_3$ (Baeyer and Villiger, *loc. cit.*), and the analogous product from benzaldehyde and hydrogen peroxide (Nef, A., 1898, i, 102). Hydrogen is, however, eliminated at low temperatures in the presence of silver or palladium black.

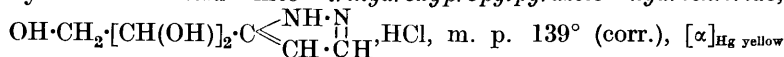
Many views have been expressed concerning the constitution of the oily residue, which is left from the distillation of ethyl ether which has been kept for some time, and has oxidising properties (cf. Clover, A., 1922, i, 619). It is now shown to be identical with dihydroxyethyl peroxide. The first stage in its formation may be dehydrogenation, with production of hydrogen peroxide: $\text{Et}_2\text{O} + \text{O}_2 \rightarrow \text{Et}\cdot\text{O}\cdot\text{CH}\cdot\text{CH}_2 + \text{HO}\cdot\text{OH}$. The vinyl ether so formed would then undergo hydrolytic fission into alcohol and acetaldehyde, the latter then reacting with the hydrogen peroxide.

It is regarded as probable that dihydroxymethyl peroxide is an intermediate stage in the production of formic acid by the electrolysis of aqueous formaldehyde solution (Müller, A., 1920, i, 709), or by the action of metallic oxides, whilst the formation of acetic acid from acetaldehyde by the action of silver oxide in alkaline solution proceeds in an analogous manner. W. S. N.

Optical Rotations of the Sugars. II. The Methyl Pentoses and the Glucosides. JOHN GWILLIAM MALTY (T., 1923, 123, 1404—1409).

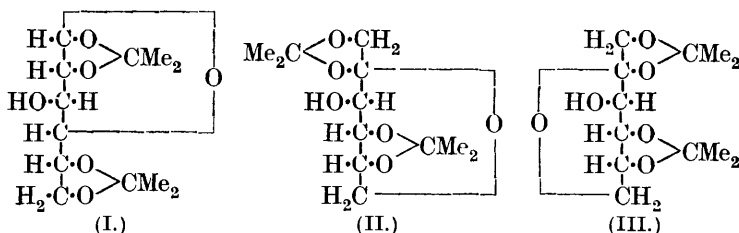
The Structure of the Normal Monosaccharides. I. Xylose. EDMUND LANGLEY HIRST and CLIFFORD BURROUGH PURVES (T., 1923, 123, 1352—1360).

Acetone Sugars. III. The Constitution of the Diacetone [Diisopropylidene] Compounds of Dextrose and Lævulose. KARL FREUDENBERG and ARNOLD DOSER (*Ber.*, 1923, 56, [B], 1243—1247).—Toluene-*p*-sulphonyldextrosediacetone (Freudenberg and Ivers, A., 1922, i, 523) is slowly converted by boiling hydrazine into hydrazinodiacetoneglucose (Freudenberg and Brauns, A., 1922, i, 1117). The latter compound is converted by cold, concentrated hydrochloric acid into trihydroxypropylpyrazole hydrochloride,



—5.6° in aqueous solution. The constitution of the salt is deduced from the observation that it is oxidised by potassium permanganate

to pyrazole-3-carboxylic acid, m. p. 215° (corr.). It follows therefore that the hydroxy-group in position 3 of diacetoneglucose is unsubstituted. The constitution shown in formula I is therefore assigned to diacetonedextrose [dextrose diisopropylidene ether]; it is regarded as definitely established as far as the upper half is concerned, and very probable with regard to the lower half. The constitutions II and III are assigned to the two diacetonealævuloses.

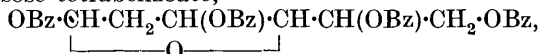


H. W.

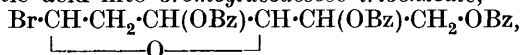
Unsaturated Reduction Products of the Sugars and their Transformations. V. 2-Deoxyglucose (Glucodesose). II. MAX BERGMANN, HERBERT SCHOTTE, and WOLFGANG LESCHINSKY (*Ber.*, 1923, **56**, [B], 1052—1059).—A fuller account of 2-deoxyglucose and its derivatives (cf. A., 1922, i, 227).

β -2-Deoxyglucose has $[\alpha]_D^{18} + 15.03^\circ$ in pyridine after the solution has been prepared for five minutes and $[\alpha]_D^{20} + 90.21^\circ$ after twenty-four hours. α -2-Deoxyglucose has $[\alpha]_D^{19} + 90.11^\circ$ in pyridine after five minutes. The mutarotation of the β -variety in pyridine is greatly affected by the presence of water or, particularly, of methyl alcohol. In aqueous solution, either form has $[\alpha]_D + 46.6^\circ$; since mutarotation cannot be observed, it appears that the change proceeds so rapidly that it is complete before polarimetric readings can be taken. Crystals of either form can be obtained at will by concentrating the aqueous solutions and seeding with the desired variety if care is taken to exclude accidental seeding from the atmosphere.

Glucodesose tetrabenzoate,



m. p. 148—149° (corr.), $[\alpha]_D^{16} + 8.96^\circ$ in tetrachloroethane, has been isolated in the homogeneous condition by the action of benzoyl chloride on α -glucodesose in the presence of pyridine and chloroform. It is converted by hydrogen bromide in the presence of glacial acetic acid into *bromoglucodesose tribenzoate*,



long needles or broad hexagonal plates, m. p. 139° (corr.) when rapidly heated, $[\alpha]_D^{16} + 121.4^\circ$ when dissolved in tetrachloroethane, which is transformed by silver carbonate in the presence of moist acetone into *glucodesose tribenzoate*, long needles, m. p. 123° (corr.), $[\alpha]_D^{19} + 38.39^\circ$ in tetrachloroethane. *Deoxymethylglucoside tribenzoate*, m. p. 88°, $[\alpha]_D^{19} - 34.31^\circ$ in tetrachloroethane, is prepared

by treating the bromo-derivative with an excess of dry silver carbonate and anhydrous methyl alcohol; dibenzoylation by means of alcoholic ammonia and subsequent acetylation of the product of the reaction leads to the isolation of β -2-deoxymethylglucoside triacetate, m. p. 96—97°, $[\alpha]_D -30.3^\circ$ when dissolved in tetrachloroethane.

Reduction of 2-deoxyglucose by sodium amalgam in as neutral as possible solution yields 2-deoxysorbitol [2-deoxymannitol], $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$, prisms, m. p. 105—106° to a turbid liquid after softening at 104°, $[\alpha]_D^{18} +15.61^\circ$ in aqueous solution. It does not exhibit the reactions characteristic of deoxy-sugars. The corresponding diisopropylidene ether, $\text{C}_{12}\text{H}_{22}\text{O}_5$, is a syrupy liquid which distills at 120—125°/1 mm. (temperature of bath), $[\alpha]_D^{20} +11.08^\circ$ in tetrachloroethane.

Deoxygluconic acid, $\text{OH}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, is prepared by oxidising 2-deoxyglucose with bromine in aqueous solution at the atmospheric temperature; it has m. p. 146—147° (corr.) after previous softening, $[\alpha]_D^{17} +4.30^\circ$ in aqueous solution which becomes constant at $+10.85^\circ$ after twenty-four hours. When heated in a high vacuum at 100°, it appears partly to sublime and to pass into the corresponding lactone, $\text{C}_6\text{H}_{10}\text{O}_5$. Barium deoxygluconate, $(\text{C}_6\text{H}_{11}\text{O}_6)_2\text{Ba}\cdot\text{H}_2\text{O}$, $[\alpha]_D^{19} +13.37^\circ$ in aqueous solution, crystallises in long prisms which are very sparingly soluble in water. H. W.

A Revision of Rosanoff's Diagram of the Aldose Sugars.

J. J. WILLAMAN and CLARENCE A. MORROW (*J. Amer. Chem. Soc.*, 1923, **45**, 1273—1280).—Rosanoff's diagram of the aldose sugars (*ibid.*, 1906, **28**, 114) has been modified in such a way as to include (1) all the known sugars, and (2) the name of the sugar, its specific rotation, and an indication whether it occurs in nature. Also, diagrams have been constructed for the known ketoses and the methyl hexoses. For further details, the original should be consulted, as it does not lend itself to abstraction. W. S. N.

The Structure of Sucrose. MAX BERGMANN (*Ber.*, 1923, **56**, [B], 1227).—In connexion with the recent observations of Haworth and Linnel (*T.*, 1923, **123**, 294, 301) that the presence of the ethylene oxide ring in sucrose is improbable, it is pointed out that the author has previously drawn a similar conclusion by his work on the methylcycloacetal of δ -acetylbutyl alcohol (*cf.* A., 1922, i, 618). H. W.

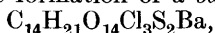
Two New Derivatives of Trehalose and Mannitol and a α -Methylglucoside Dichlorohydrin. BURCKHARDT HELFERICH, ALBRECHT LÖWA, WALDEMAR NIPPE, and HANS RIEDEL (*Ber.*, 1923, **56**, [B], 1083—1087).—In a preliminary communication, the reaction between glucosides, pyridine, and sulphuryl chloride has been discussed and crystalline derivatives of α - and β -methylglucosides have been described. Similar compounds have now been obtained from trehalose and mannitol, but not, however, from a large number of non-aldehydic sugars and sugar derivatives.

It appears that the configuration present in α -methylglucoside is essential for the production of these derivatives.

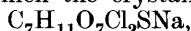
Mannitol tetrachlorohydrin sulphate, $C_6H_8O_4Cl_4S$, is prepared by the addition of a suspension of finely-divided mannitol in chloroform to a mixture of pyridine, chloroform, and sulphuryl chloride; it crystallises in leaflets, m. p. 107° , $[\alpha]_D^{15} + 105.13^\circ$ when dissolved in tetrachloroethane.

Trehalose tetrachlorohydrin disulphate, $C_{12}H_{14}O_{11}Cl_4S_2$, colourless, lustrous needles which become carbonised at about 175° , is prepared in a similar manner; it has $[\alpha]_D^{17} + 151.9^\circ$, $[\alpha]_D^{20} + 152.29^\circ$ when dissolved in chloroform.

α -Methylglucoside dichlorohydrin sulphate, for which an improved method of preparation is given, has been examined in greater detail. It is slowly hydrolysed by aqueous barium hydroxide solution at 37° with the formation of a *barium* salt,



an amorphous, white precipitate, of which the homogeneity appears somewhat doubtful. Methyl-alcoholic ammonia transforms it into the amorphous *ammonium* salt of an α -methylglucoside dichlorohydrin sulphate, from which the crystalline *sodium* salt,



broad needles, *copper* salt, $(C_7H_{11}O_7Cl_2S)_2Cu \cdot 3.5H_2O$, blue, rhombic leaflets, $[\alpha] + 123.87^\circ$ to $+125.56^\circ$ in aqueous solution, and the amorphous *barium* salt (which is not identical with the salt described above) are derived. The sodium salt is converted when in boiling aqueous solution in the presence of an excess of copper sulphate into α -methylglucoside dichlorohydrin, $C_7H_{12}O_4Cl_2$, colourless needles, m. p. 155° , $[\alpha]_D^{20} + 180.7^\circ$ in alcoholic solution. H. W.

Hydrolysis of Starch by Salts. II. W. BIEDERMANN (*Biochem. Z.*, 1923, **137**, 35—52).—A few experiments are described where a comparison is made of the colour produced by iodine on various dilutions of (1) an amylose solution mixed with a phosphate mixture and shaken continuously in a stream of air, (2) an unshaken amylose solution mixed with a phosphate mixture, the solutions being kept a few hours before testing with iodine. Instead of phosphate mixtures, $N/5$ -sodium and potassium chlorides were also employed. The results are interpreted as indicating hydrolysis of the amylose by the salts in presence of oxygen. A long discussion follows as to a possible explanation on a purely physical basis.

H. K.

Polysaccharides. XX. Polymeric Carbohydrates. P. KARRER (*Helv. Chim. Acta*, 1923, **6**, 402—409).—When Zulkowsky's soluble starch is treated at 0° with acetyl bromide, as much acetylbromomaltose, and finally hepta-acetylmaltose, is obtained as from an equal quantity of maltose, and only a trace of tetra-acetylglucose is obtained. If a proportion of glucose is added to the starch, the expected yield of tetra-acetylglucose is obtained. If, as Irvine claims, starch were derived from a triamylose, by the action of acetyl bromide, it should give half as much acetylbromoglucose as acetylbromomaltose. Irvine's conclusion cannot therefore be

maintained, and Pictet's trihexosan theory also falls to the ground for similar reasons (A., 1922, i, 987). Irvine's view that cellobiose is contained in the starch molecule is also not confirmed, since no cellobiose derivative is found among the reaction products from the action of acetyl bromide. Irvine's methylation process by which he obtained 2:3:6-trimethylglucose is too drastic and cannot be trusted for the determination of constitution. The fact that by the methylation of inulin sometimes dextrorotatory and sometimes levorotatory products are obtained shows that methylation may lead to decomposition. The remainder of the paper is a polemical reply to Irvine (T., 1922, **121**, 1060, 1213).

E. H. R.

Soluble Starch or Amylodextrin. A. REYCHLER (*Bull. Soc. chim. Belg.*, 1923, **32**, 221—227).—The author reviews the processes previously described for the preparation of soluble starch both by means of hydrolysing and oxidising reagents, and describes a new procedure whereby a preparation can be obtained which gives a very stable and limpid solution. One hundred parts of starch are digested for about twenty hours with 130—150 parts of a 0.75% solution of potassium dichromate in *N*/4-hydrochloric acid, the dichromate is then reduced with a trace of sulphur dioxide, and the product is collected by filtration, washed, and dried at a low temperature. Potassium permanganate may be substituted for the dichromate, if desired. The starch oxidised in this way swells, but does not dissolve in boiling water, but on the addition of a trace of alkali hydroxide, or even of ammonia or alkali carbonate, the mucilage is rapidly transformed into a limpid solution absolutely free from microscopic particles. The soluble starch solution has all the properties usually attributed to amylodextrin, and is not precipitated by acidification. It has but little reducing action on Fehling's solution, and is strongly dextrorotatory, $[\alpha]_D$ about $+200^\circ$.

G. F. M.

The Composition of Glycogen. M. SAMEC and V. ISAJEVIĆ (*Compt. rend.*, 1923, **176**, 1419—1421).—A comparison of the physico-chemical properties of glycogen with those of starch shows that the molecular weights are of the same order. On submitting solutions of the two substances to electro-dialysis similar phenomena are observed, the chief difference being that a starch solution deposits about 80% of the solute in the form of gel, whereas a glycogen solution yields but little gel: this is consistent with the low viscosity of the latter solution. The phosphorus content of the glycogen sol is high, although its electrical conductivity is low. The authors suggest that this quantity of phosphorus is of great physiological importance, and that glycogen may function as a reserve of phosphorus in addition to one of carbohydrate.

H. J. E.

Some Physico-chemical Properties of Laminarin. (MME) L. GRUZEWSKA (*Bull. Soc. Chim. biol.*, 1923, **5**, 216—226).—Laminarin (cf. Kylin, A., 1915, i, 931) forms a colloidal solution in water which is unstable and slowly deposits the substance in

the form of grains. The author regards this spontaneous precipitation as the result of polymerisation or condensation. The presence of oxygen appears to be necessary for its production; it is also accelerated by acids and by hydrogen peroxide and retarded by alkalis. Although laminarin forms colloidal solutions it diffuses slowly through a collodion membrane, and hence cannot be purified by dialysis. Crystalline deposits have been obtained from alkaline solutions of laminarin after the addition of alcohol and ether.

E. S.

Hydrocellulose. EMIL HEUSER and GEORG JAYME (*Ber.*, 1923, 56, [B], 1242—1243; cf. Heuser and von Neuenstein, this vol., i, 17).—The molecular weight of dimethylhydrocellulose has been determined cryoscopically in aqueous solution. The results are in harmony with the authors' conception that the compound is a dimethyl derivative of a dimeric anhydrocellobiose, which receives further confirmation from the observation that the molecular weight does not increase beyond the theoretically required value with increasing concentration of the solution. H. W.

Hydrocellulose. II. Hydrolysis of Cellulose by Oxalic Acid. EMIL HEUSER and FRITZ EISENRING (*Cellulosechemie*, 1923, 4, 25—31).—In the preparation of hydrocellulose from viscose cellulose by the action of hydrogen chloride gas in the presence of limited quantities of moisture according to the method of Knoevenagel and Busch (*A.*, 1922, i, 636), the attack on the cellulose is more severe and the yield of product reprecipitable from its solution in 8% sodium hydroxide solution is lower the greater the quantity of moisture present during the action of the hydrogen chloride. By secondary hydrolysis of the hydrocellulose with dilute sulphuric acid, the quantity of dextrose formed is also larger when more moisture is present. The composition of the product reprecipitated by alcohol from solutions of the viscose hydrocellulose in alkali hydroxide corresponds with a compound of the formula $C_{12}H_{20}O_{10} \cdot 2NaOH$. Viscose hydrocellulose, when submitted to total hydrolysis with 41% hydrochloric acid for twenty-eight hours at 18—20°, yielded more than 95% of fermentable dextrose. Hydrocellulose completely soluble in alkali hydroxide solution is produced by digesting viscose cellulose with 10—20% oxalic acid solution in a sealed tube at 100° without serious loss in the form of soluble products. With 5% oxalic acid solution at higher temperatures (140—180°), considerable quantities of reducing sugar are formed, depending on the time and temperature, and the yield of hydrocellulose residue is correspondingly reduced. At 180°, large quantities of gaseous products are formed owing to the decomposition of the oxalic acid. Ordinary cotton cellulose when heated with oxalic acid yields a hydrocellulose which is only partly soluble in 10% sodium hydroxide solution. When digested with oxalic acid solution at 180°, viscose hydrocellulose yields large proportions of ω -hydroxymethylfurfuraldehyde, viscose cellulose yields much less, and cotton cellulose only a small quantity [Cf. *J.S.C.I.*, 1923, July]. J. F. B.

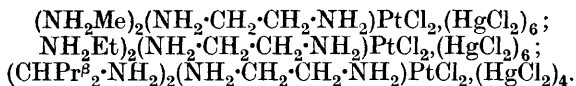
Derivatives of Straw-lignin. II. F. PASCHKE (*Cellulose-chemie*, 1923, 4, 31—32).—When heated at 180° with aniline and oxalic acid, straw-lignin forms a condensation product in which 1 mol. of lignin is combined with 3 mols. of aniline. When straw-lignin is fused with sulphur and sodium sulphide, a sulphur dye is formed having a composition corresponding with the formula $C_{36}H_{49}O_{21}S_6$. This points to the presence of four methoxyl groups in the lignin molecule, and probably also of four hydroxyl groups. In its condensation reactions, lignin exercises tervalent aldehydic or ketonic functions, and the presence of six sulphur atoms in the above formula falls in the same category. In faintly alkaline solution, straw-lignin and wood-lignin prepared by the alkaline process of digestion have a tanning action on animal skin, which after twenty-four hours' immersion in the solution is converted into a soft brown leather without gain in weight. An alkaline solution of ligninsulphonic acid, on the other hand, has no tanning action on skin but a large proportion of the extract is absorbed. The gain in weight is considerable but the product after drying becomes extremely brittle.

J. F. B.

A Note on the Photosynthesis of Amines. OSCAR WALTER SNOW and JOHN FREDERICK SMERDON STONE (*T.*, 1923, 123, 1509—1515).

Double Salts of Mercuric Chloride with the Chloroplatinites of Amines. D. STRÖMHOLM (*Z. anorg. Chem.*, 1923, 126, 129—140; cf. A., 1902, i, 138).—Mercurichlorides of compounds of the type $(NH_2R)_4PtCl_2$ are described. Of the 27 compounds mentioned, eight contain 6 molecular proportions of mercuric chloride (which appears to be the maximum amount possible), four contain 5 molecular proportions, one contains 4.5, nine contain 4, and the rest contain less than 4 molecular proportions.

The following compounds are described: $(NH_3)_4PtCl_2, HgCl_2$;
 $(NH_3)_4PtCl_2, (HgCl_2)_4, 3H_2O$; $(NH_2Me)_4PtCl_2, (HgCl_2)_4$;
 $(NH_2Et)_4PtCl_2, (HgCl_2)_6$; $(NH_2Pr^a)_4PtCl_2, 2H_2O$;
 $(NH_2Pr^a)_4PtCl_2, (HgCl_2)_{2.5}$; $(CH_2Pr^a \cdot NH_2)_4PtCl_2, 2H_2O$;
 $(CH_2Pr^a \cdot NH_2)_4PtCl_2, (HgCl_2)_2$; $(NH_2 \cdot CH_2 \cdot CH_2 \cdot NH_2)_2PtCl_2$;
 $(NH_2 \cdot CH_2 \cdot CH_2 \cdot NH_2)_2PtCl_2, (HgCl_2)_5$; $(C_5H_5N)_4PtCl_2, (HgCl_2)_2$;
cis-(NH_3)₂(NH_2Pr^a)₂ $PtCl_2, (HgCl_2)_{4.5}$;
trans-(NH_3)₂(NH_2Pr^a)₂ $PtCl_2, (HgCl_2)_6$;
cis-(NH_2Me)₂(NH_2Pr^a)₂ $PtCl_2, (HgCl_2)_3$;
trans-(NH_2Me)₂(NH_2Pr^a)₂ $PtCl_2, (HgCl_2)_5$ or $_6$;
cis- and *trans*-(NH_2Et)₂(NH_2Pr^a)₂ $PtCl_2, (HgCl_2)_6$;
cis-(NH_3)₂($CH_2Pr^a \cdot NH_2$)₂ $PtCl_2, (HgCl_2)_{3.5}$;
trans-(NH_3)₂($CH_2Pr^a \cdot NH_2$)₂ $PtCl_2, (HgCl_2)_6$;
trans-(NH_2Me)₂($CH_2Pr^a \cdot NH_2$)₂ $PtCl_2, (HgCl_2)_5$;
trans-(NH_2Et)₂($CH_2Pr^a \cdot NH_2$)₂ $PtCl_2, (HgCl_2)_5$;
 $(NH_3)_2(NH_2 \cdot CH_2 \cdot CH_2 \cdot NH_2)PtCl_2, (HgCl_2)_4$;
cis- and *trans*-(NH_3)₂(NH_2Me)₂ $PtCl_2, (HgCl_2)_4$;
cis- and *trans*-(NH_3)₂(NH_2Et)₂ $PtCl_2, (HgCl_2)_4$;
cis-(NH_2Me)₂(NH_2Et)₂ $PtCl_2, (HgCl_2)_6$;
trans-(NH_2Me)₂(NH_2Et)₂ $PtCl_2, (HgCl_2)_4$;



H. H.

A New Class of Complex Compounds of Ruthenium. A. GUTBIER (*Ber.*, 1923, **56**, [B], 1008—1011; cf. Gutbier and Krauss, A., 1915, i, 120).—Complex ruthenium compounds of the type $\text{RuX}_3\cdot 4\text{NH}_3\text{R}\cdot\text{X}$ are uniformly obtained when the necessary proportion of the organic base dissolved in dilute halogen acid is added very rapidly to a solution of the ruthenium halide in the presence of a sufficient amount of halogen acid; the precipitates are recrystallised from water or alcohol acidified with halogen acid. The salts are highly sensitive to pure water, so that their physico-chemical behaviour in this medium cannot be studied. The constitution has not yet been definitely elucidated, but, for the present, the author adopts Werner's conception and considers that the four molecules of the substituted ammonium halide are each united to the ruthenium atom by a subsidiary valency of the halogen atom, thus giving a kation with the co-ordination number 6; the general formula for the salts is therefore $[\text{RuX}_2(\text{NH}_3\text{RX})_4]\text{X}$.

The following individual salts are described: Chloro-series, the *methylammonium* salt, $[\text{RuCl}_2(\text{NH}_3\text{MeCl})_4]\text{Cl}$, reddish-brown, lustrous needles; the *ethylammonium* salt, reddish-brown, feathery needles or irregular plates; the *n-propylammonium* salt, small, red, lustrous needles; the *isopropylammonium* salt, brownish-red, irregular leaflets; the *n-butylammonium* salt, lustrous, brownish-red, matted needles; the *isobutylammonium* salt, reddish-brown needles; the *ethylenediammonium* salt, $[\text{RuCl}_2(\text{C}_2\text{H}_4\text{N}_2\text{H}_6\text{Cl}_2)_2]\text{Cl}$, very small, red, lustrous needles or brownish-red leaflets; the *propylenediammonium* salt, purplish-red, lustrous needles or leaflets; the *pyridinium* salt, small, reddish-brown needles; the *quinolinium* salt, lustrous, brownish-red leaflets. Bromo-series: *methylammonium* salt, $[\text{RuBr}_2(\text{NH}_3\text{MeBr})_4]\text{Br}$, small, very dark leaflets; the *ethylammonium* salt, almost black leaflets; the *n-propylammonium* salt, dark, lustrous leaflets; the *isopropylammonium* salt, small, dark leaflets; the *n-butylammonium* salt, dark leaflets; the *isobutylammonium* salt, almost black leaflets; the *ethylenediammonium* salt, very dark, irregular leaflets; the *propylenediammonium* salt, black needles; the *pyridinium* salt, dark needles or leaflets; the *quinolinium* salt, very dark, thin leaflets.

H. W.

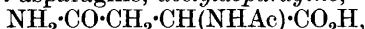
Changes undergone by Amino-acids in Presence of Sugar. S. KOSTYTSCHEV and W. BRILLIANT (*Z. physiol. Chem.*, 1923, **127**, 224—233).—If yeast autolysate is allowed to remain with sugar at 30—55° a decrease in the amino-nitrogen takes place, and a compound which can be precipitated by copper hydroxide is formed, containing nitrogen closely corresponding in amount with that lost by the amino-acids. A spontaneous reaction between sugar and amino-acids takes place in alkaline media, with the

formation of a compound precipitable by copper hydroxide. From the precipitate the sugar, but not the amino-acids, can be recovered.

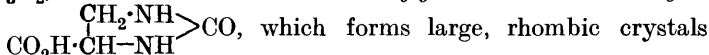
W. O. K.

Synthesis of γ -Amino- β -hydroxybutyric Acid. MAX BERGMANN (*Z. physiol. Chem.*, 1923, **127**, 260—261).— γ -Amino- β -hydroxybutyric acid, synthesised by Tomita (this vol., i, 190) has also been synthesised by the author and his collaborators, who have also prepared the *anhydride*, and the *hydrobromide*, m. p. 78°; the *N*-benzoyl derivative, m. p. 177°; *O*-benzoyl derivative (*hydrochloride*, m. p. 215° decomp.), the isomeric benzoyl derivatives of the ester, and the amide of the acid. W. O. K.

The Configuration of Amino-acids. I. P. KARRER and A. SCHLOSSER (*Helv. Chim. Acta*, 1923, **6**, 411—418).—These experiments were started with the object of obtaining an optically active serine from *l*-asparagine, and although this has not yet been accomplished, a number of interesting results were obtained. By acetylation of *l*-asparagine, *acetyl*asparagine,



was obtained in 60% yield, stout prisms, m. p. 165°; a 1.5% aqueous solution is optically inactive. When treated with bromine in barium hydroxide solution, this was converted into a compound, $\text{C}_4\text{H}_6\text{O}_3\text{N}_2$, which was shown to be *l*-glyoxalid-2-one-5-carboxylic acid,



[$a:b:c=0.8601:1:0.6356$, $[\alpha]_D^{18} -16.5^\circ$]; it decomposes at 184°. With diazomethane, it gives a *methyl* ester, m. p. 78°, crystallising in fine needles. It does not form salts with mineral acids, is not affected by nitrous acid, and when heated with hydrochloric acid is converted into *d*- β - γ -diaminopropionic acid, which was isolated as the monohydrochloride, $[\alpha]_D^{20} +25.0^\circ$. It follows that *l*-asparagine and *d*-diaminopropionic acid must have the same configuration as *l*-glyoxalid-2-one-5-carboxylic acid, since no change takes place at the asymmetric carbon atom. *d*-Diaminopropionic acid has previously been converted into *d*-glyceric acid (lævorotatory) through *d*-isoserine, and *l*-asparagine has also been converted into *l*-glyceric acid (dextrorotatory) through *l*-aspartic acid, *l*-malic acid, and *l*-isoserine. It follows that at one of these stages a Walden inversion must occur.

l-Acetylaspargine forms a *methyl* ester, $[\alpha]_D^{19} -41.14^\circ$, and an *amide* (which is the diamide of *l*-acetylaspargic acid) decomposing at 230°; practically it is optically inactive. E. H. R.

The Amides of Hypothiocyanic Acid. HANS LECHER, MAX WITTWER, and WALTER SPEER (*Ber.*, 1923, **56**, [B], 1104—1112).—The term, hypothiocyanic acid, has been applied to the compound $\text{NCS}\cdot\text{OH}$, by Bjerrum and Kirschner ("Die Rhodanide des Goldes und das freie Rhodan," Kopenhagen, 1918, p. 11). Attempts to prepare amides of the acid have been described by Söderbäck (*A.*, 1920, i, 219), who however, did not obtain products which could be purified. A slight modification of his procedure, however,

which consists in adding the solution of thiocyanogen to that of an excess of ammonia or amine, leads to the desired result. The *diethylamide*, $\text{NCS}\cdot\text{NEt}_2$, is thus obtained as a colourless liquid with a pleasant odour, b. p. 37° (corr.)/3 mm.; it is unstable at the atmospheric temperature. The *amide*, $\text{NCS}\cdot\text{NH}_2$, can be prepared similarly in ethereal solution which is relatively stable. It remains as a colourless liquid with an odour of formaldehyde when the solvent is removed at a low temperature in a high vacuum. It is not possible to purify it, since it explodes spontaneously at 0° and at a lower temperature has not a sufficiently high vapour tension to permit its distillation in a high vacuum.

Hydrolysis of the amides by acids results in the immediate production mainly of ammonium or amine salt and hypothiocyanic acid: $\text{NCS}\cdot\text{NR}_2 + \text{H}_2\text{O} + \text{HX} = \text{NCS}\cdot\text{OH} + \text{NHR}_2, \text{HX}$. Subsequently, hypothiocyanic acid yields thiocyanic acid, sulphuric acid, and hydrocyanic acid, but a portion of it is decomposed in a different direction, since the amounts of the two latter acids which are formed are less than the theoretical. Similar observations are recorded in the case of the hydrolysis of thiocyanogen by water; the process therefore does not occur quantitatively in accordance with Söderbäck's equation: $3(\text{SCN})_2 + 4\text{H}_2\text{O} \rightarrow 5\text{HSCN} + \text{H}_2\text{SO}_4 + \text{HCN}$.

Diethylrhodanamine is relatively stable towards water and aqueous ammonia. It is decomposed more slowly by solutions of alkali hydroxides than by acids. Hydrolysis occurs in a completely different manner, and gives cyanate, sulphur, and amine in such quantities that the main change must follow the course: $\text{NC}\cdot\text{S}\cdot\text{NR}_2 + \text{KOH} \rightarrow \text{NC}\cdot\text{OK} + \text{S} + \text{NHR}_2$. Apparently the first phase of the reaction consists in the rupture of the bond between the sulphur and carbon atoms: $\text{NC}\cdot\text{S}\cdot\text{NR}_2 + \text{KOH} \rightarrow \text{NC}\cdot\text{OK} + \text{HS}\cdot\text{NR}_2$. Diethylthiohydroxylamine is thereby formed, which is either decomposed further in accordance with the scheme:



or is hydrolysed to $\text{HS}\cdot\text{OH}$, which yields water and sulphur.

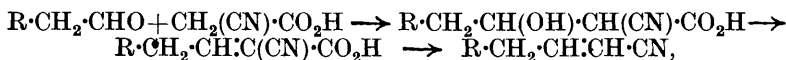
Rhodanamine is decomposed in fundamentally the same manner when its ethereal solution is shaken with alkali hydroxide solution. The bulk of the sulphur is obtained, however, in the form of polysulphide and thiosulphate. In the presence of an organic solvent such as ether, which preserves the sulphur in the molecular-disperse condition, the element appears to react readily with alkali hydroxide.

The acid hydrolysis of rhodanamine appears to proceed in part according to the scheme given for the alkaline hydrolysis, since the formation of carbon dioxide and an excess of ammonium salt points to a primary production of cyanic acid. H. W.

Nitriles of Olefine Monocarboxylic Acids. K. VON AUWERS [with O. JORDAN, TH. MEISSNER, and O. SEYDEL] (*Ber.*, 1923, 56, [B], 1172—1185).—The constitution of the product obtained by the action of potassium cyanide on allyl bromide or iodide has been the subject of considerable discussion, since its mode of production causes it to be regarded as allyl cyanide, $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{CN}$,

whereas its properties indicate that it is crotononitrile, $\text{CHMe}\cdot\text{CH}\cdot\text{CN}$. The authors have endeavoured to apply spectrochemical methods to the elucidation of its constitution, in the expectation that allyl cyanide would be optically normal, whereas crotononitrile should exhibit optical exaltation in consequence of the conjugation of the double and treble bonds. Pure allyl cyanide is most conveniently prepared from allyl bromide and cuprous cyanide; it has $d_4^{14.8}$ 0.8407, $n_D^{14.8}$ 1.40626, $n_D^{14.8}$ 1.40868, $n_D^{14.8}$ 1.41511, $n_D^{14.8}$ 1.41996. It is characterised by the unusual ease with which it becomes isomerised to crotononitrile under the influence of alkali hydroxide, and, for this reason, the use of potassium cyanide in its preparation is inadvisable. Three specimens of crotononitrile, prepared respectively from crotonaldoxime and acetic anhydride (I and II) and from crotonamide and phosphoric oxide have been examined, with the following results. (i) $d_4^{11.5}$ 0.8378, d_4^{20} 0.829, d_4^{23} 0.8259; $n_D^{11.5}$ 1.42859, $n_D^{11.5}$ 1.43198, $n_D^{11.5}$ 1.44097, $n_D^{11.5}$ 1.44879. (ii) $d_4^{19.1}$ 0.8226, $n_D^{19.1}$ 1.41566, $n_D^{19.1}$ 1.41966, $n_D^{19.1}$ 1.42795, $n_D^{19.1}$ 1.43518. (iii) $d_4^{14.1}$ 0.8304, $n_D^{14.1}$ 1.42164, $n_D^{14.1}$ 1.42488, $n_D^{14.1}$ 1.43361, $n_D^{14.1}$ 1.44103. The expected difference in the spectroscopic behaviour is therefore observed. The differences appear to be shown quite generally between Δ^{α} - and Δ^{β} -nitriles.

The action between aldehydes and cyanoacetic acid has been examined. The expectation that it would proceed in accordance with the scheme :

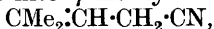


is fulfilled as far as the production of the nitrile-acid is concerned, but it is found that when the latter is decomposed with loss of carbon dioxide a displacement of the double bond occurs in such a manner that a conjugated passes into a non-conjugated system. The Δ^{β} -nitrile is therefore the final product, the formation of which is not due to isomerisation of primarily formed Δ^{α} -nitrile, since the latter is stable under the experimental conditions adopted.

The following nitrile acids are obtained by the condensation of cyanoacetic acid with the requisite aldehyde in the presence of piperidine at 60–70°. They are converted into nitriles by heating them until evolution of carbon dioxide ceases; the yields are uniformly very poor, since the bulk of the material becomes resinified.

α -Cyanocrotonic acid, thin leaflets, m. p. 80°, yields an *ethyl* ester, a colourless liquid, b. p. 112°/20 mm., $d_4^{18.8}$ 1.0255, d_4^{20} 1.024; $n_D^{18.8}$ 1.44988, $n_D^{18.8}$ 1.45302, $n_D^{18.8}$ 1.46172, $n_D^{18.8}$ 1.46888, $n_D^{18.8}$ 1.4525; the nitrile obtained from it is a mixture of much crotononitrile and little vinylacetonitrile. Propaldehyde and cyanoacetic acid yield α -cyano- Δ^{α} -pentenoic acid, coarse, lustrous needles, m. p. 82–84° (*ethyl* ester, a colourless liquid, b. p. 121–122°/25 mm., $d_4^{19.9}$ 1.0004, d_4^{20} 1.000, $n_D^{19.9}$ 1.44988, $n_D^{19.9}$ 1.45292, $n_D^{19.9}$ 1.46152, $n_D^{19.9}$ 1.46869, n_D^{20} 1.4529) which is converted by heat into Δ^{β} -*penteno-nitrile*, b. p. 85–87°/110 mm., $d_4^{18.8}$ 0.8430, d_4^{20} 0.842, $n_D^{18.8}$ 1.42397, $n_D^{18.8}$ 1.42650, $n_D^{18.8}$ 1.43374, $n_D^{18.8}$ 1.43968, n_D^{20} 1.4260. *iso*Butalde-

hyde and cyanoacetic acid give a small yield of the corresponding acid which is converted into γ -methyl- Δ^{β} -pentenenitrile,



a colourless liquid, b. p. $63^{\circ}/14$ mm., d_4^{188} 0.8556, d_4^{20} 0.855, n_a^{188} 1.43529, n_D^{188} 1.43796, n_p^{188} 1.44529, n_{γ}^{188} 1.45129, n_D^{20} 1.4374. *iso*-Valeraldehyde and cyanoacetic acid yield α -cyano- Δ^{α} -*iso*-heptenoic acid, m. p. 53° , d_4^{100} 0.9711, whence $d_4^{99.6}$ 0.9715, $n_a^{99.6}$ 1.44367, $n_D^{99.6}$ 1.44690, $n_p^{99.6}$ 1.45599, $n_{\gamma}^{99.6}$ 1.46409, which is converted by ozone into a mixture of *isovaleraldehyde* and a little *isobutaldehyde*. The corresponding *ethyl* ester is a colourless liquid of agreeable odour, b. p. $121-122^{\circ}/13$ mm., $d_4^{19.7}$ 0.9666, d_4^{20} 0.966, $n_a^{19.7}$ 1.45198, $n_D^{19.7}$ 1.45502, $n_p^{19.7}$ 1.46340, $n_{\gamma}^{19.7}$ 1.47037, n_D^{20} 1.4549. Δ^{β} -*iso*-Heptenenitrile, obtained from the α -cyano-acid, has b. p. $57-88^{\circ}/11$ mm., $d_4^{22.3}$ 0.8241, d_4^{20} 0.826, $n_a^{22.3}$ 1.42691, $n_D^{22.3}$ 1.42932, $n_p^{22.3}$ 1.43614, $n_{\gamma}^{22.3}$ 1.44166, n_D^{20} 1.4304; its optical characteristics and its behaviour towards ozone prove it to be almost exclusively the Δ^{β} -derivative. It is converted by boiling potassium hydroxide solution into a mixture of Δ^{α} - and Δ^{β} -*iso*heptenoic acids. H. W.

[The Catalytic Reduction of Aliphatic Azines. II. Reduction of Dimethylketazine and *iso*Butyraldazine in the Presence of Glacial Acetic Acid]. K. A. TAIPALE (*Ber.*, 1923, 56, [B], 1247; cf. this vol., i, 547).—An addendum. The lack of foreign scientific literature in Russia during the last few years has caused the author to be in ignorance of the work of Lochte, Bailey, and Noyes (*A.*, 1922, i, 329; this vol., i, 26) on the hydrogenation of dimethylketazine. H. W.

A Possible Asymmetry of Aliphatic Diazo-compounds. IV. P. A. LEVENE and L. A. MIKESKA (*J. Biol. Chem.*, 1923, 55, 795—800).—In previous communications (*A.*, 1921, i, 233; 1922, i, 818), experiments have been described which resulted in the production of optically active diazosuccinic ester; the rotation observed, however, was extremely small. The crude diazo-ester has now been converted into bromosuccinic ester by treatment with gaseous hydrogen bromide in ethereal solution. Hydrolysis of the bromo-ester with 10% hydrochloric acid yielded a product, $[\alpha]_D^{20} +0.2^{\circ}$, which was a mixture of bromosuccinic, chlorosuccinic, and fumaric acids. By fractional crystallisation of 800 g. of this product, a fraction was finally obtained which melted at 176° and had $[\alpha]_D^{20} +60.45^{\circ}$ in ethereal solution. Analysis indicated that it contained about 10% of chlorosuccinic and 90% of bromosuccinic acids. Since pure bromosuccinic acid has $[\alpha]_D^{20} +67.92^{\circ}$ and m. p. 172° , it is considered that the activity of the final product was due entirely to the bromosuccinic acid, and hence that the previously observed activity of preparations of diazosuccinic ester was due, not to contaminating substances, but to the diazo-ester itself. This is supported by the observation that active malic ester is not converted into active chlorosuccinic acid when treated with hydrochloric acid under the conditions used above. An explanation of the mechanism of the asymmetry will be dealt with in a later publication.

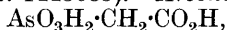
The observations of Chiles and Noyes (A., 1922, i, 924), that optically active glutamic and aspartic acids are produced by the reduction of ethyl diazoglutarate and ethyl diazosuccinate, respectively, have not been confirmed. Further, starting from *l*-asparagine, the authors have consistently obtained dextrorotatory diazosuccinic and malic esters; Chiles and Noyes, however, state that *lævo*-compounds are produced.

E. S.

Preparation of Aliphatic Arsenical Compounds. LES ÉTABLISSEMENTS POULENC FRÈRES and CARL OECHSLIN (Brit. Pat. 191029).—An arsenical aliphatic acid of the formula $[\text{CHAs}(\text{OH})_2]_x$ is obtained by heating at 180° , until the evolution of carbon dioxide and acetic acid ceases, the acetylarsenious anhydride prepared by dissolving arsenious oxide in acetic anhydride. The residual mass is dried in a vacuum, reduced to a fine powder, extracted several times with sodium hydroxide or hydrochloric acid, and the insoluble, grey powder remaining, which has the composition $(\text{AsCH})_x$, is suspended in sodium carbonate solution and oxidised with hydrogen peroxide. The resulting solution containing the sodium salt of the acid is decolorised with charcoal, and acidified with hydrochloric acid, when the acid is precipitated as a white powder, sparingly soluble in water and alcohol, but readily soluble in alkalis.

G. F. M.

Arsonoacetic acid. J. HUISMANN, J. CALISEN, and W. GRÜTTEFIEN (U.S. Pat. 1445685).—*Arsonosoacetic acid*,



is prepared by addition of sulphuric acid to the calcium salt, the latter being obtained by interaction of arsenious oxide, chloroacetic acid, sodium hydroxide, acetic acid, ammonia and calcium chloride, successively added. It forms colourless crystals from glacial acetic acid solution, m. p. 152° .

CHEMICAL ABSTRACTS.

The Action of Sulphuryl Chloride on Organic Substances. II. THOMAS HAROLD DURRANS (T., 1923, 123, 1424—1429).

The Walden Inversion. A. E. USPENSKI (*J. Russ. Phys. Chem. Soc.*, 1920, 51, 275—288).—An explanation of the Walden inversion is given for cyclic compounds in which *cis-trans*-isomerism may exist, and the possibility of ring formation as an intermediate stage in the Walden inversion in open-chain compounds is pointed out.

R. T.

Recent Investigations on Substitution in the Benzene Nucleus. A. F. HOLLEMAN (*Rec. trav. chim.*, 1923, 42, 355—379).—A lecture delivered at the Universities of London and Oxford, June 7th and 9th, 1922, in which a general survey of the subject is made. No entirely satisfactory theoretical explanation of the problem of replacing a hydrogen atom in substances of the type $\text{C}_6\text{H}_5\text{X}$ has yet been put forward. In dealing with the entry of a third substituent into a compound of the type $\text{C}_6\text{H}_4\text{XY}$, the quantitative aspect is also far from a satisfactory explanation, but greater progress has been made from the qualitative point of view. The replacement of substituents gives still greater scope for research,

for although many substances have been prepared in this manner, the work has not been done as regards systematic replacement, and is therefore irrelevant for this purpose. A consideration of some of the more systematic investigations on comparative substitution includes references to papers by Beyer (A., 1922, i, 37), Böeseken (A., 1912, i, 430), Davies (T., 1921, **119**, 853, 876; 1922, **121**, 785), Dimroth and von Schmaedel (A., 1907, i, 620), Holleman (A., 1913, i, 844), Holleman and de Mooy (A., 1916, i, 22), Holleman and Rinkes (A., 1911, i, 535), Holleman and Wibaut (A., 1913, i, 169), de Lange (A., 1919, i, 122), Lobry de Bruyn (A., 1904, i, 388), and Wibaut (A., 1915, ii, 680).

H. J. E.

Low Temperature Coal Tar and the Products of its Superheating. FRANZ SCHÜTZ, WILHELM BUSCHMANN, and HEINRICH WISSEBACH (*Ber.*, 1923, **56**, [B], 1091—1096; cf. Schütz, this vol., i, 195).—A reply to Fischer (this vol., i, 313).

Evidence is brought forward to prove that the low temperature tar examined by the authors had not, as Fischer suggested, been subjected to superheating. The temperature (600°) cited in the original paper is that of the heating chambers, and not of the coal itself, which did not exceed 480° . The authors agree with Fischer that a temperature of 400 — 500° suffices for the production of low temperature tar, but do not share his view that "benzine" escapes from the coal at 300° . Tar, and simultaneously also gas, commences to be produced at 370 — 380° and is freely evolved at 400° . The pyrogenic decomposition of the tar-forming constituents of coal takes place within narrow limits of temperature (400 — 450°). With rise of temperature above 450° , the formation of tar diminishes rapidly, whereas that of gas falls more slowly. At about 500° , the change is complete in six to seven hours. The yields of the various products depend greatly on the type of coal. Ninety kg. of low temperature tar and 50 cubic metres of gas per ton were obtained from a gas coal "Zeche Fürst Hardenberg" at 500° , and smaller yields at 450° . (The datum 110 cubic metres per ton given in the previous paper is due to an error in measurement.)

The light oils obtained from coal at a temperature not exceeding 450° have been re-examined; the results confirm those obtained previously by the authors. The fractions boiling below 75° have a high content of unsaturated hydrocarbons, whereas paraffins are not present in amount exceeding 25%. The occurrence of acetone is confirmed. The fractions of higher boiling point contain benzene, toluene, the xylenes, and phenol. There is no essential difference between the products obtained in the technical, continuous retorts and in the experimental, intermittent furnaces of Fischer and Glud. A possible explanation of the discrepancies between the authors' observations and those of Fischer lies in the fact that the products obtained by the latter were subjected to a preliminary treatment with aluminium chloride.

The origin of benzene in low temperature tar is discussed at length. Tetrahydrobenzene does not appear to suffer marked dehydrogenation at temperatures below 500° .

H. W.

3 : 3-Dimethyl-0 : 1 : 3-bicyclohexane in Connexion with Isomeric Change in Cyclic Compounds, and the Stereoisomeric 3 : 5-Dibromo-1 : 1-dimethylcyclohexanes. A. E. USPENSKI (*J. Russ. Phys. Chem. Soc.*, 1920, **51**, 257—263).—Two 3 : 5-dibromo-1 : 1-dimethylcyclohexanes, one, m. p. 36·5—37·5°, and the other, b. p. 124°/10 mm., n_D^{20} 1·5301, d_4^{20} 1·5771, and probably the *trans*- and *cis*-isomerides, respectively, are prepared by the action of phosphorus tribromide on 1 : 1-dimethylcyclohexane-3 : 5-diol. Both isomerides yield, on heating with zinc dust in aqueous alcohol, a mixture of 3 : 3-dimethyl-0 : 1 : 3-bicyclohexane, $\text{CH}_2 \begin{smallmatrix} \text{CH} \cdot \text{CH}_2 \\ | \quad | \\ \text{CH} \cdot \text{CH}_2 \end{smallmatrix} \text{CMe}_2$, b. p. 115·2—115·4°/760 mm., n_D^{20} 1·4385, d_4^{20} 0·8125, together with an isomeric hydrocarbon, $\text{CH}_2 \begin{smallmatrix} \text{CH} = \text{CH} \\ | \quad | \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{CMe}_2$ or $\text{CH} \begin{smallmatrix} \text{CH} - \text{CH}_2 \\ | \quad | \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{CMe}_2$, which is eliminated from the mixture by oxidation with potassium permanganate. R. T.

The Synthesis of the Stereoisomeric 1 : 4-Dibromocyclohexanes. A. E. USPENSKI and I. TURIN (*J. Russ. Phys. Chem. Soc.*, 1920, **51**, 263—274).—The synthesis of 1 : 4-dibromocyclohexane (Baeyer, A., 1894, i, 174) is repeated. The starting-point is diethyl succinate, which is converted successively into diethyl succinylsuccinate, 1 : 4-diketocyclohexane, 1 : 4-dihydroxycyclohexane, and 1 : 4-dibromocyclohexane. The dihydroxycyclohexane is obtained as a mixture of the *cis*- and *trans*-isomerides, which are separated by fractional crystallisation of their diacetyl derivatives, m. p. 34—36°, and 102—103°, respectively. These give on hydrolysis *cis*- and *trans*-1 : 4-dihydroxycyclohexanes, m. p. 100—102°, and 199°, respectively. Each of these, on heating in a sealed tube with hydrogen bromide, yields a mixture in the same proportions of the *cis*- and *trans*-dibromides, b. p. 137—138°/25 mm., d_4^{20} 1·7737, $n_D^{24.5}$ 1·5500, and m. p. 113°, respectively. R. T.

Catalytic Reduction of Nitro-compounds. I. $\alpha\beta$ -Unsaturated Nitro-compounds. E. P. KOHLER and N. L. DRAKE (*J. Amer. Chem. Soc.*, 1923, **45**, 1281—1289).—The reduction of nitrostyrene by means of hydrogen in methyl-alcoholic or ethereal solution in the presence of platinum black, or in alcohol in the presence of nickel, leads mainly to the dimeric compound, $\text{NO}_2 \cdot \text{CH}_2 \cdot \text{CHPh} \cdot \text{CHPh} \cdot \text{CH}_2 \cdot \text{NO}_2$ (Sonn and Schellenberg, A., 1918, i, 9), together with *syn*- and *anti*-phenylacetaldoximes. The formation of complex compounds is largely inhibited by the presence of mineral acids. The reduction of nitrostilbene by means of hydrogen and platinum black, in ethereal solution, gives deoxybenzoin oxime. β -Nitro- $\alpha\alpha$ -diphenylethylene is reduced by the same method to diphenylacetaldimine, $\text{CHPh}_2 \cdot \text{CH} : \text{NH}$, long, white needles, which passes, on heating, with loss of ammonia, into a compound, probably $\text{CHPh}_2 \cdot \text{CH}(\text{N} : \text{CH} \cdot \text{CPh}_2)_2$, slender, white needles, m. p. 129° (decomp.). The aldimine gives benzophenone

on oxidation by means of chromic acid in glacial acetic acid solution; it reacts with hydroxylamine, giving diphenylacetaldoxime, and a small quantity of a *substance*, m. p. about 85°, and with semicarbazide acetate giving diphenylacetaldehydesemicarbazone. $\beta\beta$ -Dinitro- $\alpha\alpha$ -diphenylethylene is reduced in alcoholic or ethereal solution in the presence of colloidal platinum to diphenylacetoneitrile and tetraphenylacetoneitrile, together with an oil which gives benzophenone on being distilled in steam. The reduction of 6-nitro-2-benzoyl-1-phenylcyclopropane in methyl-alcoholic solution by means of platinum black and hydrogen leads to the formation of γ -nitro- β -phenylbutyrophenone. W. S. N.

Halochromism. II. Halochromic Phenomena of Ethylenic Hydrocarbons and their Significance for the Theory of Halochromic Compounds. SIEGFRIED SKRAUP and LEO FREUNDLICH (*Annalen*, 1923, **431**, 243—270; cf. A., 1922, i, 539).—The figure previously given for the basicity of benzhydrol is meaningless, because the latter cannot be recovered unchanged, subsequently to the basicity determination; the addition of alcohol to the solution in acetic acid and sulphuric acid gives benzhydryl ethyl ether, whilst benzhydryl acetate is produced when water is added.

Dilution of a halochromic solution of a mixed aliphatic-aromatic carbinol causes elimination of water, with formation of an ethylenic hydrocarbon, which gives the same coloration in acetic acid-sulphuric acid solution as the original carbinol. Moreover, the same figure for the basicity is obtained, whether the hydrocarbon or the alcohol is used, *e.g.* ethyldiphenylcarbinol, 0·343, $\alpha\alpha$ -diphenylpropylene, 0·343; diphenylpropylcarbinol, 0·368, $\alpha\alpha$ -diphenylbutylene, 0·370. It follows that either quantitative conversion into the carbinol occurs under the conditions used in the basicity determination, or the same equilibrium is attained, starting from either side, $\text{OH}\cdot\text{CR}_2\cdot\text{CH}_2\text{R} \rightleftharpoons \text{R}_2\text{C}\cdot\text{CHR} + \text{H}_2\text{O}$. By addition of bromine in acetic acid solution to a solution of diphenylpropylene or the corresponding carbinol in acetic acid, or acetic acid and sulphuric acid, followed by addition of potassium iodide, and titration by means of sodium thiosulphate, it is shown that at least 86% of the solute, in the halochromic solution, exists as the unsaturated hydrocarbon. The figures so obtained are, however, too uncertain to use in calculating the basicity of pure carbinols from previous "basicity" measurements. Moreover, the unsaturated hydrocarbons themselves exhibit halochromy (see below); the results of Hess and Weltzien (A., 1922, i, 35), and particularly of Ziegler and Ochs using unsaturated carbinols (A., 1922, i, 1047), are therefore to be accepted with caution. Nevertheless, the figures quoted in the earlier paper (*loc. cit.*) may have a qualitative significance, since possibly the addition of acid to the hydrocarbon and salt formation from the carbinol may lead to the same product.

The formation of the carbinol, the possibility of which is never entirely excluded when sulphuric acid is used, may be avoided, since derivatives of ethylene give colour reactions in benzene solution with stannic chloride or stannic bromide. These are true

halochromic solutions, since on dilution the intensity of the colour decreases more rapidly than the concentration. For the lemon-yellow complex from diphenylbutylene and stannic bromide the dissociation constant corresponds with the composition: 2 mol. hydrocarbon+1 mol. halide, and has the value $K=0.090$. The other additive compounds examined are formed from equimolecular proportions of the components. The values of K are as follows. With stannic chloride: stilbene, yellow, 23.8; phenylstilbene, orange-yellow, 6.74; $\alpha\alpha$ -diphenylpropylene, yellow, 2.75; $\alpha\alpha$ -diphenylbutylene, yellowish-green, 0.280; $\alpha\alpha$ -diphenylethylene, greenish-yellow, 0.192; α -phenyl- α -*p*-anisylpropylene, orange, 0.0259. With stannic bromide: phenylstilbene, faintly orange, 23.8; $\alpha\alpha$ -diphenylpropylene, orange-yellow, 12.8; $\alpha\alpha$ -dianisylpropylene, red, 0.553; α -phenyl- α -anisylpropylene, reddish-orange, 0.114; phenyl-*p*-anisylethylene, greenish-yellow, 1.61. Since these values for K are so high, it is not surprising that none of these additive compounds can be isolated. It is noticeable that the bromine compounds have greater dissociation constants than the chlorine derivatives (cf. Pfeiffer, A., 1914, i, 923); there is, moreover, no parallelism between ease of dissociation and colour (cf. Kaufmann, A., 1917, i, 391; Lifschitz, A., 1917, i, 558).

Pfeiffer (A., 1918, i, 62) believes that the tendency to form additive complexes shown by ketones, quinones, nitro-compounds, and acid anhydrides is a function of the whole molecule, but that addition occurs on the oxygen of the carbonyl group or of the nitro-group. The free valency of the carbon atom of the carbonyl group, or of the nitrogen atom of the nitro-group, is thus increased, this being the cause of the production of colour. Pfeiffer separates halochromic additive compounds into two classes, which are directly opposed, in respect to the effect, on colour, of substituents in the components: (1) quinhydrones, and products derived from nitro-compounds or acid anhydrides, (2) products derived from quinones, unsaturated nitro-compounds, or unsaturated ketones and acids or metallic halides. Pfeiffer can only conclude that the carbonyl group may behave in two entirely different ways, without suggesting any cause. The authors, in view of the new type of halochromism described above, regard the halochromy of quinones, unsaturated ketones, or unsaturated nitro-compounds with acids or metallic halides as a reaction of the ethylene linking, whilst the formation of quinhydrones is a reaction of the carbonyl group. In agreement with this view, the influence of substituents on colour is the same for the new additive compounds described as for the compounds of the first class.

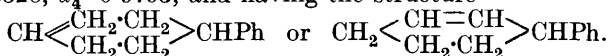
Additive compounds exhibiting halochromy are tabulated and classified, several new examples, in addition to those already mentioned, being given. Maleic anhydride gives the following colorations: with stannic chloride, faint red; with stannic bromide, deep red; with dibenzylideneacetone, orange; with di-*p*-methoxystyryl ketone, red; with diphenylpropylene, yellow; with anisylpropylpropylene, reddish-orange; with dianisylpropylene, a deeper reddish-orange. Distyryl ketone and tetranitromethane

give a lemon-yellow coloration. Di-*p*-methoxystyryl ketone and tetranitromethane, orange-red. Chloranil, dissolved in diphenylpropylene, phenylanisylpropylene, or dianisylpropylene, gives, respectively, a red, reddish-violet, or violet solution. In the same three solvents, *p*-benzoquinone is coloured yellow, reddish-orange, or red, whilst thymoquinone is coloured yellow, yellowish-orange, or reddish-orange. A fused mixture of di-*p*-methoxystyryl ketone and diphenylpropylene is scarcely coloured more deeply than the ketone itself, but an appreciable deepening of colour is observed on fusion with phenylanisylpropylene, dianisylpropylene, or diphenylbutylene. The following solutions are coloured. Distyryl ketone in benzene, lemon-yellow; in dimethylaniline, orange-yellow. Di-*p*-methoxystyryl ketone in benzene, faintly yellow; in anisole, pale yellow; in dimethylaniline, orange-yellow.

p-Anisyldimethylcarbinol is a colourless liquid which loses water when distilled under reduced pressure, giving β -*p*-anisylpropylene, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CMe}\cdot\text{CH}_2$. Phenyl-*p*-anisylpropylene, m. p. 52° , is obtained by the action of excess of magnesium ethyl bromide on *p*-methoxybenzophenone. The action of magnesium ethyl bromide on di-*p*-methoxybenzophenone gives di- α -*p*-anisylpropylene, colourless leaflets, m. p. 101° , which not only gives the expected (red) coloration with sulphuric acid, but is oxidised by means of chromic acid to di-*p*-methoxybenzophenone. The compound described by Gattermann (A., 1889, 862) as di- α -*p*-anisylpropylene gives neither of these reactions; moreover, a mixed melting-point determination with the substance now described showed a depression of 20° . It is concluded that the material prepared by Gattermann has some other constitution.

W. S. N.

3-Phenyl-0 : 1 : 3-bicyclohexane and the Unsaturated Cyclic Hydrocarbon, $\text{C}_{12}\text{H}_{14}$, in Connexion with Isomeric Change in Cyclic Compounds. ALEXEI EUGENIEVITSCH USPENSKI (*J. Russ. Phys. Chem. Soc.*, 1920, **51**, 245—257).—3 : 5-Dibromo-1-phenylcyclohexane, b. p. $173\text{—}175^\circ/5\text{ mm.}$, n_D^{20} 1.5998, d_4^{20} 1.5977, is prepared from 1-phenylcyclohexane-3 : 5-diol by the action of phosphorus tribromide. The dibromo-derivative, on boiling with zinc dust in aqueous alcoholic solution, yields 5-phenyl-0 : 1 : 3-bicyclohexane, $\text{CH}_2\langle\begin{smallmatrix} \text{CH}\cdot\text{CH}_2 \\ | \\ \text{CH}\cdot\text{CH}_2 \end{smallmatrix}\rangle\text{CHPh}$, b. p. $241.5\text{—}242.5^\circ/745\text{ mm.}$, $n_D^{16.5}$ 1.5452, d_4^{20} 0.9830, contaminated with an unsaturated isomeride, which can be removed by mild oxidation with potassium permanganate. The chief product of the oxidation of the phenylcyclohexene is benzoic acid, traces of other unidentified substances being also obtained. A small quantity of a more volatile dibromide, b. p. $155^\circ/15\text{ mm.}$, was obtained as a by-product in the preparation of the above dibromide, and this, on treatment with zinc dust, yields a hydrocarbon, $\text{C}_{12}\text{H}_{14}$, b. p. $243.2\text{—}244.2^\circ/756\text{ mm.}$, $n_D^{19.5}$ 1.5528, d_4^{20} 0.9793, and having the structure



R. T.

The Styphnates of some Hydrocarbons. N. N. EFREMOV (*J. Russ. Phys. Chem. Soc.*, 1919, **51**, 353—398).—Styphnic acid (*s*-trinitroresorcinol) forms equimolecular compounds with a number of aromatic compounds; these styphnates are analogous to the picrates, but are less readily formed and less stable. The formation of these substances was studied by plotting cooling curves of mixtures of the components, and it was found that the following gave definite compounds with styphnic acid, the melting point of the dystectic being indicated in brackets: naphthalene (165.5°) (cf. Noeltling and v. Salis, A., 1883, 59), phenanthrene (132.7°) acenaphthene (156.0°), retene (135.7°), and α -benzyl-naphthalene (doubtful, curve nearly horizontal at 134.3°). The compounds formed with the following decompose on melting and the cooling curves show a transition point indicated in brackets: α -bromonaphthalene (101.2°), β -bromonaphthalene (131.7°), α -chloronaphthalene (109.8°), fluorene (127.5°), stilbene (142.4° , very unstable). No compounds are obtained from diphenyl and dibenzyl or nitro-compounds (α -nitronaphthalene, nitroacenaphthene, 1 : 3 : 5-trinitrobenzene, 2 : 4 : 6-trinitrotoluene, 2 : 4 : 6-trinitro-*m*-xylene); whilst diphenylmethane and triphenylmethane are only partly miscible with styphnic acid in the molten state. G. A. R. K.

The Stepwise Addition of Hydrogen to Tetraphenylallene. D. VORLÄNDER and PAUL WEINSTEIN (*Ber.*, 1923, **56**, [B], 1122—1124).—Although the constitution of tetraphenylallene, $\text{CPh}_2\text{:C:CPh}_2$, has been placed beyond doubt by its synthesis and degradation (cf. Vorländer and Siebert, A., 1906, i, 345; Vorländer, Osterburg, and Meye, this vol., i, 682), the presence of the two unsaturated linkings has not previously been directly established by additive reactions. It is now shown that the hydrocarbon may be reduced by regulated treatment with a mixture of glacial acetic acid, hydriodic acid (d 1.7), and red phosphorus to tetraphenylpropylene, $\text{CHPh}_2\text{:CH:CPh}_2$, m. p. $127\text{--}128^\circ$ (cf. Vorländer and Siebert, *loc. cit.*) which may be reduced further to tetraphenylpropane. The unsaturated compound can be supercooled to an unusual degree. It is oxidised by chromic acid in the presence of glacial acetic acid to benzophenone and diphenylacetic acid.

Tetraphenylallene, dissolved in carbon tetrachloride, is converted by short treatment with chlorine into the *chloride*, $\text{C}_6\text{H}_4\text{<CPh}_2\text{>CCl}$, m. p. 167° .

Tetraphenylallene and nitrogen trioxide dissolved in cold benzene yield a colourless, crystalline compound, $\text{C}_{27}\text{H}_{20}\text{O}_3\text{N}_2$, m. p. $141\text{--}142^\circ$, which is possibly a nitrosite, from which, however, tetraphenylallene cannot be recovered. It is converted by alcoholic stannous chloride solution or by hydrogen chloride in the presence of alcohol or glacial acetic acid into the dioxide, $\text{Ph}_2\text{C}=\text{C}=\text{CPh}_2$, m. p. 198° , which is identical with the product obtained by Vorländer and Siebert (*loc. cit.*) by the action of chromic acid on tetraphenylallene.

H. W.

The Stereochemistry of the Hexahydrotoluidines [Methylcyclohexylamines]. A. SKITA (*Ber.*, 1923, **56**, [B], 1014—1023).—It has been shown previously (Skita and Berendt, A., 1920, i, 27) that the catalytic hydrogenation of the toluidines in the presence of platinum leads in each case to the production of two methylcyclohexylamines which are separable in the form of their crystalline benzoyl derivatives. The latter compounds have now been hydrolysed to the corresponding free bases which, however, are not readily prepared in this manner, as it involves the expenditure of much time and material. It is more convenient to use the acetotoluidides as the starting points, since these substances are converted into the corresponding *cis*-hexahydro-derivatives when hydrogenated in the presence of colloidal platinum, chloroplatinic acid, and a sufficiency of hydrochloric acid, and into the *trans*-hexahydro-compounds when treated with hydrogen and colloidal platinum in neutral, aqueous solution. The methylcyclohexylamines are colourless liquids which readily absorb carbon dioxide from the atmosphere, the ability being more pronounced with the *trans*- than with the *cis*-amines. The isomerides differ from one another in odour, that of the *cis*-series being penetratingly ammoniacal, whereas that of the *trans*-compounds resembles conine. The electrical conductivity is the same for each isomeride. When treated with nitrous acid the *cis*- and *trans*-amines pass into the corresponding *cis*- and *trans*-methylcyclohexanols (cf. this vol., 460).

[With HANS HÄUBER and WILHELM SCHARENBERG.]—The following individual substances are described: *cis*-Aceto-o-methylcyclohexylamide, b. p. 162—163°/18 mm., m. p. 82°, the corresponding meta-derivative, granular crystals, b. p. 156·5—157·5°/15 mm., m. p. 74—75°, and the para-compound, pointed needles, b. p. 160·5°/18 mm., m. p. 79°, *trans*-aceto-o-methylcyclohexylamide, b. p. 153—155°/17 mm., m. p. 57°, the corresponding meta-derivative, b. p. 159°/20 mm., m. p. 63°, and para-compound, b. p. 156—158°/17 mm., m. p. 68—69°. The acetyl derivatives are hydrolysed by concentrated hydrochloric acid at 130—140°, to the free amines of which the complete series is described as follows: *cis*-o-methylcyclohexylamine, b. p. 153·5—154·5° (corr.), d_4^{20} 0·8778, n_D^{20} 1·4688 (benzoyl derivative, m. p. 107°; phenylcarbamide compound, $C_{14}H_{20}ON_2$, m. p. 85°); *trans*-o-methylcyclohexylamine, b. p. 149·7—150·2° (corr.), d_4^{20} 0·8688, n_D^{20} 1·4650 (benzoyl derivative, m. p. 146°; phenylcarbamide compound, m. p. 130—131°); *cis*-m-methylcyclohexylamine, b. p. 152·7—153·4°, d_4^{20} 0·8552, n_D^{20} 1·4538 (benzoyl derivative, m. p. 98°; phenylcarbamide compound, m. p. 138·5°); *trans*-m-methylcyclohexylamine, b. p. 151·5—152·5° (corr.), d_4^{20} 0·8572, n_D^{20} 1·4547 (benzoyl derivative, m. p. 127°; phenylcarbamide compound, m. p. 178—179°); *cis*-p-methylcyclohexylamine, b. p. 153·3—153·7° (corr.), d_4^{20} 0·8567, n_D^{20} 1·4559 (benzoyl derivative, m. p. 116°; phenylcarbamide compound, m. p. 102°); *trans*-p-methylcyclohexylamine, b. p. 151·5—151·9° (corr.), d_4^{20} 0·8543, n_D^{20} 1·4550 (benzoyl derivative, m. p. 180°, phenylcarbamide compound, m. p. 176°).

The methylcyclohexylamines have also been prepared by the

reduction of the corresponding methylcyclohexanoneoximes, the *cis*-compounds being formed when the action is effected by sodium amalgam in the presence of alcohol and glacial acetic acid, and the *trans*-derivatives resulting when sodium amalgam and alcohol are used. The physical constants of the substances themselves and their derivatives agree with those of the compounds prepared as described in the preceding paragraph. The following derivatives are also described: *cis*-o-methylcyclohexylthiocarbimide, a pungent smelling liquid, b. p. 228—229°/769 mm., d_4^{20} 0.9680, n_D^{20} 1.5338, and *phenyl-cis*-o-methylcyclohexylthiocarbimide, $C_{14}H_{20}N_2S$, colourless leaflets, m. p. 114°: *trans*-o-methylcyclohexylthiocarbimide, b. p. 224—225°/770 mm., d_4^{20} 0.9620, n_D^{20} 1.5303, and the corresponding 3-phenylthiocarbimide, leaflets, m. p. 145°; *cis*-m-methylcyclohexylthiocarbimide, b. p. 226—227°, d_4^{20} 0.9479, n_D^{20} 1.5204, and the corresponding phenylthiocarbimide, m. p. 105—106°; *trans*-m-methylcyclohexylthiocarbimide, b. p. 224.5—225.5°, d_4^{20} 0.9487, n_D^{20} 1.5206, and the corresponding phenylthiocarbimide, m. p. 94—95°, after softening at 90°; *cis*-p-methylcyclohexylthiocarbimide, b. p. 227—228°/765 mm., d_4^{20} 0.9470, n_D^{20} 1.5208, and the corresponding phenylthiocarbimide, m. p. 149°; *trans*-p-methylcyclohexylthiocarbimide, b. p. 225.5—226.5°/765 mm., d_4^{20} 0.9450, n_D^{20} 1.5200, and the corresponding phenylthiocarbimide, m. p. 159°.

cis-p-Methylcyclohexylmethylamine, prepared by the action of an ethereal solution of methyl sulphate on *cis*-p-methylcyclohexylamine, has b. p. 157.5—158.5°/766 mm., d_4^{20} 0.8485, n_D^{20} 1.4529; its *picrate* has m. p. 179°. It is transformed by an ethereal solution of methyl iodide into *cis*-p-methylcyclohexyldimethylamine, b. p. 160—161°/767 mm., d_4^{20} 0.8355, n_D^{20} 1.4507 (*picrate*, yellow crystals, m. p. 181°). *trans*-p-Methylcyclohexylmethylamine has b. p. 154—155°/767 mm., d_4^{20} 0.8440, n_D^{20} 1.4522; it yields a *picrate*, m. p. 182.5°. *trans*-p-Methylcyclohexyldimethylamine has b. p. 156.5—157°/764 mm., d_4^{20} 0.8320, n_D^{20} 1.4494 (*picrate*, m. p. 184°). H. W.

Solubility of Tetranitroaniline in Organic Solvents. C. A. TAYLOR and W. H. RINKENBACH (*J. Amer. Chem. Soc.*, 1923, **45**, 1218—1220).—The solubility of tetranitroaniline has been determined in water, methyl alcohol, ethyl alcohol, diethyl ether, acetone, chloroform, carbon tetrachloride, carbon disulphide, and toluene at 0° and in benzene at 3.9°. The following solubilities in grams per 100 g. of solvent are recorded: water, 0.007; methyl alcohol, 0.45; ethyl alcohol, 0.34; diethyl ether, 0.081; acetone, 7.50; chloroform, 0.010; carbon tetrachloride, 0.0036; carbon disulphide, 0.0056; benzene (3.9°) 0.13; and toluene, 0.188. Attempts to determine the solubility at higher temperatures were unsuccessful, owing to the tendency of tetranitroaniline to decompose. The solubility is slightly lower than that of tetryl in the same solvents (this vol., i, 315, 320). J. F. S.

The Electrical Conductivity, Viscosity and Diagrams of State of the Systems formed by Benzoic Acid with Diphenylamine, the Naphthylamines and Quinoline. III. ALEXANDER BASILEVITSCH BASKOV (*J. Russ. Phys. Chem. Soc.*, 1920, **50**, 589—618; cf. A., 1913, ii, 1016; 1915, ii, 408).—The investigation of

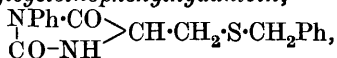
the above systems by the thermal method shows that benzoic acid does not form compounds with diphenylamine, or α - or β -naphthylamines, simple eutectics being obtained corresponding with about 8, 25, and 50 mol. % of benzoic acid, respectively. The system benzoic acid-quinoline shows a definite transition point corresponding with 23° and 50 mol. % of the components, whilst the eutectic point corresponds with -40° and 17 mol. % of benzoic acid.

The conductivity curves of the systems consisting of benzoic acid with the naphthylamines show breaks corresponding with 50 mol. % of acid, but these are due to the formation of naphthalides, which were isolated; the conductivity of the system benzoic acid-diphenylamine could not be measured at all.

The conductivity, viscosity, and density measurements on the system benzoic acid-quinoline point to the existence of a compound, but its composition corresponds with 66.6% of acid, not 50%; the same is true of the system benzoic acid-pyridine (cf. A., 1915, ii, 408). It is suggested that compounds of the type of acid salts may be formed at higher temperatures and serve as electrolytes; or the excess of benzoic acid may serve as a dielectric medium, although in that case it is difficult to understand why the point of maximum conductivity should correspond so exactly with a definite molecule complex.

G. A. R. K.

Some Derivatives of Cystine and Cysteine. GEORGE J. SHIPLE and CARL P. SHERWIN (*J. Biol. Chem.*, 1923, 55, 671—686).—The following derivatives have been prepared: *diphenylacetylcystine*, short rods or needles, m. p. $119-121^\circ$; *phenylacetylbenzylcysteine*, $\text{CH}_2\text{Ph}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CH}(\text{NH}\cdot\text{CO}\cdot\text{CH}_2\text{Ph})\cdot\text{CO}_2\text{H}$, bunches of long, fine needles, m. p. $87-89^\circ$; *phenylcarbamylbenzylcysteine*, $\text{CH}_2\text{Ph}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CH}(\text{NH}\cdot\text{CO}\cdot\text{NHPh})\cdot\text{CO}_2\text{H}$, feathery crystals, m. p. $145-146.5^\circ$; *benzylcysteinophenylthydantoin*,



fine needles, m. p. $118-119.5^\circ$, *acetylbenzylcysteine*, fine needles, m. p. $156-157^\circ$; *p-chlorobenzylcysteine*, m. p. $219-220^\circ$; *phenylcarbamylcysteine*, fine, short needles, m. p. $134-136^\circ$. E. S.

Picryl Sulphide. Study of the Binary System Trinitroanisole-Picryl Sulphide. CHAUMEL and V. THOMAS (*Compt. rend.*, 1923, 176, 1323—1325).—Thermal study of the binary mixture gave a normal curve which is shown diagrammatically. Certain abnormal results were also obtained in the case of mixtures containing more than 90% of trinitroanisole. On solidification, the rise of the thermometer occurred in two separate stages, but no intermediate maximum was detected. The authors put forward the hypothesis of formation of an unstable system which separates into trinitroanisole and the eutectic mixture at a temperature below that corresponding with the eutectic temperature of the stable system.

H. J. E.

Electrolytic Preparation of o-Aminophenol. Effect of Cathode Materials. O. W. BROWN and J. C. WARNER (*J. Physical Chem.*, 1923, 27, 455—465).—The electrolytic reduction

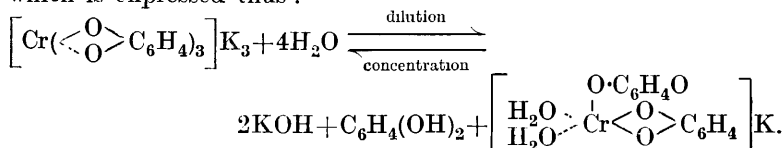
of *o*-nitrophenol in 15% sodium hydroxide solution has been investigated, using cathodes of various materials under a series of different conditions. It is shown that at low current densities (1—2 amps. per dm.²) copper, zinc, zinc amalgam, and nickel are the most efficient cathodes for this reduction. At current densities, from 4.0—10.0 amps. per dm.² lead cathodes give the highest yield (95.4%), whilst zinc and zinc amalgam give a little lower yield (about 93%). Except in the case of lead, increase in the current density causes a decrease in the yield, but in no case is the decrease greater than 15% for an increase from 1 amp. to 10 amps. Discharge potentials and depolarisation values are not criterions of the usefulness of a material as cathode in carrying out this reduction. The efficiency of a metal in the reduction of *o*-nitrophenol to *o*-aminophenol is generally reduced slightly by amalgamation. Since the factors on which the efficiency of a material as an electrode depends are many and variable, the best method of ascertaining what is the most suitable material for an electrode in any given reduction appears to be that of an experimental test under various conditions of temperature, current density, and concentration. J. F. S.

Acyl Derivatives of *o*-Aminophenol. R. E. NELSON and H. L. DAVIS (*Proc. Indiana Acad. Sci.*, 1921, 201—202; cf. Ransom, A., 1900, i, 218; Stieglitz and Upson, A., 1904, i, 575; Ransom and Nelson, A., 1914, i, 269; Raiford, A., 1920, i, 156).—When the groups COR- and CO·OR- are introduced into *o*-aminophenol, the latter group always becomes attached to the nitrogen atom, regardless of the order of introduction. If the group COR- is at first in that position, it is removed to the oxygen atom when the group CO·OR- is introduced. CHEMICAL ABSTRACTS.

Preparation of 2-Hydroxy-1-arylnaphthylamines. SOCIÉTÉ ANONYME DES MATIÈRES COLORANTES ET PRODUITS CHIMIQUES DE ST. DENIS, ANDRÉ RASUL WAHL, and ROBERT LANTZ (*Brit. Pat.* 182084).—2-Hydroxy-1-arylnaphthylamines are obtained by heating primary aromatic amines with α -chloro- or α -bromo- β -naphthols, either in presence or absence of a suitable solvent and with or without the addition of powdered zinc, tin, iron, lead, or copper, which accelerates the reaction but at the same time favours the formation of secondary products. Example: 1 part of α -chloro- β -naphthol is boiled for three to four hours with 5 parts of aniline, the excess of aniline is removed by steam distillation, the residue washed with dilute sodium hydroxide, the alkaline solution acidified, and the precipitated 2-hydroxy-1-phenylnaphthylamine, m. p. 153—154°, thus obtained purified by recrystallisation first from benzene, and then from a mixture of acetic and formic acids. 2-Hydroxy-1-*p*-tolyl-naphthylamine, similarly prepared, has m. p. 137—138°. G. F. M.

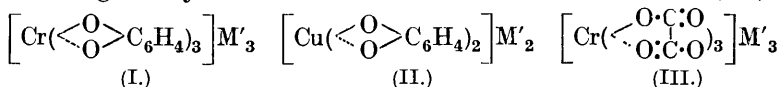
Compounds of Tervalent Chromium and of Bivalent Copper with Pyrocatechol. R. WEINLAND and EDMUND WALTER (*Z. anorg. Chem.*, 1923, 126, 141—166; cf. A., 1912, i, 184, 445, 850).—When excess of ammonia is added to a solution of pyrocatechol and green chromium chloride hexahydrate, the precipitate

of chromium hydroxide which first forms is dissolved to a dark green solution, owing to the formation of a complex ion containing pyrocatechol. Many salts of this type have been isolated. They are green, crystalline solids, with the exception of those containing pyridine, which are green with a tinge of yellow, and those containing the chloropentamminechromic complex, which exhibit reddish-green dichroism; they become dark coloured on exposure to the air. The alkali, barium, and guanidine salts are easily soluble in water, the barium-ammonium salt is less soluble, and the remainder are sparingly soluble. Dilution of the aqueous solution causes the green colour to change to Bordeaux red—a reversible reaction which is expressed thus :



Similar copper salts can be obtained which are olive-green in colour, except the basic sodium salt, which is yellowish-green.

The constitution assigned to these compounds (I, II) is similar to that given by Werner to the blue trioxalatochromic salts (III).



The following salts are described: Chromium salts $[\text{Cr}(\text{O} \cdot \text{C}_6\text{H}_4\text{O})_3] = \text{R}; \text{R}(\text{NH}_4)_3, \text{H}_2\text{O}; \text{R}(\text{NH}_4)_2 \cdot \text{H}; \text{R}(\text{NH}_4)_2 \cdot \text{H}, \text{H}_2\text{O}; \text{RK}_3, \text{H}_2\text{O}; \text{RH}_2\text{K}; \text{RNa}_3, 9\text{H}_2\text{O}; \text{RLi}_3, 9\text{H}_2\text{O}; \text{RMg} \cdot \text{NH}_4; \text{RKC}_2, 2\text{H}_2\text{O}; \text{R}_2\text{Sr}_3, 9\text{H}_2\text{O}; \text{R}_2\text{Ba}_3, 9\text{H}_2\text{O}; \text{R}(\text{NH}_4)\text{Ba}, 6\text{H}_2\text{O}; \text{RNaBa}, 6\text{H}_2\text{O}; \text{RKBa}, 6\text{H}_2\text{O}; \text{RMnK}; \text{RCoK}, 6\text{H}_2\text{O}; \text{R}[\text{Al}(\text{H}_2\text{O})_6]; \text{R}[\text{Cr}(\text{H}_2\text{O})_6];$

$$\text{R} \left[\begin{array}{c} (\text{NH}_3)_5 \\ \text{Cr} \quad \text{Cl} \\ \text{Na} \end{array} \right] 3\text{H}_2\text{O}; \quad \text{RK}(\text{HC}_5\text{H}_5\text{N})_2; \quad \text{RH}_3(\text{C}_5\text{H}_5\text{N})_3;$$

$$\text{RH}_3[\text{NH}:\text{C}(\text{NH}_2)_2].$$

Copper salts $[\text{Cu}(\text{O} \cdot \text{C}_6\text{H}_4\text{O})_2] = \text{R}'; \text{R}'(\text{NH}_4)_2, 2\text{H}_2\text{O}; \text{R}'(\text{NH}_4)_2; \text{R}'\text{Li}_2, 9\text{H}_2\text{O}; \text{R}'\text{K}_2, 2\text{H}_2\text{O}; \text{R}'\text{Na}_2, \text{NaOH}, 7\text{H}_2\text{O}; \text{R}'\text{Ba}; \text{R}'\text{Mn}, 4\text{H}_2\text{O}; \text{R}'\text{Co}, 4\text{H}_2\text{O}; \text{R}'\text{H}_2(\text{NH}:\text{C}[\text{NH}_2]_2)_2; \text{Cu}(\text{O} \cdot \text{C}_6\text{H}_4\text{O}), 2\text{H}_2\text{O}. \quad \text{H. H.}$

An Explosive (Lead Trinitroresorcinoxide). E. HERZ (U.S. Pat. 1443328).—*Lead trinitroresorcinoxide*, $\text{C}_6\text{H}(\text{NO}_2)_3 \cdot \text{O}_2\text{Pb}$, is prepared by adding a boiling solution of 650 g. of lead nitrate in 1.4 litres of water to a boiling solution of 245 g. of resorcinol and 290 g. of crystalline sodium carbonate in 12.8 litres of water and 77 c.c. of glacial acetic acid. It is a dark orange-coloured, granular, crystalline powder, *d* 3.09, and is a powerful explosive (cf. Brit. Pat. 187012/1921).

CHEMICAL ABSTRACTS.

A Verification of the Antioxygenising Power of Polyphenols: The Relation between "Fastness to Light" of Dyes on Fibres and the Presence in their Molecule of the (Ortho or Para) Diphenolic Function. ALFRED GILLET (*Compt. rend.*, 1923, 176, 1402—1405).—A study of the stability of dyes

towards atmospheric oxidation from the point of view of chemical constitution shows that it is apparently correlated with the existence in the molecule of an ortho- or para-dihydroxyphenol. This function is possibly analogous to the anti-oxygenising properties of the dihydroxyphenols described by Moreu and Dufraisse (this vol., i, 91), but in the dyes the replacement of hydroxyl by other groups such as $-N=NAr$, $-NHAr$, $-NHAc$, $-OAr$, $-SH$, $-SAr$, also results in stable substances. The author points out that, in addition to the view of such groups as auxochromes, they should also be considered in respect of their stabilising properties.

H. J. E.

Molecular Rearrangements accompanying the Dehydration of Phenylethyl- $\beta\beta$ -disubstituted Primary Alcohols. (MME)

PAULINE RAMART and J. BLONDEAU (*Compt. rend.*, 1923, **176**, 1320—1323; cf. Haller and Bauer, A., 1918, i, 428; Haller and Ramart, *Compt. rend.*, 1922, **174**, 1211).—Further study of the dehydration of disubstituted primary alcohols of the type $CR^1R^2Ph\cdot CH_2\cdot OH$ shows that in each case the principal substance produced is $CR^1R^2\cdot CHPh$. In addition to the migration of the phenyl group, a small proportion of the resulting product is formed by similar shifting of another substituting group to yield either $CR^1Ph\cdot CHR^2$ or $CR^2Ph\cdot CHR^1$. The alcohols investigated were β -phenyl- β -methyl- α -butanol, β -phenyl- β -ethyl- α -butanol, and β -benzoyl- β -phenyl- α -butanol.

H. J. E.

A New Series of Hypnotics: the Aryldialkylglycols.

M. TIFFENEAU and H. DORLENCOURT (*Compt. rend.*, 1923, **176**, 1343—1346; cf. A., 1907, i, 130).—The aryldialkylglycols exhibit hypnotic properties as shown by experiments on dogs, mice, and sticklebacks. These properties appear to be due to the glycol group, they are increased by the presence of the three substituents, and appear to vary with the number of carbon atoms in the molecule. The relative positions of the substituents also affect the results obtained.

H. J. E.

Retrograde Precipitation of Salts of Aromatic Acids.

A. SMITS (*Z. physikal. Chem.*, 1923, **104**, 481—486).—The author shows that the results obtained by Ephraim (this vol., i, 32), on the precipitation of salts of aromatic acids are readily explained on the basis of the theory of allotropy.

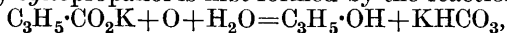
J. F. S.

***n*-Butyl *p*-Aminobenzoates.** R. ADAMS and E. H. VOLWILER

(U.S. Pat. 1440652).—*n*-Butyl *p*-nitrobenzoate, white plates, m. p. 35°, is prepared by reaction between *n*-butyl alcohol and *p*-nitrobenzoic acid in the presence of sulphuric acid. Reduction with iron and hydrochloric acid yields *n*-butyl *p*-aminobenzoate, m. p. 57—58·5°, which is a local anæsthetic. *n*-Butyl 3:5-dinitrobenzoate is similarly reduced to *n*-butyl 3:5-diaminobenzoate, a viscous liquid which does not solidify at the ordinary temperature (*monohydrochloride*, m. p. 255° [decomp.]).

CHEMICAL ABSTRACTS.

The Behaviour of Alkali Salts of *cyclo*Propanecarboxylic Acid at the Anode and the Thermal Decomposition of Perbutyric Acid. FR. FICHTER and HANS REEB (*Helv. Chim. Acta*, 1923, 6, 450—457).—When potassium *cyclo*propanecarboxylate is electrolysed using a platinum anode, preferably in presence of excess of *cyclo*propanecarboxylic acid, the allyl ester of *cyclo*propanecarboxylic acid is formed, together with a considerable quantity of high boiling, presumably polymerised products. Apparently *cyclo*propanol is first formed by the reaction



but this unstable alcohol isomerises to allyl alcohol which in presence of excess of the carboxylic acid forms the ester. For comparison with the product of electrolysis, allyl *cyclo*propanecarboxylate was prepared from silver *cyclo*propanecarboxylate and allyl chloride. It is a colourless, mobile oil of pleasant odour, b. p. 154—155°. It was accompanied by a high-boiling fraction similar to that obtained with the electrolytically prepared ester. The formation of *cyclo*propanol and subsequently of ester is to be attributed to the decomposition of per-acid formed at the anode. In confirmation of this, it is found that, by the thermal decomposition of perbutyric acid, propyl butyrate is formed, and among the decomposition products of a preparation of *cyclo*propaneper-carboxylic acid, allyl *cyclo*propanecarboxylate was recognised. E. H. R.

Hydroxynaphthoic Acids. I. FRANK ALBERT ROYLE and JACK ARNOLD SCHEDLER (T., 1923, 123, 1641—1647).

Abietic Acid. A. W. SCHORGER (*J. Amer. Chem. Soc.*, 1923, 45, 1339—1340).—Exception is taken to the view (Steele, A., 1922, i, 739) that the crystallisation of rosin is due to hydration, and that rosin consists of abietic anhydride (Knecht and Hibbert, A., 1919, i, 338), and has not been crystallised from anhydrous solvents, for the following reasons. The solvent previously employed (A., 1915, i, 431) was petroleum naphtha, dried over calcium chloride. From this solvent it is possible to crystallise rosin which has been (1) heated at 220—225° under 25 mm. for thirty minutes, or (2) distilled under reduced pressure in such a way that any water present would not be condensed. Moreover, rosin becomes opaque on the surface more rapidly when kept in water than when kept in sulphuric acid, whereas the hydration of an anhydride should proceed more rapidly in the presence of mineral acid. The loss of weight observed by Knecht and Hibbert when abietic acid is heated at 180° in an atmosphere of carbon dioxide has not been shown to be due entirely to loss of water. W. S. N.

Racemic *apo*Fenchocamphoric Acid. SERGEI SEMENOVITSCH NAMETKIN and (MLLE) ANNA MICHAILOVNA CHUCHRIKOVA (*J. Russ. Phys. Chem. Soc.*, 1917, 49, 426—428; cf. *ibid.*, 1915, 47, 433).—*cis-apo*Fenchocamphoric acid on treatment with acetyl chloride gives an *anhydride*, m. p. 136—137°, which on solution in alkali hydroxides and reprecipitation by acids regenerates the *cis*-acid; the *anilide*, m. p. 155—157°, and *dianilide*, m. p. 148—150°, were

also prepared, the former probably consisting of a mixture of the anilides of the *cis*- and *trans*-isomerides. *trans*-apo*Fenchocamphoric* acid, m. p. 147—148°, is prepared by the action of concentrated hydrochloric and acetic acids on the *cis*-isomeride, and does not form an anhydride with acetyl chloride. The *anilide*, m. p. 138—142°, also a mixture of isomerides, and the *dianilide*, m. p. 215—216°, were prepared. R. T.

Derivatives of cycloHexane-3 : 6-dione-1 : 2-dicarboxylic Acid. BURCKHARDT HELFERICH and HELLMUT GUSTAV BODENBENDER (*Ber.*, 1923, 56, [B]. 1112—1116; cf. A., 1921, i, 185).—Methyl *cyclohexane*-3 : 6-dione-1 : 2-dicarboxylate is converted by acetic anhydride in the presence of concentrated sulphuric acid into the corresponding *diacetate*, C₁₄H₁₆O₈, m. p. 87—88°. It gives a *dithallium* salt. Methyl 2-benzylcyclohexane-3 : 6-dione-1 : 2-dicarboxylate crystallises in short, thick prisms, m. p. 109° (corr.) after softening at 105°; it yields a *diphenylhydrazone*, C₂₉H₃₀O₄N₄, m. p. (indefinite) 75—80°.

cycloHexane-3 : 6-dione-1 : 2-dinitrile, CO<CH₂—CH₂>CO, crystallises in slender, colourless needles, m. p. 160—170° (decomp.) after darkening at about 100°. The *sodium* salt, C₈H₄O₂N₂Na₂, and the *thallium* salt, C₈H₄O₂N₂Tl₂, were analysed. The *semicarbazone*, C₁₀H₁₂O₂N₈, darkens at about 200°, but does not melt below 280°. With phenylhydrazine in acetic acid solution (80%), the dinitrile yields a *compound* (? *diphenylhydrazone*), C₂₀H₁₅N₈, a reddish-brown, amorphous precipitate, m. p. (indefinite) 226—232° after becoming discoloured at about 180°. The crystalline *diacetate*, C₁₂H₁₀O₄N₂, has m. p. 162° (corr.). *cycloHexane*-3 : 6-dione-1 : 2-dinitrile is converted by boiling dilute sulphuric acid into *cyclohexane*-1 : 4-dione and by diazomethane in ethereal solution into the *dimethyl ether*, OMe·C<C(CN)·C(CN)>C·OMe, m. p. 202° (corr.) after softening at 200°. The latter substance is converted by sulphuric acid into *cyclohexane*-1 : 4-dione and by aqueous potassium hydroxide solution into a mixture of 2 : 5-dimethylgentisic acid and succinic acid. H. W.

Bile Acids. IX. MARTIN SCHENCK (*Z. physiol. Chem.*, 1923, 128, 53—58).—α-Diketocholanic acid reacts with hydrazine to yield the *dioxime*, C₂₄H₃₈O₄N₂, decomp. 184—187°, forming characteristic double pyramids. When heated with sulphuric acid, this yields an isomeric *compound*, decomp. 196—197°, microscopic bundles of needles. From the *dioxime*, when heated with 25% hydrochloric acid, a *compound* is formed, m. p. 188—189°, insoluble in acid, whilst the isomeric *compound* yields no such *compound* insoluble in acid under similar conditions. W. O. K.

Preparation of Intermediate Products for Dyes. [4 : 4'-Dihydroxy-1 : 1'-ketodinaphthalene-3 : 3'-dicarboxylic Acid, and α-Naphthol-2 : 4-dicarboxylic Acid.] SOCIETY OF CHEMICAL INDUSTRY IN BASLE (Brit. Pat. 195513, addition to 172177).—In the preparation of trihydroxytrinaphthylmethane dyes

from α -naphthol- β -carboxylic acid and a tetrahalogen derivative of methane the above two substances are also formed as by-products. Their formation at the expense of the dye is favoured by increasing the proportion of carbon tetrachloride, using potassium hydroxide for neutralising the liberated hydrogen chloride, and carrying out the reaction in a highly diluted medium. The keto-acid can readily be separated from the naphtholdicarboxylic acid by taking advantage of the difference in solubility of the alkali and alkaline-earth salts of the two acids. Thus the mother-liquor from the dye separation may be acidified, the precipitate dissolved in sodium carbonate solution, and the disodium salt of the keto-acid precipitated by the addition of sodium chloride. The keto-acid itself is a white powder, which decomposes without melting at about 259° . The mother-liquor from the keto-acid separation is then acidified, and the precipitate extracted with boiling baryta water. Acidification of the extract causes the precipitation of α -naphthol-2 : 4-dicarboxylic acid, a whitish powder, decomp. about 286° .
G. F. M.

Substitution in Vicinal Trisubstituted Benzene Derivatives.

I. WILLIAM DAVIES (T., 1923, 123, 1575—1593).

The Isomeric Transformations of Cyclic 2-Monochloro-ketones. II. A. E. FAVORSKI and VADIM NIKOLAEVITSCH BOSHOVSKI (*J. Russ. Phys. Chem. Soc.*, 1920, 50, 582—588).—In the first part (A., 1915, i, 411) it was shown that 2-chlorocyclohexanone is converted by alcoholic potassium hydroxide into cyclopentanecarboxylic acid, 2-chloromethylcyclohexanone behaving in a similar manner. The reaction has now been extended to 2-chlorocyclopentanone and 2-chlorosuberone.

The former compound is readily obtained and boils at 80 — $81^{\circ}/17$ mm. (cf. Koetz, A., 1913, i, 1200; Godchot and Taboury, *ibid.*, 278), d_4^{20} 1.2061, d_4^{20} 1.1854 $[R_L]_D$ 28.08; it is significant that the action of alcoholic alkali on it leads to complete resinification, no trace of cyclobutanecarboxylic acid being obtained.

2-Chlorosuberone is obtained in 56% yield, b. p. 106 — $107^{\circ}/24$ mm. (cf. Koetz, *loc. cit.*), d_4^{20} 1.1513, d_4^{20} 1.1328, $[R_L]_D$ 37.18; a dichlorosuberone, m. p. 55 — 56° after crystallisation from light petroleum, is obtained as a by-product. By the action of alcoholic potassium hydroxide, a 50% yield of cyclohexanecarboxylic acid is obtained from the monochloro-ketone, m. p. 29.5 — 30.5° . A small amount of cyclohexan-2-olcarboxylic acid, m. p. 108 — 109° (A., 1913, i, 728), is also produced in this reaction. The formation of the hydroxy-acid is due to oxidation, as is shown by carrying out the reaction with 2-chlorocyclohexanone in the presence of copper sulphate, when cyclopentan-2-olcarboxylic acid is almost the sole product of the reaction. In the reaction with 2-chlorocyclohexanone (*loc. cit.*), a small amount of a neutral oil was produced. This is now shown to be ethyl cyclopentanecarboxylate, b. p. 172 — $174^{\circ}/752$ mm., and can be made the principal product of the reaction by avoiding excess of alkali; a little 2-cyclohexanolone,

m. p. 118—119°, and cyclopentan-2-olcarboxylic acid are also produced. G. A. R. K.

Dehydration of Secondary-Tertiary α -Alcohols; Derivatives of Hydrobenzoin. I. STEFAN NIKOLAEVITSCH DANILOV (*J. Russ. Phys. Chem. Soc.*, 1920, **51**, 97—128).—Some observations previously published (this vol., i, 579) are repeated, with some additions. Triphenylethanol on reduction with hydriodic acid undergoes molecular rearrangement, yielding $\alpha\beta$ -triphenylethane; with phosphorus pentachloride, triphenylchloroethylene is produced. R. T.

Allyldeoxybenzoin. S. N. DANILOV (*J. Russ. Phys. Chem. Soc.*, 1920, **51**, 128—132).—Allyldeoxybenzoin,
 $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{COPh}$,

is prepared by the action of allyl iodide on deoxybenzoin in the presence of sodium ethoxide. The product thus obtained is a mixture of two isomerides; one an oil, b. p. 178—179°/9—10 mm., d_4^{20} 1.0742, n_D^{20} 1.57989, and the other a solid, m. p. 35.5°, b. p. 178—179°/9—10 mm. Both give on oxidation β -benzoyl- β -phenylpropionic acid; on heating with alcoholic potash, they yield a mixture of hydrocarbons, containing stilbene and the three phenylbutenes. Two semicarbazones of allyldeoxybenzoin, m. p. 177—178° and 117.5°, are obtained, and two oximes, m. p. 140—141° and 127°, respectively. R. T.

Disubstituted Deoxybenzoins. I. S. N. DANILOV (*J. Russ. Phys. Chem. Soc.*, 1920, **51**, 133—138).—Two methods for the preparation of the hitherto unknown disubstituted deoxybenzoins are described. The first of these consists in heating phenyldeoxybenzoin with solid sodium hydroxide and ethyl iodide in a sealed tube. Better results are obtained by first forming the sodium salt of phenyldeoxybenzoin and then heating this with ethyl iodide in a sealed tube. By the former method, a 15% yield and by the latter method a 40% yield of *ethyldeoxybenzoin*, m. p. 120°, are obtained. Attempts at the preparation of the oxime and semicarbazone of this substance were unsuccessful. Reduction with sodium ethoxide yields α -hydroxy- $\alpha\beta$ -triphenylbutane. R. T.

The Chemistry of the Three-carbon System. I. The Influence of the cycloHexane Ring on the $\alpha\beta$ - $\beta\gamma$ -Change. STANLEY FRANCIS BIRCH, GEORGE ARMAND ROBERT KON, and WOODFORD STANLEY GOWAN PLUCKNETT NORRIS [with an Introductory Note by J. F. THORPE] (*T.*, 1923, **123**, 1361—1374).

The Action of Sodium on Diphenylacetic Ester. D. VORLÄNDER and EDGAR RACK (*Ber.*, 1923, **56**, [B], 1125—1129).—To explain the production of tetraphenylallene by the dry distillation of barium diphenylacetate, Vorländer and Siebert (*A.*, 1906, i, 345) have been led to presume the intermediate formation of the then unknown tetraphenylacetone [dibenzhydriyl ketone], $\text{CHPh}_2\cdot\text{CO}\cdot\text{CHPh}_2$. The substance, m. p. 134°, has now been

prepared by the action of sodium on diphenylacetic ester in the molten state or in ethereal solution. It is identical with the product obtained by Staudinger (A., 1911, i, 306) by the action of alkalis on diphenylketen. It can be distilled unchanged over phosphoric oxide, calcium oxide, or barium carbonate. It crystallises unchanged from acetic anhydride, thionyl chloride, or phosphoryl chloride and does not react readily with phosphorus pentachloride. It does not unite with bromine, neither does it exhibit the characteristic ketonic reactions with semicarbazide, phenylhydrazine, or hydroxylamine. When passed through a red hot tube, it gives a mixture of products containing some tetraphenylethane, m. p. 207°. When distilled with zinc dust, it gives diphenylmethane and other substances. It is oxidised by chromic acid in the presence of glacial acetic acid to benzophenone and carbon dioxide, by permanganate in acetone solution to benzophenone and a little benzoic acid, and by nitric acid in glacial acetic acid solution to diphenylacetic acid. Concentrated nitric and sulphuric acids convert it into a mixture of nitro-compounds, m. p. (indefinite) 140—145°. Zinc and acetic acid, sodium and ethyl or amyl alcohol, and boiling hydriodic acid are practically without action on it. Fuming hydriodic acid and red phosphorus at 200—210° convert it partly into diphenylmethane. It reacts with magnesium ethyl iodide or magnesium phenyl bromide, but the products have not been completely identified. Under the action of bromine in cold carbon tetrachloride solution in the presence of sunlight or arc light, it appears to yield a *monobromo*-derivative, $C_{27}H_{21}OBr$, m. p. about 78°.

It appears, therefore, impossible that dibenzhydryl ketone is an intermediate product in the transformation of barium diphenylacetate into tetraphenylallene.

H. W.

***as*-Benzylidenediphenylacetone [Benzhydryl Styryl Ketone].**

EDGAR RACK (*Ber.*, 1923, 56, [B], 1130—1131).—The substance closely resembles dibenzhydryl ketone in its extreme stability (cf. Vorländer and Rack, preceding abstract).

Benzhydryl styryl ketone, $CHPh:CH\cdot CO\cdot CHPh_2$, pale yellow, prismatic crystals, m. p. 102—103°, is prepared by the addition of aqueous potassium hydroxide solution to a mixture of benzhydryl methyl ketone and benzaldehyde dissolved in alcohol. The corresponding *dibromide* crystallises in colourless needles, m. p. 147—150°. It is transformed by magnesium phenyl bromide in ethereal solution into $\alpha\alpha\delta\delta$ -tetraphenylbutane- β -one, $CHPh_2\cdot CH_2\cdot CO\cdot CHPh_2$, colourless, prismatic crystals, m. p. 89—91°.

Benzhydryl p-methoxystyryl ketone forms pale yellow crystals, m. p. 130—131°.

H. W.

The Action of Sodium on $\beta\beta$ -Diphenylpropionic Ester.

D. VORLÄNDER, EDGAR RACK, and WALTER LEISTER (*Ber.*, 1923, 56, [B], 1131—1135).—Methyl $\beta\beta$ -diphenylpropionate, m. p. 48°, or ethyl $\beta\beta$ -diphenylpropionate, b. p. 183—185°/15 mm., is converted by sodium in the presence of anhydrous ether at the atmospheric temperature into a mixture of $\alpha\alpha\zeta\zeta$ -tetraphenylhexane- γ -ol-

b b*

δ -one, $\text{CHPh}_2\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CHPh}_2$, small, colourless prisms or needles, m. p. $147\text{--}148^\circ$, and $\alpha\alpha\zeta\zeta$ -tetraphenylhexane- $\gamma\delta$ -dione, $\text{CHPh}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CHPh}_2$, short, yellow prisms, m. p. $188\text{--}189^\circ$, which are separated from one another by taking advantage of their widely differing solubilities in alcohol. The hexanol is converted into the diketone by treatment with nitric acid ($d\ 1.4$) on the steam-bath, whereas the reverse transformation is effected with fuming, aqueous hydriodic acid and red phosphorus. The diketone is oxidised by chromic and acetic acids mainly to $\beta\beta$ -diphenylpropionic acid. The hexanecolone gives an *acetate*, colourless, lustrous needles, m. p. 93° , and an *oxime*, small, colourless needles, m. p. 169° . The hexanedione yields a *monoxime*, $\text{C}_{30}\text{H}_{27}\text{O}_2\text{N}$, colourless rodlets or needles, m. p. 162° after softening at 158° , a *dioxime*, $\text{C}_{30}\text{H}_{28}\text{O}_2\text{N}_2$, colourless, lustrous needles, m. p. $211\text{--}212^\circ$ (decomp.), and a *phenylosazone*, $\text{C}_{42}\text{H}_{38}\text{N}_4$, pale yellow needles, m. p. $198\text{--}203^\circ$. $\alpha\alpha\zeta\zeta$ -Tetraphenylhexane- γ -ol, colourless needles, m. p. $139\text{--}141^\circ$, is prepared by the reduction of the keto-alcohol or the diketone with sodium and boiling amyl alcohol. $\alpha\alpha\zeta\zeta$ -Tetraphenyl- n -hexane, colourless leaflets, m. p. $124\text{--}125^\circ$, is obtained from the keto-alcohol or the diketone by means of zinc dust and concentrated hydrochloric acid in the presence of acetic acid or from the keto-alcohol by the action of amalgamated zinc and concentrated hydrochloric acid. It could not be prepared by these methods from $\alpha\alpha\zeta\zeta$ -tetraphenylhexane- γ -ol.

The action of sodium on $\alpha\beta$ -diphenylpropionic ester does not yield a crystalline condensation product. H. W.

β -Phenylbenzylidenacetophenone [Phenyl Diphenylvinyl Ketone]. D. VORLÄNDER, JOHANNES OSTERBURG, and OTTO MEYE (*Ber.*, 1923, **56**, [B], 1136—1144).—The experiments were undertaken with the object of obtaining tetraphenylallene, $\text{CPh}_2\text{:C:CPh}_2$, from a ditertiary alcohol, $\text{OH}\cdot\text{CPh}_2\cdot\text{CH}_2\cdot\text{CPh}_2\cdot\text{OH}$. The action of magnesium phenyl bromide on an ethereal solution of dibenzoylmethane does not proceed beyond the stage which results in the formation of β -hydroxy- $\beta\beta$ -diphenylpropiophenone, $\text{OH}\cdot\text{CPh}_2\cdot\text{CH}_2\cdot\text{COPh}$, colourless prisms, m. p. 119° , which is also obtained from methyl or ethyl malonate and magnesium phenyl bromide even when a large excess of the latter is employed. It is converted by potassium hydroxide solution into a mixture of benzophenone and acetophenone and by aqueous hydrochloric acid into *phenyl diphenylvinyl ketone*, $\text{CPh}_2\text{:CH}\cdot\text{COPh}$, pale yellow prisms, m. p. 91° . The latter substance and several related compounds (tetraphenylpropylene, tetraphenylallene, etc.) exhibit the property of remaining viscous for weeks or months in the supercooled condition at the atmospheric temperature. They do not immediately solidify when seeded, although crystallisation can then be generally induced by a slight rise of temperature. It can also be caused by chemical agents. Thus the ketone remains as an oil when the solvent is removed from its ethereal solution, but crystallises if the ethereal solution is evaporated in contact with dilute sulphuric acid. Substances with unsymmetrical, branched

or angular molecules appear particularly prone to remain liquid in the undercooled state.

Hydroxydiphenylpropiophenone is converted by phenylhydrazine in acetic acid solution into a *substance*, $C_{27}H_{22}N_2$, lustrous, yellow leaflets, m. p. 222—223°; the compound is derived from phenyl diphenylvinyl ketone, and appears to be a tetraphenylpyrazoline. Phenyl diphenylvinyl ketone appears to be converted by hydroxylamine into a normal *oxime*, $C_{21}H_{17}ON$, colourless, transparent leaflets, m. p. 146°. With a molecular proportion of bromine in chloroform solution the ketone gives a *monobromo-derivative*, $CPh_2.CBr.COPh$, prismatic crystals, m. p. 168° after softening at 155°. Reduction of the ketone with zinc dust and glacial acetic acid yields the *pinacone* of diphenylpropiophenone, $C_{42}H_{38}O_2$, colourless needles, m. p. 192°. The ketone does not react readily with hydrogen chloride, hydrogen bromide, or picric acid under widely varied conditions; with a saturated solution of hydrogen bromide in glacial acetic acid at 100°, it gives a *bromide*, pale yellow needles, m. p. (indefinite) 135—137°, which is possibly not homogeneous. It reacts with ethyl malonate in the presence of sodium ethoxide, but the product of the action has not been fully investigated. It does not appear to react with concentrated sulphuric acid. Phenyl styryl ketone, on the other hand, combines with sulphuric acid in the presence of benzene, giving a *compound*, $C_{15}H_{12}O.2H_2SO_4$, whilst phenyl methoxystyryl ketone gives a similarly constituted *substance*, reddish-violet crystals.

Phenyl diphenylvinyl ketone is converted by magnesium phenyl bromide in the presence of ether into tetraphenylpropylene alcohol, which is smoothly transformed by boiling acetic anhydride into tetraphenylallene.

Benzylideneacetylacetone hydrochloride-*B* exhibits a pronounced tendency to the further addition of hydrogen chloride when it is very powerfully cooled. Benzylideneacetylacetone reacts in the usual manner with ethyl sodiomalonate, giving a monobasic acid, colourless crystals, m. p. 128—130°. Anisylideneacetylacetone readily yields a *hydrochloride*, $C_{13}H_{15}O_3Cl$, colourless, slender needles, m. p. 48—50°; benzylidenebenzoylacetone reacts with hydrogen chloride, but the product could not be isolated. Ethyl sodiomalonate and benzylidenebenzoylacetone give the monobasic acid, $C_{22}H_{20}O_5$, m. p. 54°. H. W.

The Action of Benzene and Aluminium Chloride on $\alpha\beta$ -Unsaturated Ketones and their Halogenated Derivatives. D. VORLÄNDER and ALEXANDER FRIEDBERG (*Ber.*, 1923, 56, [B], 1144—1150).—The action of benzene and aluminium chloride on a number of unsaturated diketones has been studied. The change appears to occur only with those compounds which unite readily with hydrogen chloride, and consists therefore in the substitution of the β -chlorine atom of the primarily formed hydrochloride by phenyl, and not in the addition of benzene at the $\alpha\beta$ -unsaturated linking.

Phenyl styryl ketone, benzene, and aluminium chloride give
bb*2

diphenylpropiophenone, m. p. 96° ; resinous products are also formed and a portion of the unsaturated ketone is decomposed with production of acetophenone. The side reactions can be largely avoided by using phenyl styryl ketone hydrochloride in place of the ketone, or by a preliminary saturation of the solution of the latter in benzene with hydrogen chloride. Under similar conditions, phenyl *p*-methoxystyryl ketone remains unchanged. On the other hand, phenylanisylidenepropiophenone, m. p. 90° , is obtained from magnesium phenyl bromide and anisylidenacetophenone, which therefore resembles closely phenyl styryl ketone in its behaviour towards this reagent. Phenyl styryl ketone dibromide, benzene, and aluminium chloride yield $\alpha\beta$ -triphenylpropiophenone, $\text{CHPh}_2\cdot\text{CHPh}\cdot\text{COPh}$, colourless needles, m. p. 182° , which is also obtained in a similar manner from bromodiphenylpropiophenone, m. p. 160 — 162° . Benzylidenementhone gives menthone and diphenylmethylmenthone, $\text{C}_{10}\text{H}_{17}\text{O}\cdot\text{CHPh}_2$, m. p. 157° .

$\beta\beta$ -Diphenylpropiophenone is converted by hydrogen chloride in the presence of benzaldehyde to $\beta\beta$ -diphenyl- α -benzylidenepropiophenone hydrochloride, $\text{CHPh}_2\cdot\text{CHBz}\cdot\text{CHPhCl}$, needles, m. p. 185° , from which the benzylidene group is removed by treatment with aluminium chloride and warm benzene.

The additive compound, $\text{C}_{21}\text{H}_{18}\text{O}_3\text{S}$, of phenyl styryl ketone and benzenesulphinic acid is obtained from its components in ethereal solution or when a solution of the ketone in benzene is saturated with sulphur dioxide and subsequently treated with aluminium chloride. If the latter reaction is prolonged the benzenesulphinyl residue is replaced by phenyl, thus yielding diphenylpropiophenone. Phenyl *p*-methoxystyryl ketone, benzene, sulphur dioxide, and aluminium chloride similarly yield the additive compound, $\text{C}_{22}\text{H}_{20}\text{O}_4\text{S}$, colourless crystals, m. p. about 177° (decomp.).

Distyryl ketone and benzenesulphinic acid give the product, $\text{C}_{23}\text{H}_{20}\text{O}_3\text{S}$, colourless needles, m. p. 168 — 170° , and 1:3-dibenzylidenecyclopentan-2-one gives the substance, $\text{C}_{25}\text{H}_{23}\text{O}_3\text{S}$, m. p. 155° ; in neither case could the ketone be caused to combine with more than one molecular proportion of benzenesulphinic acid. H. W.

The Additive Products of α -Unsaturated Ketones and Mercury Halides. D. VORLÄNDER and EGON EICHWALD (*Ber.*, 1923, 56, [B], 1150—1152).—The additive compound of phenyl styryl ketone and mercuric chloride, $\text{C}_{15}\text{H}_{12}\text{O}\cdot\text{HgCl}_2$, pale yellow needles, decomp. 92 — 93° , is obtained when a hot, concentrated solution of its components in alcohol is allowed to cool; it appears to have a limited ability to unite with hydrogen chloride. The compound from phenyl styryl ketone and mercuric bromide forms pale yellow, prismatic crystals, decomp. 88 — 90° . Phenyl *p*-methoxystyryl ketone mercuric chloride, $\text{C}_{16}\text{H}_{14}\text{O}_2\cdot\text{HgCl}_2$, crystallises in pale yellow needles, decomp. about 114° , whereas the corresponding compound with mercuric bromide, pale yellow needles, decomposes at 115 — 117° . Di-*p*-methoxystyryl ketone mercuric chloride, $\text{C}_{19}\text{H}_{18}\text{O}_3\cdot\text{HgCl}_2$, decomp. about 159° , is also described. H. W.

The Velocity of Addition of Hydrogen Chloride to α -Unsaturated Ketones. D. VORLÄNDER and EGON EICHWALD (*Ber.*, 1923, 56, [B], 1153—1156).—The rate of combination of hydrogen chloride and certain α -unsaturated diketones to form the so-called *B*-hydrochlorides has been measured in glacial acetic acid at 65°. Aliquot portions of the solution after definite intervals of time are poured into water and the combined acid in the precipitated mixture of ketone and ketone hydrochloride or the hydrochloric acid in the filtrate is estimated. Under suitable conditions, the additions take place in accordance with the law of mass action, and are catalytically accelerated by excess of hydrogen chloride. Since, however, the presence of the latter facilitates the dissociation of the additive compounds probably by altering the nature of the medium, the expected bimolecular course of the change has not been observed. In the presence of a large excess of hydrogen chloride, the reaction is of the first order. The velocity of addition of hydrogen chloride to phenyl styryl ketone dissolved in glacial acetic acid is eighteen times greater than that observed with anisylidenedibenzylketone, which exceeds that of benzylidenedeoxybenzoin.

In the case of acetophenone, the formation of a *B*-hydrochloride is facilitated by the introduction of a benzylidene residue, but hindered by an anisylidene group. In the case of dibenzyl ketone, on the other hand, the anisylidene derivative gives a very stable *B*-hydrochloride, whereas the benzylidene compound does not unite with hydrogen chloride to yield a *B*-salt. Conversely, the tendency to yield *A*-additive compounds preponderates in the case of the anisylidene derivative of acetophenone. It appears, therefore, that the readiness of formation of *A*-derivatives is paralleled by difficulty in the production of *B*-compounds and *vice versa*. H. W.

Benzopyrylium Salts of Distyryl Ketones. II. Salts and Metallic Complexes of 4'-Dimethylamino-2-styrylbenzopyrylium. JOHANNES SYBRANDT BUCK and ISIDOR MORRIS HEILBRON (*T.*, 1923, 123, 1395—1404).

The Mobility of Symmetrical Triad Systems. II. The Conditions Relating to Systems Terminated by the *o*-Phenylene Group. Derivatives of Indene. CHRISTOPHER KELK INGOLD and HENRY ALFRED PIGGOTT (*T.*, 1923, 123, 1469—1509).

A New Method of Preparing Dibenzoyl ethylene and Related Compounds. JAMES B. CONANT and ROBERT E. LUTZ (*J. Amer. Chem. Soc.*, 1923, 45, 1303—1307).—*trans*-Dibenzoyl ethylene is prepared in 74% yield by gradually adding fumaryl chloride to a suspension of aluminium chloride in benzene, and decomposing the product by means of ice. The use of toluene in place of benzene leads to the formation of *trans*-ditoluoyl ethylene, $C_6H_5(CO \cdot C_6H_4Me)_2$, pale yellow needles, m. p. 148°, yield 75%; this is converted into *cis*-ditoluoyl ethylene, colourless needles, m. p. 123°, by the action of sunlight in acetone solution, the reverse change being effected by the action of iodine in chloroform solution. Either isomeride is reduced to ditoluoyl ethane by means of sodium hyposulphite in hot alcoholic solution, or by means of zinc and acetic acid. *trans*-Di-*p*-chlorobenzoyl ethylene, pale yellow crystals, m. p. 172°, is

formed by the gradual addition of aluminium chloride to a mixture of fumaryl chloride, carbon disulphide, and chlorobenzene, the whole being subsequently heated at 45—50° for two and a half hours and decomposed by means of ice, yield 51%. *cis*-*Di*-*p*-chlorobenzoyl*ethylene*, slender, white needles, m. p. 102°, is formed from the *trans*-isomeride in chloroform solution by the action of sunlight; the *trans*-form is reproduced in the presence of iodine. *Di*-*p*-chlorobenzoyl*ethane*, colourless crystals, m. p. 151°, is obtained by the reduction of the *cis*- or *trans*-form of the ethylene derivative, by means of sodium hyposulphite, or of zinc dust and acetic acid. *trans*-*Di*-(2:4:6-*trimethylbenzoyl*)*ethylene*, pale yellow crystals, m. p. 174°, is produced in 75% yield from fumaryl chloride, aluminium chloride, mesitylene, and carbon disulphide; when an alcoholic solution containing a slight amount of undissolved substance is exposed to sunlight in a quartz vessel, incomplete conversion occurs to *cis*-*di*-2:4:6-*trimethylbenzoyl**ethylene*, colourless needles, m. p. 120°. Either the *cis*- or *trans*-isomeride is reduced to *di*-2:4:6-*trimethylbenzoyl**ethane*, colourless crystals, m. p. 138.5°. *Di*-*p*-methoxybenzoyl*ethylene* has been obtained as a pale yellow solid, m. p. 165.5°, from fumaryl chloride, aluminium chloride, carbon disulphide, and anisole. The yield is poor, and, so far, a colourless isomeride has not been prepared. W. S. N.

Quinonemethides [Methylenequinones] and Pseudophenolhalogenides. HANS LINDEMANN (*Annalen*, 1923, **431**, 270—300).—Although the pseudophenolhalogenides (*o*- or *p*-hydroxybenzyl halides) give acetates on treatment with acetyl chloride, they do not give salts by the action of alkali, but are converted into insoluble products. Zincke's explanation (*A.*, 1907, i, 322), that these compounds possess a semiquinonoid structure but are capable of reacting in the hydroxybenzenoid form, is insufficient, since an equilibrium between such forms would unquestionably be disturbed in the presence of alkali, with formation of the normal alkali salt. It is now suggested that actually a salt is first produced, but concurrently hydrogen halide is eliminated giving a quinonemethide (methylenequinone), which then undergoes polymerisation. The possibility of tautomerism is, of course, not excluded.

The existence of derivatives of methylenequinone, unsubstituted in the methylene group, has been questioned by Pummerer (*A.*, 1915, i, 417), dimeric formulæ being assigned to these compounds. Nevertheless, whilst the polymerides of methylenequinones, not substituted in the methylene group, are yellow and dimeric, those derived from methylene substituted quinonemethides are colourless, and nearly always trimeric. This difference is unexplained by means of Pummerer's formulæ. In order, therefore, to obtain further evidence on the subject, methylenequinones containing halogen in the methylene group have been prepared from the corresponding *p*-hydroxybenzylidene halides, and their reactions investigated.

The benzylidene halide is prepared by the action of phosphorus pentahalide in benzene solution on the relevant aldehyde, into which it is reconverted by means of hot glacial acetic acid, or of

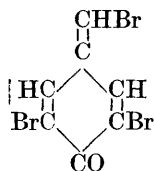
aqueous or alcoholic alkali. If the reaction with alkali is conducted in the cold, an unstable blue intermediate compound is formed; it is suggested that the change takes place through the quinone halogen methide. In prolonged contact with cold alcohol, or more rapidly in the boiling solution, the benzylidene halide is converted into the aldehyde. If, however, it is quickly dissolved in cold alcohol, or if an ethereal solution is shaken with aqueous sodium acetate, hydrogen halide is eliminated with formation of the quinonehalogenmethide, the reverse change being effected by means of hydrogen halide in glacial acetic acid solution. The action of hydrogen chloride on a quinonebromomethide gives a *p*-hydroxybenzylidenechloridebromide, from which hydrogen bromide, not hydrogen chloride, is eliminated by the action of alcohol or sodium acetate.

The quinonehalogenmethides described are unimolecular, but polymerise somewhat readily, particularly in hot benzene solution. Moreover, they exhibit no tendency to form ethane derivatives (cf. Fries and Kann, A., 1907, i, 613), but are converted with extraordinary ease by means of aqueous alkali, or even hydroxylic solvents, into the original hydroxyaldehydes. The dimeric structure is therefore excluded for these quinonehalogenmethides.

During the reaction with alkali, a blue coloration appears, which may be due to an intermediate compound containing bivalent carbon. This is most readily observed when gaseous ammonia is led into a benzene solution of the halogenmethide, or of the benzalhalide; a blue precipitate is formed, which gradually changes into the yellow benzalimine. The latter immediately passes into the aldehyde in contact with warm dilute acid. The same anil is formed by the action of aniline on the halogenmethide, the benzalhalide, or the original aldehyde.

The action of warm acetic anhydride and concentrated sulphuric acid on 3 : 5-dibromo-4-hydroxybenzaldehyde gives the *triacetate*, $\text{OAc} \cdot \text{C}_6\text{H}_2\text{Br}_2 \cdot \text{CH}(\text{OAc})_2$ (1), m. p. 125°, which is converted by boiling with dilute hydrochloric acid and acetic acid into the *monoacetate*, $\text{OAc} \cdot \text{C}_6\text{H}_2\text{Br}_2 \cdot \text{CHO}$, m. p. 112°. The solid *sodium* salt of the aldehyde reacts at 100° with dimethyl sulphate, giving 3 : 5-dibromo-4-methoxybenzaldehyde, white needles, m. p. 82–86°; the latter is converted by warming with phosphorus pentabromide into 3 : 5-dibromo-4-methoxybenzylidene bromide, large, white leaflets, m. p. 60–64°. Incidentally, anisaldehyde is converted by treatment with bromine in glacial acetic acid solution into 3 : 5-dibromo-4-methoxybenzoic acid. The following compounds, the reactions of which are described above, have been obtained.

3 : 5-Dibromo-4-hydroxybenzylidene bromide, white needles, m. p. 98–101·5°, and its *acetate*, m. p. 80°. 3 : 5-Dibromo-quinonebromomethide (annexed formula), small, yellow needles, m. p. 120°. 3 : 5-Dibromo-4-hydroxybenzylidene chloride bromide, $\text{OH} \cdot \text{C}_6\text{H}_2\text{Br}_2 \cdot \text{CHClBr}$, white needles, m. p. 70–74°. 3 : 5-Dibromo-4-hydroxybenzylideneaniline, large, orange prisms, m. p. 150–152°. Unstable, yellow *imine* of 3 : 5-dibromo-4-hydroxybenzaldehyde. 2-Hydroxy-4 : 6-dimethylbenzaldehyde, large,



colourless, vitreous needles, m. p. 48° , is obtained as a by-product in the preparation of 4-hydroxy-2:6-dimethylbenzaldehyde by the action of hydrogen cyanide on xylol in the presence of aluminium chloride. It is volatile in steam and gives a *phenylhydrazone*, m. p. 127° . 3:5-Dibromo-4-hydroxy-2:6-dimethylbenzaldehyde, long, white needles, m. p. 181° , is obtained by the bromination of 4-hydroxy-2:6-dimethylbenzaldehyde in glacial acetic acid solution. It gives an *acetate*, large, white leaflets, m. p. 149° , and a *triacetate*, white needles, m. p. 114° . 3:5-Dibromo-4-hydroxy-2:6-dimethylbenzylidene bromide, long, white needles, m. p. 154° , its *acetate*, white prisms, m. p. 152° , and its *anil*, white prisms, m. p. 212° . 3:5-Dibromo-2:6-dimethylquinonebromomethide, m. p. 200° (indefinite). 3:5-Dibromo-4-hydroxy-2:6-dimethylbenzylidene chloride, white needles, m. p. 153° , does not depress the melting point of the corresponding bromide. 3:5-Dibromo-2:6-dimethylquinonechloromethide, pale yellow needles, m. p. 132° . 3:5-Dibromo-4-hydroxy-2:6-dimethylbenzylidene chloride bromide, white needles, m. p. 151° , does not depress the melting point of the bromide or chloride, and gives an *acetate*, m. p. 138° .

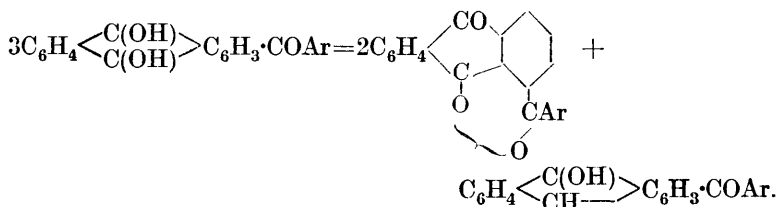
The author describes an apparatus (cf. Ziegler, A., 1921, i, 165) by means of which one litre of anhydrous hydrocyanic acid may be prepared in one hour.

W. S. N.

Derivatives of β -Methylanthraquinone. II. The Synthesis of Chrysophanic Acid. [1:8-Dihydroxy-3-methylanthraquinone.] R. EDER and C. WIDMER (*Helv. Chim. Acta*, 1923, 6, 419—424; cf. A., 1922, i, 260).—The condensation of α -nitrophthalic acid with *m*-cresol in presence of aluminium chloride is much improved if a large excess of *m*-cresol is used instead of an indifferent solvent, and if the use of any alkali is avoided a 40% yield of 3-nitro-*o*-3'-hydroxy-*p*-toluoylbenzoic acid is obtained. Under the same conditions but using α -nitrophthalic anhydride, the yield of the same product is practically theoretical. In a similar manner, α -acetylaminophthalic anhydride can be condensed with *m*-cresol to give 3-amino-*o*-3'-hydroxy-*p*-toluoylbenzoic acid, and α -hydroxyphthalic anhydride with *m*-cresol to give 3-hydroxy-*o*-3'-hydroxy-*p*-toluoylbenzoic acid; the yields are, however, comparatively poor. The above 3-amino-*o*-3'-hydroxy-*p*-toluoylbenzoic acid, when heated at 150° with concentrated sulphuric acid, is converted into 8-amino-1-hydroxy-3-methylanthraquinone, lustrous, bronze needles, m. p. 245 — 246° . In boiling sodium hydroxide solution, it is sparingly soluble with a reddish-violet colour, and in concentrated sulphuric acid it dissolves with an orange-yellow colour. From a mixture of pyridine and water, it crystallises in violet-black needles containing pyridine. By diazotising in concentrated sulphuric acid and subsequent heating, it can be converted into chrysophanic acid. When 6-amino-*o*-3'-hydroxy-*p*-toluoylbenzoic acid is heated in sulphuric acid it forms 5-amino-1-hydroxy-3-methylanthraquinone, bronze needles, m. p. 248 — 249° , which can also be diazotised and converted into the previously described 1:5-dihydroxy-3-methylanthraquinone.

E. H. R.

A New Class of Free Organic Radicles. III. ROLAND SCHOLL and HERBERT HÄHLE (*Ber.*, 1923, **56**, [B], 1065—1075; cf. A., 1921, i, 872; this vol., i, 584).—The only method of preparative importance for the production of the benzoyloxanthronyls has consisted hitherto in the reduction of 1-benzoylanthraquinones with metallic powders in the presence of concentrated sulphuric acid. This process, however, only leads readily to the isolation of homogeneous substances when the sulphates are insoluble or sparingly soluble in cold concentrated sulphuric acid. An alternative method is now described in which the 1-benzoylanthraquinones are reduced to the corresponding quinols, and the latter are converted by dehydrogenation and disproportioning into the required compounds in accordance with the scheme :



p-Chlorobenzoylanthraquinone is reduced by zinc dust and glacial acetic acid to *p*-chlorobenzoylanthraquinol under conditions which are very exactly described in the original, and the reddish-brown solution is poured into boiling concentrated hydrochloric acid which contains sodium chloride and a little potassium dichromate. A vigorous action is observed whereby the green oxonium chloride is produced. The mixture is poured into ammonia and the precipitated *p*-chlorobenzoyloxanthronyl is crystallised from acetic anhydride containing a little sodium acetate.

Protracted treatment with boiling acids causes the disproportioning of the benzoyloxanthronyls to benzoylanthraquinones and, probably, arylanthraquinonylcarbinols, $\text{C}_6\text{H}_4\begin{matrix} \text{CO} \\ \text{CO} \end{matrix} > \text{C}_6\text{H}_3\cdot\text{CHAr}\cdot\text{OH}$.

The photochemical disproportioning of *p*-chlorobenzoyloxanthronyl dissolved in nitrobenzene has been investigated further by titration with bromine solution. The change occurs very slowly at the atmospheric temperature in darkness, somewhat more rapidly in diffused daylight, and completely in about one and three-quarter hours in direct sunlight. In boiling solution, the change takes place fairly readily in diffused daylight.

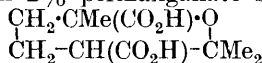
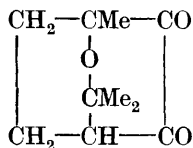
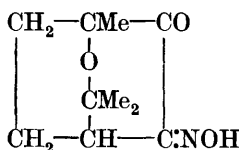
The disproportioning of the benzoyloxanthronyls by acids, alkalis, or phosphorus trichloride is described; the course of the changes has not yet been elucidated definitely. H. W.

Ketocineole. V. GUIDO CUSMANO (*Gazzetta*, 1923, **53**, i, 195—200; cf. A., 1919, i, 212, 213; 1920, i, 346).—In spite of its relationship to ketoterpin, ketocineole exhibits the chemical behaviour, not of the monocyclic, but of the bicyclic, terpenic ketones, especially of camphor. It is now found that the α -carbonylic

derivative of ketocineole, to which the name diketocineole is given, is a yellow compound behaving solely as a diketone and is hence closely analogous to camphorquinone.

Oximinoketocineole (annexed formula), prepared by the action of ethyl nitrite on ketocineole in presence of sodium or, better, of hydrochloric acid, forms large crystals (+H₂O), m. p. about 90° or (anhydrous) 132°. When treated with phenylhydrazine, it yields *diketocineole oxime phenylhydrazone*, C₁₆H₂₁ON₃, which forms pale yellow crystals, m. p. 186°. *Diketocineole dioxime*, C₁₀H₁₆O₃N₂, separates in minute crystals, m. p. 195° (decomp.), and, when dissolved in ether containing nitrous fumes gives, not the diketone, but the *anhydride* of the dioxime or *furazan*, C₁₀H₁₄O₂N₂, which forms lozenge-shaped crystals, m. p. 89°.

Diketocineole (annexed formula), obtained by heating oximinoketocineole in acetic acid solution with sodium hydrogen sulphite and decomposing the resulting compound with dilute hydrochloric or sulphuric acid, forms colourless crystals (+H₂O) with a rhombic base and becomes yellow and volatile when dehydrated in a vacuum over sulphuric acid. It reduces neither Fehling's solution nor ammoniacal silver nitrate solution, and gives no coloration with ferric chloride. When oxidised with 2% permanganate solution, it gives a good yield of cineolic acid,



T. H. P.

Homologues of Camphor. II. β -Methylcamphene and β -Methylcamphenilone. S. S. NAMETKIN (*J. Russ. Phys. Chem. Soc.*, 1920, **51**, 139—144).—6-Methylisoborneol (cf. this vol., i, 586) when heated with potassium hydrogen sulphate, loses water, yielding α - and β -methylcamphenes, principally the latter. β -Methylcamphene, b. p. 170—170.5°/760 mm., m. p. 98—100°, when warmed with glacial acetic acid yields acetyl-6-methylisoborneol, which on hydrolysis gives the corresponding alcohol. β -Methylcamphene, on treatment with oxides of nitrogen and subsequent warming with alcoholic potash, yields β -methylcamphenilone, m. p. 141—142°, the *semicarbazone*, m. p. 231—232° (decomposition), of which is prepared. The action of sodamide on β -methylcamphenilone is to yield the *amide* of β -methylcamphenylic acid, C₁₀H₁₉ON, m. p. 124—125°.

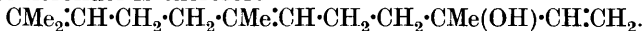
R. T.

Homologues of Camphor. III. Tertiary Methylbornyl Alcohol and its Dehydration. S. S. NAMETKIN and M. A. SCHLESINGER (*J. Russ. Phys. Chem. Soc.*, 1920, **51**, 144—147; cf. preceding abstract).—Tertiary methylbornyl alcohol easily loses water, yielding, not methylfenchene, as might be expected, but α -methylcamphene, which was previously obtained by the dehydration of tertiary methylisobornyl alcohol.

R. T.

The Conversion of Carvone into Carvacrol. FRIEDRICH RICHTER (*Chem. Ztg.*, 1923, 47, 489).—*d*-Carvone was heated for five hours at 205° and, after cooling, the carvacrol estimated by extraction with 5% potassium hydroxide. The quantity of carvacrol formed was inappreciable. This observation is in agreement with that of Baeyer (A., 1894, i, 297), who found that carvone remains unchanged when boiled for one hour, whilst eucarvone, under similar conditions, undergoes complete transformation, and contrary to that of Dormaar (A., 1905, i, 222), according to whom carvone, when heated at 205° for five hours, undergoes 36% transformation and eucarvone only 21%. W. T. K. B.

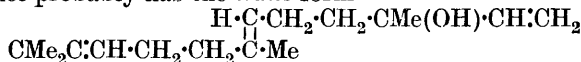
Higher Terpene Compounds. VIII. The Constitution of Nerolidol (Peruviol). L. RUZICKA (*Helv. Chim. Acta*, 1923, 6, 483—492).—A comparison of the physical and chemical properties of the aliphatic sesquiterpene derivatives farnesol and nerolidol, on the one hand, with those of geraniol and linalool, on the other, suggests that nerolidol bears the same relation to farnesol as linalool does to geraniol. The hydroxyl group of geraniol and farnesol is far more reactive than that of linalool and nerolidol. These considerations suggest that nerolidol, like linalool, is a tertiary alcohol, and its molecular refraction indicates the presence of three double bonds, but not of conjugated double bonds. The probable constitution of nerolidol is therefore



In confirmation of this reasoning, it is found that nerolidol is oxidised by chromic acid to farnisal, just as linalool is oxidised to citral, and by the action of acetic anhydride on nerolidol it is converted into farnesol, just as linalool is converted into geraniol. The hydrolysed product of the action of acetic anhydride on nerolidol gave on distillation three fractions. The first fraction consisted principally of sesquiterpenes, a considerable proportion of which consisted of farnesene; the second consisted of unaltered nerolidol, and the third contained the farnesol, which was identified by its semicarbazone [cf. *J.S.C.I.*, 1923, July]. E. H. R.

Higher Terpene Compounds. IX. The Complete Synthesis of *dl*-Nerolidol and Farnesol. L. RUZICKA (*Helv. Chim. Acta*, 1923, 6, 492—502; cf. preceding abstract).—The synthesis of *dl*-nerolidol was accomplished in the following manner. $\alpha\beta$ -Dihydro- ψ -jonone, $\text{CMe}_2\text{:CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe}\text{:CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COMe}$, was condensed with acetylene and sodamide, giving in almost quantitative yield *homogeranylmethylcarbinol*, or *dehydro-dl-nerolidol*, $\text{CMe}_2\text{:CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe}\text{:CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe(OH)}\cdot\text{C}\text{:CH}$. This is a colourless oil with a faint odour, b. p. 146—147°/12 mm., d_4^{20} 0.8908, n_D^{20} 1.4789. Its phenylurethane could not be crystallised. By reduction with sodium in ether solution, this gave *dl-nerolidol*, a colourless oil with a pleasant odour, b. p. 145—146°/12 mm., 98—100°/0.3 mm., d_4^{16} 0.8788, n_D^{16} 1.4801. This did not give a crystalline phenyl- or naphthyl-urethane. It was identified by conversion by acetic anhydride into farnesol (cf. preceding abstract). A *cis*- and *trans*-form of nerolidol is possible, and four stereoisomeric

forms of farnesol. Whilst the densities of natural and synthetic nerolidols are the same, farnesols of different origins differ considerably. If, as has been suggested, geraniol is a *trans*-form, then since the above synthesis starts from geraniol, the synthetic *dl*-nerolidol probably has the *trans*-form



and the farnesol prepared from it has either a *trans-cis*- or a *trans-trans*-form, or is more probably a mixture of the two, just as a mixture of geraniol and nerol is formed by the action of acetic anhydride on linalool.

When farnesol is heated at 170° and 12 mm. with potassium hydrogen sulphate, a sesquiterpene distills over, b. p. 128—130°/12 mm., d_4^{18} 0.8385, n_D^{18} 1.4965, which from its molecular refraction is taken to be farnesene. Its constants agree with those of the aliphatic sesquiterpene found by Semmler and Spornitz in Java citronella oil (A., 1914, i, 193). When this farnesene is heated at 140° with 90% formic acid it is converted into a monocyclic sesquiterpene, b. p. 126—128°/12 mm., d_4^{16} 0.8776, n_D^{16} 1.4961. It appears to be the same product as that obtained from nerolidol in the same manner.

Geranyl chloride can be obtained by the action of phosphorus pentachloride on geraniol in light petroleum, but is best prepared on a large scale with phosphorus trichloride by the method of Tiemann and Schmidt (A., 1896, i, 382). E. H. R.

Pinane. S. S. NAMETKIN (*J. Russ. Phys. Chem. Soc.*, 1920, **51**, 147—151).—Pinene on reduction by the Sabatier-Senderens process (Zielinski, *Ber.*, 1911, **44**, 2782) gave a mixture of hydrocarbons not possessing the pinene structure, principally *isobornylane*. This work is repeated at a lower temperature (155—158° instead of 180°), when a product, b. p. 155—156°, d_4^{20} 0.8606, n_{20} 1.4669, $[\alpha]_D$ —42.38°, is obtained, which is probably *pinane*, $\text{C}_{10}\text{H}_{18}$, as its refractive index corresponds with the presence of the pinene ring. It does not react with nitric acid, d 1.4, even on warming; with bromine it slowly evolves hydrogen bromide. *Nitropinane*, $\text{C}_{10}\text{H}_{17}\text{NO}_2$, b. p. 134—135°/23 mm., d_4^{20} 1.0416, n_{20} 1.4814, was prepared and appears also to possess the pinene structure. R. T.

Fenchylene. II. S. S. NAMETKIN and (MLLE) A. K. RUSHENCEVA (*J. Russ. Phys. Chem. Soc.*, 1920, **51**, 152—156; cf. *ibid.*, 1916, **48**, 450).—Two *amides* of xanthylisofenchyl alcohol, $\text{C}_{10}\text{H}_{17}\text{O} \cdot \text{C} \cdot \text{S} \cdot \text{NH}_2$, one m. p. 69—70°, d_4^{15} 0.8134, $[\alpha]_D$ —37.77°, and the other an oil, are obtained by the action of 10% ammonia on the corresponding methyl or ethyl esters. The solid amide gives on hydrolysis pure *isofenchyl alcohol*, m. p. 60—61°, $[\alpha]_D$ —27.04° in alcoholic solution, d_4^{15} 0.8037; both amides on heating at 180° yield fenchylene; that from the crystalline amide has b. p. 140—141°/740 mm., d_4^{20} 0.8397, n_{20} 1.4502, $[\alpha]_D$ —57.28°, the *nitrosylchloride*, m. p. 131°, of which yields fenchylcamphoric acid on oxidation. The fenchylene obtained from the liquid amide has

b. p. 140.5—141°/760 mm., d_4^{20} 0.8398, n_{20} 1.4505, $[\alpha]_D - 50.98^\circ$, and is probably contaminated with *cyclofenchene*. R. T.

Constituents of some Indian Essential Oils. VIII. The Essential Oil from the Gum-oleo-resin of *Boswellia serrata* (Roxb.). JOHN LIONEL SIMONSEN (*Indian For. Rec.*, 1923, 9, 289—306).—This oil does not consist of *d*- α -pinene and β -pinene as stated by Pearson and Puran Singh (*Indian For. Rec.*, 1918, 6, 303), but is mainly *d*- α -thujene, containing a little α -pinene and probably a little *d*- α -phellandrene, but no β -pinene. The thujene was characterised by conversion into *d*- α -thujaketonic acid [mixed with *l*- α -thujaketonic acid, identified as the semicarbazone, m. p. 197° (cf. Thomson, T., 1910, 97, 1511)], *l*- α -thujadicarboxylic acid, β -thujaketonic acid (oxime, m. p. 111—112° [cf. Wallach, A., 1893, i, 105]; semicarbazone, m. p. 195—196° [cf. Seyler, A., 1902, i, 229]) and β -thujadicarboxylic acid.

The purified *d*- α -thujene had b. p. 152—152.5°/699 mm., d_{20}^{20} 0.8314, n_D^{30} 1.4502, and $[\alpha]_D^{30} + 37.69^\circ$ (after two months, $[\alpha]_D^{30} + 37.13^\circ$ [cf. Fowler and Malandkar, *J. Ind. Inst. Sci.*, IV, 27]). E. E. T.

The Essential Oils of Two Species of *Homoranthus* and the Occurrence of Ocimene. A. R. PENFOLD (*Perf. Essent. Oil Rec.*, 1923, 14, 145—148).—*Homoranthus virgatus*, a slender, upright shrub growing in New South Wales and Queensland, contains an average of 0.7% of essential oil, having the following characters: d_{15}^{15} 0.8660, $\alpha + 28^\circ$, n_D^{20} 1.4743, saponification value 6.16 before, and 27.65 after acetylation. It contains about 80% of *d*- α -pinene, and the remainder consists of a sesquiterpene, b. p. 129—132°/10 mm., d_{15}^{15} 0.9171, n_D^{20} 1.5049, together with small amounts of amyl alcohol, isovaleraldehyde, and a paraffin, m. p. 65—66°. The essential oil of *H. flavescens*, on the other hand, contains about 80% of the olefinic terpene ocimene, together with *d*- α -pinene, sesquiterpene, and the minor constituents mentioned above. The oil has the following characters: d_{15}^{15} 0.8429, $\alpha - 1.75^\circ$, n_D^{20} 1.4836, saponification value after acetylation 51—85. The high alcohol and ester numbers are not due to the presence of actual ester and alcohol, but to some resinous substances which appear to increase in amount soon after the distillation of the oil. G. F. M.

Aggregation and Disaggregation. Hydrolysis of Shellac Resin. Hydrogenation of Caoutchouc. C. HARRIES (*Ber.*, 1923, 56, [B], 1048—1051).—The terms “polymerisation” and “depolymerisation” are frequently applied to alterations in the state of aggregation of colloids. Since, however, these expressions have a definite meaning in organic chemistry and denote a type of change which is probably not identical with that observed in the case of colloids, it is proposed that they should be replaced in connexion with the latter by the terms “aggregation” and “disaggregation.”

In a recent communication, Harries and Nagel (this vol., i, 120) have described two forms of purified shellac resin one of which is soluble in alcohol and readily hydrolysed, whereas the other is

insoluble in alcohol and only hydrolysed with great difficulty. The products, however, appear to be structurally identical and differentiated only by difference in the state of aggregation. The unreactive can be transformed into the active variety by solution in glacial acetic or, preferably, formic acid and reprecipitation by water, whilst the reverse change can be effected by treatment with ether containing a little hydrogen chloride. It is supposed that the inability of one product to enter into chemical change is due to the mechanical arrangement of the particles in such a manner that an inadequate point of attack is offered to a reagent.

Many unsuccessful attempts have been made to hydrogenate caoutchouc catalytically and this has been effected by Pummerer and Burkard (this vol., i, 49) and by the author by the use of highly purified material in very dilute solution. If, however, crude caoutchouc is first rendered highly plastic mechanically, it can be subsequently hydrogenated to perhydrocaoutchouc at the atmospheric temperature in the presence of light petroleum under a pressure of a few atmospheres. The product behaves as saturated towards bromine; it becomes decomposed at 220—230°. It appears, therefore, that the ability of caoutchouc to unite with hydrogen depends directly on its degree of dispersion or aggregation.

It is suggested that the vulcanisation of rubber is due to a displacement of the aggregation. H. W.

Rutin, Sophorin, and the Sugar which they yield on Hydrolysis. H. TER MEULEN (*Rec. trav. chim.*, 1923, **42**, 380—386).—Rutin, prepared from the dried leaves of *Ruta graveolens*, was hydrolysed in glycerol solution by a solution of rhamninase obtained from *Rhamnus infectoria*, the results, as shown by a series of control experiments, indicating that the sugar of the glucoside is rhamninose. Evidence is adduced, based on the work of Wachs (A., 1894, i, 299), of Zwenger and Dronke (*Annalen*, 1862, **123**, 145), and of the present author, to show that sophorin and rutin are identical, the formula being $C_{33}H_{42}O_{20} \cdot 4H_2O$. Attempts to obtain crystalline rhamninose from the glucoside were unsuccessful. No enzyme present in *Ruta graveolens* or *Sophora japonica* hydrolyses rutin, but seeds of *Rhamnus cathartica* contain a substance which may be used as a substitute for rhamninase. H. J. E.

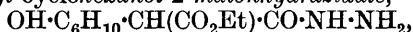
Synthesis of *m*-Nitrotolyl-glucoside and the Disinfecting Value of *m*-Nitrocresol. E. GLASER and H. PRÜFER (*Biochem. Z.*, 1923, **137**, 429—438).—3-Nitro-*p*-tolylglucoside tetra-acetate was prepared from 3-nitro-*p*-cresol and β -acetobromoglucose. It melts at 201—203° and has $[\alpha]_D +26.8^\circ$ in chloroform. It was hydrolysed in methyl-alcoholic solution by dry ammonia. 3-Nitro-*p*-tolylglucoside melts at 128—129°, and has $[\alpha]_D -77.5^\circ$ in water. Emulsin effects partial hydrolysis. 3-Nitro-*p*-cresol is six times as powerful a disinfectant as phenol when tested on *Staphylococcus pyogenes citreus*. The glucoside has no disinfectant action in vitro, but is readily hydrolysed by *Staphylococcus*, the dextrose acting as a growth promoter. H. K.

The Constitution of Cantharidin. SAMUEL COFFEY (*Rec. trav. chim.*, 1923, **42**, 387—436; cf. Gadamer, A., 1915, i, 432).—A consideration of Gadamer's review of the subject (A., 1914, i, 707) together with work subsequently published (Auwers, A., 1913, i, 1319; Danckwort, A., 1915, i, 432, 433; Gadamer, A., 1915, i, 432; 1917, i, 659, 704; 1920, i, 859; Haworth, T., 1913, **103**, 1242; Rudolf, A., 1917, i, 468) leads to the general conclusion that one of the three formulæ considered possible by Gadamer for cantharidin is correct, although there appears to be insufficient evidence for accepting any particular formula in preference to the other two. An attempt was therefore made to prepare synthetically the three substances which, according to deductions from Gadamer's three formulæ, are the three possible deoxycantharidins viz., (a) *ciscyclohexane*-1 : 2-diacetic anhydride, (b) *cis*-1 : 2-dimethyl*cyclohexane*-4 : 5-dicarboxylic anhydride, (c) *cis*-1 : 2-dimethyl*cyclohexane*-1 : 2-dicarboxylic anhydride.

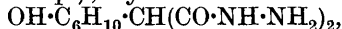
The first-named substance was prepared by Leroux (*Ann. chim. phys.*, 1910, [viii], **21**, 458), but only in small amount. As some quantity of this acid was required, the action of ethyl sodiomalonate on dibromocyclohexene was studied and found to take two courses, one yielding hexahydroisocoumaranone, the other cyclohexene and ethyl ethanetetracarboxylate. The last-named substance behaves towards hydrazine as a normal ester (cf. Salomon and Pohl, A., 1895, i, 508). It was anticipated that ethyl sodiomalonate and the cyclohexenehalogenohydrins would yield hexahydroisocoumaranone in quantity, but the results were poor owing to the large proportion of useless by-products, and the preparation of this substance was found to be most satisfactorily effected from ethyl sodiomalonate and cyclohexene oxide. It was not possible, however, to prepare 1 : 2-cyclohexenediacetic acid from it, and therefore attempts were made to prepare and reduce *o*-phenylenediacetic acid, the method of Moore and Thorpe (T., 1908, **93**, 165) being found the most suitable. The acid is unaffected by treatment with sodium and either ethyl or amyl alcohol, but is quantitatively reduced to a mixture of *cis*- and *trans*-cyclohexanediactic acids by means of platinum black and hydrogen. The separation of these acids was effected by very slow crystallisation from water or ethyl acetate and the *cis*-form was eventually obtained pure. On distillation, it yielded the anhydride, but this is a somewhat unstable substance. The acid and anhydride are not identical with deoxycantharidic acid and deoxycantharidin, respectively, as the m. p. of the pure acid is 162—163°, whilst that of deoxycantharidinic acid is 160—165°, and the silver salts crystallise with $\frac{1}{2}$ H₂O and 1H₂O, respectively. Further, the two acids behave very differently on distillation with steam. Attention was therefore directed to the preparation of *cis*-1 : 2-dimethylcyclohexane-4 : 5-dicarboxylic acid. A substance to which the constitution of 4 : 5-dimethylphthalic acid was attributed was described by von Korzyński (A., 1902, i, 274), but a repetition of that worker's experiments showed that the acid prepared by him was not a dimethylphthalic acid, but a dimethylisophthalic acid identical with the acid that

may be obtained directly by the oxidation of durene. 4 : 5-Dimethylphthalic acid was thus apparently unknown, and attempts were made to prepare it. For this purpose, 4 : 5-dibromo-*o*-xylene and 4 : 5-dibromophthalic acid were used, but no successful result was obtained. *p*-Xylic acid was then used as a starting-point, this was heated with mercuric acetate, giving a mixture of the anhydrides of the two possible *o*-hydroxymercuri-*p*-xylic acids. These were treated with fuming sulphuric acid, and converted into the corresponding *o*-sulpho-*p*-xylic acids, which were purified by the fractional crystallisation of their barium and finally of their sodium salts. The orientation of these acids was demonstrated to be of the ortho-type by treatment with bromine water, which resulted in the elimination of carbon dioxide and the sulphonic group with formation of known dibromo-*o*-xylenes. On fusing the sodium salt of 5-sulpho-*p*-xylic acid with sodium formate, 4 : 5-dimethylphthalic acid was obtained. Attempts to reduce this acid to the corresponding hexahydro-derivative have as yet been unsuccessful.

In the course of the above work, the following substances, hitherto not described, have been prepared : The lactone of 2-cyclohexanol-2-malonic acid, $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{CH} \cdot \text{CO}_2\text{H} \\ | \\ \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{O} \end{array} > \text{CO}$, a pale yellow, viscous oil, not obtained crystalline, b. p. 190—200°/10 mm. (decomp.); ethyl cyclohexanol-2-malonhydrazide,



silky needles, m. p. 184—185° (corr. decomp.); cyclohexanol-2-malonamide, $\text{C}_9\text{H}_{16}\text{O}_3\text{N}_2$, a white, granular, crystalline substance, m. p. 227—228° (corr. decomp.); cyclohexanol-2-malonhydrazide,



a white, crystalline powder, m. p. 226—227° (corr.); hexahydroisocoumaranone (cyclohexanolacetolactone), $\text{C}_8\text{H}_{12}\text{O}_2$, a colourless, mobile liquid of characteristic odour, b. p. 152—153°/28 mm., 138—139°/15 mm., 262.5—263.5°/765 mm., d_4^{25} 1.0925, n_D^{25} 1.4790, m. p. —5.5°; cyclohexan-2-ol-1-acetic acid, $\text{C}_8\text{H}_{14}\text{O}_3$, crystals, m. p. 97—102°, silver and potassium salts of the acid, the latter crystallising in lustrous plates; cyclohexan-2-ol-1-acetamide, $\text{C}_8\text{H}_{15}\text{O}_2\text{N}$, large, characteristic clusters of prisms, m. p. 154° (corr.); cyclohexanolacetohydrazide, $\text{C}_8\text{H}_{16}\text{O}_2\text{N}_2$, silky needles, m. p. 167.5° (corr.); cyclohexanolacetobenzohydrazide, $\text{OH} \cdot \text{C}_6\text{H}_{10} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{NH} \cdot \text{Bz}$, colourless, feathery needles, m. p. 173—174° (corr.); cyclohexanolacetophenylhydrazide, $\text{C}_{14}\text{H}_{20}\text{O}_2\text{N}_2$, small, colourless crystals, m. p. 165.5° (corr.); dihydronaphthalenemono-ozonide, a colourless, amorphous, gummy solid, which explodes on heating to a fairly high temperature; *o*-phenylenediacetic acid monoamide, $\text{C}_{10}\text{H}_{11}\text{O}_3\text{N}$, small, brilliant needles, m. p. 207—208° (corr.); 3 : 4 : 3' : 4'-tetramethylbenzil (4 : 4-*o*-xylil), $\text{C}_{18}\text{H}_{18}\text{O}_2$, a citron-yellow solid, m. p. 128.5° (corr.), yielding a golden-yellow, crystalline osazone, m. p. 199—200° (corr.); 2 : 3-di-*o*-4'-xylilquinoxaline, $\text{C}_{24}\text{H}_{22}\text{N}_2$, colourless needles, m. p. 158° (corr.); 4 : 5-dimethylphthalic anhydride, $\text{C}_{10}\text{H}_8\text{O}_3$, characteristic, square leaves, m. p. 208.5° (corr.); 4 : 5-dimethylphthalic acid, $\text{C}_{10}\text{H}_{10}\text{O}_4$, long, colourless needles, m. p. 209° with evolution of water vapour.

1 : 2-Dibromocyclohexane has b. p. 97—98°/10 mm., 124—125°/36 mm., m. p. —6.0°, d_{16}^{16} 1.7917, d_4^{16} 1.7898, n_D^{16} 1.5540. H. J. E.

Tannins and Similar Substances. XIII. Stereoisomeric Catechins. III. KARL FREUDENBERG and LUDWIG PURBMAN (Ber., 1923, 56, [B], 1185—1194).—Four members of the catechin family have been isolated previously, viz., *d*- and *dl*-catechin and *l*- and *dl*-epicatechin. Kostanecki's Gambier catechin is pure *d*-catechin, which is convertible into a mixture of catechins from which *dl*-catechin can be isolated. The latter substance is the main component of Pega catechu (acacatechin) which contains also *l*-catechin. The isolation of the latter is now described and the relationships of the *d*-, *l*-, and *dl*-forms is firmly established. Further, it has been found possible to separate *d*-epicatechin in the homogeneous state from the products of the transformation of *d*-catechin and thence to place beyond doubt the racemic nature of *dl*-epicatechin. It is considered most probable that the epicatechin is derived from the catechin series by change in the arrangement of the groups attached to the two asymmetric carbon atoms, which occurs at appreciably different rates; a displacement of the ring is not involved.

The separation of *l*- and *dl*-catechins and *l*- and *dl*-epicatechins from the ethereal extract of Acacia catechu is described in detail, the compounds being obtained in the relative amounts : 60 : 320 : 30 : 30. Two specimens of Acacia catechu from India consisted respectively of nearly homogeneous *d*-catechin and of a mixture of approximately equal amounts of *dl*- and *l*-catechins. A specimen of Gambier catechu yielded mainly *d*-catechin with minor quantities of the *dl*-derivative.

The transformation of *d*-catechin is effected conveniently in aqueous solution at 125°, the products being *dl*-catechin and *dl*- and *d*-epicatechins.

The following compounds are described in detail : *l*-Catechin, $C_{15}H_{14}O_6 \cdot 4H_2O$, m. p. (hydrated) 93—97°, (anhydrous) 174—175°, (indefinite) $[\alpha]_{Hg}^{yellow}$ —16.7° in aqueous acetone (50%), inactive in alcoholic solution : *l*-Catechin penta-acetate, m. p. 132° $[\alpha]_{Hg}^{yellow}$ —39.4° in tetrachloroethane : Tetramethyl-*l*-catechin, colourless crystals, m. p. 142—143°, $[\alpha]_{Hg}^{yellow}$ +12.0° ($\pm 2^\circ$) : *dl*-Catechin, colourless needles, m. p. 214—216° after previous softening. *dl*-Catechin penta-acetate, m. p. 166°. *l*-Epicatechin (+4H₂O), m. p. 245° (corr. decomp.), $[\alpha]_{Hg}^{yellow}$ —68° in alcohol, —60° in aqueous acetone (50%). *l*-Epicatechin penta-acetate, colourless needles, m. p. 153—154°, $[\alpha]_{Hg}^{yellow}$ —15° when dissolved in *s*-tetrachloroethane. Tetramethyl-*l*-epicatechin, broad prisms, m. p. 153—154°, $[\alpha]_{Hg}^{yellow}$ —61.5° in *s*-tetrachloroethane. *d*-Epicatechin, m. p. 245° (decomp.), $[\alpha]_{Hg}^{yellow}$ +69° in alcohol (96%). *d*-Epicatechin penta-acetate (+4H₂O), m. p. 153°, $[\alpha]_{Hg}^{yellow}$ +16°. Tetramethyl-*d*-epicatechin, m. p. 153°, $[\alpha]_{Hg}^{yellow}$ +60.9° when dissolved in *s*-tetrachloroethane. *dl*-Epicatechin crystallises in two forms, thick, glistening plates or slender needles, which probably contain differing proportions of water of crystallisation; it

has m. p. (anhydrous), 229—232°. *dl*-Epicatechin penta-acetate has m. p. 167°.

The presence of *l*- or *dl*-catechins causes an exaltation of the specific rotation of *l*-epicatechin, whereas *d*-catechin does not appear to be influenced by the presence of the epi modification.

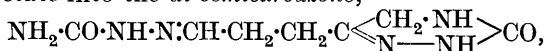
H. W.

The Fission of Furfuryl Alcohol and the Mechanism of the Production of Lævulic Acid from Hexoses. RUDOLF PUMMERER and WILHELM GUMP (*Ber.*, 1923, 56, [B], 999—1008).—Furfuryl alcohol is decomposed by hot, very dilute, methyl-alcoholic hydrogen chloride into methyl lævulate and a derivative of δ -hydroxy- γ -ketovaleraldehyde, the yield of unresinified products under these conditions being about 30—40% of the weight of the initial material. It has not been found possible to isolate δ -hydroxylævulaldehyde in substance, but it is shown that the compound, when treated with boiling mineral acids, undergoes a remarkable intramolecular Cannizzaro reaction which results in the formation of lævulic acid.

5-Hydroxymethylfurfuraldehyde, $\begin{matrix} \text{CH:C(CH}_2\cdot\text{OH)} \\ \text{CH}=\text{C(CHO)} \end{matrix} > \text{O}$, has been

shown previously to be an intermediate product in the conversion of hexoses into lævulic acid, but the further course of the reaction has not been elucidated hitherto. The present experiments make it appear probable that the next step in the series consists in the formation of δ -hydroxylævulaldehyde, the aldehydic group being hydrolytically eliminated as formic acid. It is improbable that hydrolysis occurs previous to the rupture of the furan ring, since, in this case, furfuryl alcohol would be produced which, when treated with boiling mineral acids under the customary experimental conditions, yields only 5—40% of lævulic acid (the remainder of the alcohol becomes resinified) whereas 5-hydroxymethylfurfuraldehyde gives an approximately quantitative yield of formic acid and lævulic acid. It is therefore likely that the hydroxymethyl compound is transformed into the hydroxydiketoaldehyde, $\text{OH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CHO}$, which is subsequently hydrolysed.

Furfuryl alcohol is converted by a boiling solution (0.1%) of hydrogen chloride in methyl alcohol into methyl lævulate, b. p. 85—86°/14 mm. (*p*-nitrophenylhydrazone, m. p. 136°; *semicarbazone*, lustrous leaflets, m. p. 148—149°), and δ -methoxylævulaldehyde dimethyl acetal, $\text{OMe}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH(OMe)}_2$, a colourless liquid, b. p. 97—98°/13 mm., d_4^{20} 1.0323, n_D^{20} 1.4281, the constitution of which is established by its production from furfuryl methyl ether. It is converted by semicarbazide hydrochloride and sodium acetate into the *di-semicarbazone*,



thin, pale yellow leaflets, m. p. 222°, and by *p*-nitrophenylhydrazine in acetic acid solution (50%) into the *p*-nitrophenylhydrazone, $\text{C}_{28}\text{H}_{27}\text{O}_7\text{N}_9$, m. p. 216—217°. A second *p*-nitrophenylhydrazone, $\text{C}_{11}\text{H}_{13}\text{O}_4\text{N}_3$, is also obtained when the acetal reacts with *p*-nitro-

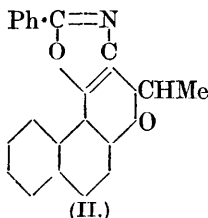
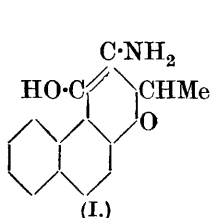
phenylhydrazine in the presence of dilute aqueous mineral acid. The acetal is converted by boiling 0.5*N* aqueous hydrochloric acid into lævulinic acid and by methyl-alcoholic hydrogen chloride (2*N*) into methyl lævulate. H. W.

Blue Dye from Furfuraldehyde and Diethylaniline. F. PASCHKE (*Cellulosechemie*, 1923, 4, 32—33).—The green colouring matters of the malachite-green type which are formed by the condensation of furfuraldehyde with dimethyl- or diethyl-aniline in the presence of oxalic acid are relatively unstable. If, however, the green mass obtained by condensation with diethylaniline is boiled for a short time with alcoholic hydrogen chloride, the green colour is discharged, owing apparently to the rupture of the oxygen bridge of the furan ring. The brown solution is filtered cold, mixed with sodium chloride solution, then acidified with acetic acid and treated with ferric chloride solution drop by drop. A blue dye is thus formed which is separated by salting out and purified by solution in glacial acetic acid; its composition corresponds with the formula $C_{25}H_{34}O_{10}N_2Cl_2$. This dye contains more oxygen than would be present if the reaction were confined to a simple rupture of the furan ring, and its behaviour suggests the presence of phenolic hydroxyl groups. It has the properties of an acid dye, having a strong direct affinity for silk in an acid bath and dyeing cotton only as a mordant dye. The mordant lakes are extremely fast. J. F. B.

Pyrylium Compounds. XII. The Constitution of Methyl-diphenylpyrylium Salts. W. DILTHEY and J. FISCHER (*Ber.*, 1923, 56, [B], 1012—1013).—It has been pointed out recently by Schneider and Ross (*A.*, 1922, i, 1171) that the compounds described by Dilthey as 2 : 6-diphenyl-4-methylpyrylium salts can be obtained from dypnone and differ from those derived from phenyl propenyl ketone and acetophenone; they are therefore to be regarded as 4 : 6-diphenyl-2-methylpyrylium compounds. Although the arguments of Schneider and Ross do not appear to be necessarily convincing, the author is led to share their view, since it is found that the action of benzaldehyde on the diphenylmethylpyrylium compounds gives 4 : 6-diphenyl-2-styrylpyrylium salts, the constitution of which is established by their production from styryl methyl ketone and phenyl styryl ketone. H. W.

The Additive Product of Ammonia and 2-Methyl- β -naphthachromone- α . WILHELM SCHNEIDER and HELMUTH BODE (*Ber.*, 1923, 56, [B], 1042—1046).—In a previous communication (Schneider and Kunau, *A.*, 1921, i, 879), it has been mentioned incidentally that an additive product of ammonia and 2-methyl β -naphthachromone- α is formed in minor amount by the action of alcoholic ammonia on 3-acetyl-2-methyl- β -naphthachromone- α . By a suitable modification of the experimental conditions, the substance may be made the main product of the change; it is remarkable, however, that it does not appear to be formed directly from

2-methyl- β -naphthachromone- α and ammonia. It crystallises in slender, yellow needles, m. p. 138—139°, is soluble in alkalis and not too dilute acids, and gives an intense, dark green coloration with ferric chloride in alcoholic or ethereal solution. It gives a picrate, $C_{20}H_{16}O_9N_4$, yellow crystals, m. p. 179—180°. Its phenolic character is established by the isolation of a methyl ether, almost colourless crystals, m. p. 198° (corresponding *picrate*, yellow crystals,



m. p. 171°). With benzoyl chloride and sodium hydroxide it loses the elements of water and gives a *mono-benzoyl* derivative, pale yellow crystals, m. p. 137°. The behaviour of the substance appears to be explained by the hypothesis that it is 3-amino-2-methyl- β -naphtha- α -chromen-4-ol (annexed formula I), and that the benzoyl derivative is an oxazole compound (formula II).

H. W.

Etheseroline. MAX POLONOVSKI and MICHEL POLONOVSKI (*Compt. rend.*, 1923, **176**, 1480—1483; cf. A., 1918, i, 504).—The preparation of etheseroline has been further studied, all the intermediate substances have been isolated in a pure condition and the following new and corrected observations made. Eseretholemethine crystallises from ether in prismatic needles, m. p. 89°, and gives a *picrate*, m. p. 196°; two methiodides were obtained in admixture, their separation was effected by an ether-alcohol mixture. The α -form is a crystalline powder of neutral reaction, m. p. 135°, $\alpha_D + 2^\circ$; for the β -compound no m. p. is indicated, but $\alpha_D - 25^\circ$. The former is decomposed quantitatively into trimethylamine and etheseroline on being heated with concentrated sodium hydroxide solution, the latter is unaffected. Etheseroline, $C_{14}H_{17}ON, H_2O$, forms large, colourless, transparent prisms, m. p. 48°, α_D (in 95% alcohol) -98° ; it is a weak base, soluble in concentrated acids, but precipitated by addition of water. The nitrogen atom appears to be tertiary and to form part of a pyrrole or indole nucleus. It is linked to a methyl group. The substance has the double bond characteristic of eserine derivatives and also their asymmetric carbon atom.

H. J. E.

The Pepper Taste of Piperine. HEINRICH RHEINBOLDT (*Ber.*, 1923, **56**, [B], 1228—1229).—The sharp taste of Indian pepper has been attributed alternately to the presence of piperine and chavicine. Piperine which has been exhaustively purified through its additive compound with tin tetrabromide has only a faint although distinct taste of pepper in substance, whereas in the finely disperse state or in alcoholic solution the physiological action is very marked. Piperine is therefore to be regarded as the active component of pepper (cf. Staudinger and Schneider, this vol., i, 361).

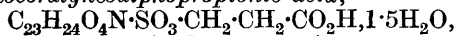
H. W.

Hydrolysis of Scopolamine. RICHARD WILLSTÄTTER and ENDRE BERNER (*Ber.*, 1923, 56, [B], 1079—1082).—The basic constituent of scopolamine has not previously been isolated, since it is very readily transformed into scopoline (cf. Gadamer and Hammer, A., 1921, i, 588; Hess and Wahl, A., 1922, i, 854). It may, however, be obtained by the hydrolysis of scopolamine in feebly alkaline solution. This can be effected by pancreatic lipase in the presence of an ammonia-ammonium chloride buffer, activation being effected by the addition of albumin and calcium chloride; the presence of olive oil is advantageous. It is simpler, however, to use the mixture of ammonia and ammonium chloride alone; hydrolysis is almost complete after thirty-five days, but during this period a portion of the new base (for which the name "scopine" is proposed) is converted into scopoline, from which it can be separated only with difficulty. It is more advantageous, therefore, to limit the duration of the experiment, since scopine is readily separated from unchanged scopolamine.

Scopine (annexed formula) crystallises in long, stable needles, m. p. 76° (corr.); it is optically inactive. It is converted when heated or under the influence of acid or, particularly, of alkalis into scopoline. *Scopine hydrochloride* crystallises from alcohol in well-defined platelets; the *picrate*, thin leaflets, has m. p. 231° (decomp.), whereas scopoline *picrate* forms coarser prisms, m. p. 236°. The two bases are, however, more readily distinguished in the chloroplatinates and chloraurates. *Scopine chloroplatinate*, (C₈H₁₃O₂N)₃.H₂PtCl₆.2H₂O, crystallises in long, domatic prisms, m. p. 219° (decomp.), whereas scopoline chloroplatinate, +1H₂O, forms plates, m. p. 203° (decomp.). *Scopine chloroaurate*, C₈H₁₄O₂NAuCl₄, small prisms, m. p. 216° (decomp.), appears to contain water of crystallisation, whilst *scopoline chloroaurate*, +½H₂O, crystallises in prismatic plates, m. p. 220° (decomp.).

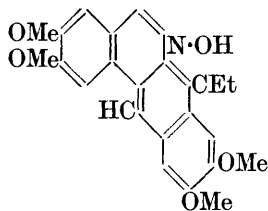
H. W.

Propionylpapaverine and Homocoralyne. WILHELM SCHNEIDER and ERHARD NITZE (*Ber.*, 1923, 56, [B], 1036—1041).—An extension of previous work (Schneider and Schroeter, A., 1920, i, 760). *Homocoralyne* sulphopropionic acid,



yellow needles, m. p. 273° (decomp.) after previous softening, is readily obtained by treating papaverine with a mixture of propionic anhydride and sulphuric acid monohydrate which has previously been warmed at 85° until a test sample does not give a precipitate with barium chloride. The following derivatives are readily prepared from it: *chloride*, C₂₃H₂₄O₄NCl.3H₂O, slender, yellow needles, m. p. 250° (decomp.); *iodide*, +H₂O, slender, yellow needles, m. p. 268° (decomp.); *nitrate*, +2H₂O, yellow needles, which soften and darken above 273° without melting; *hydrogen sulphate*, +2.5H₂O, gradual decomp. above 300°; *perchlorate*, slender, yellow needles, decomp. above 280°; *picrate*, +2H₂O, pale yellow, slender

needles, m. p. 259° (decomp.). Treatment with sodium hydroxide solution causes the conversion of the sulphopropionic acid into *propionylpapaverine* (annexed formula), pale yellow, lustrous crystals m. p. 145—146° (the intermediate, quaternary ammonium base is very unstable). It gives a *phenylhydrazone*, colourless, lustrous needles, m. p. 205—206°, an *oxime*, small, almost colourless needles, m. p. 212°, and a *methiodide*, yellow crystals, m. p.



215—216° (prepared by treating the ketonic base with methyl iodide and benzene at 100°). The substance last mentioned is converted by sodium hydroxide solution into *N-methylpropionylisopapaverine*, $C_{24}H_{27}O_5N$, a yellow, amorphous powder, m. p. 120—121°.

Homocoralyne, in the form of its sulphopropionate, is reduced by zinc filings and dilute sulphuric acid in the presence of acetic acid to an intensely yellow, unstable base which appears to be dihydrohomocoralyne. More drastic reduction converts it into *hexahydrohomocoralyne* [*homocoralydine*], $C_{23}H_{29}O_4N$, large, colourless leaflets, m. p. 145—146° (*hydriodide*, slender, colourless leaflets, m. p. 236°). H. W.

Strychnine. I. E. OLIVERI-MANDALÀ and G. COMELLA (*Gazzetta*, 1923, **53**, i, 276—284).—According to the structure proposed by Perkin and Robinson (T., 1910, **97**, 305), strychnine contains a secondary alcohol grouping, which forms part of a hydrogenated aromatic nucleus. The action of a halogen, bromine especially, in presence of water should, therefore, convert strychnine into a *cyclohexanone* derivative which, by further oxidation and consequent rupture of the hydroaromatic nucleus, should give rise to a dicarboxylic acid, or by a series of transformations should be capable of conversion into a dehydrogenated ring containing the hydroxyphenyl grouping.

The only product obtained by the authors by treating the free base with bromine water in presence of calcium carbonate is, however, monobromostrychnine (cf. Beckurts, A., 1885, 675, 911; Leuchs and Boll, A., 1910, i, 766). Treatment of strychnine oxide (cf. Pictet and Mattisson, A., 1905, i, 816) with bromine or potassium ferricyanide also fails to oxidise any functional group of the strychnine molecule, and the action of hydrogen peroxide on strychnine in acetic acid solution gives a similar result.

From various considerations, the conclusion is drawn that the cause of the isomerism of strychnine and *isostrychnine* lies in the carbon atom united with the oxygen atom, the function of which is not fully understood. None of the reagents for characterising oxygen atoms in different groupings seems capable of determining the form in which this oxygen atom exists, but the presence of the group $\cdot N \cdot CMe(OH) \cdot$ is in agreement with the behaviour of strychnine, and the conversion of such group into $\cdot NH \cdot + \cdot CO \cdot CH_3$ would explain the appearance of the ketonic function attending the transformation of strychnine into *isostrychnine*.

Oxidation of strychnine oxide by permanganate in the cold yields the acid, $C_{21}H_{20}O_6N_2 \cdot 2H_2O$, obtained by Leuchs (A., 1908, i, 563) by the oxidation of strychnine, suspended in acetone, by means of permanganate. Oxidation of the oxide by hot permanganate gives, however, a compound, m. p. about 200° (decomp.), which is undoubtedly a derivative of indole, the presence of an indole nucleus in the strychnine molecule being, therefore, certain.

T. H. P.

Some Transformations of 2:4-Dimethylpyrrole. HANS FISCHER, BERNHARD WEISS, and MAX SCHUBERT (*Ber.*, 1923, **56**, [B], 1194—1202).—Further experiments with 2:4-dimethylpyrrole are recorded (cf. Fischer and Bäumer, A., 1915, i, 309; Fischer and Zerweck, A., 1922, i, 758; this vol., i, 364).

2:4-Dimethylpyrrole condenses with acetonitrile in anhydrous ether under the influence of hydrogen chloride to give the *ketimine* of 5-acetyl-2:4-dimethylpyrrole, slender needles, m. p. 141° , in which the new side chain is only loosely attached, since it is removed by the action of hydrogen in the presence of spongy platinum with re-formation of 2:4-dimethylpyrrole. The ketimine is converted by boiling water into 5-acetyl-2:4-dimethylpyrrole, colourless needles, m. p. 121° , which is conveniently prepared in this manner. It does not appear capable of further condensation.

5-Chloroacetyl-2:4-dimethylpyrrole,
$$NH \begin{array}{l} \diagup C(CO \cdot CH_2Cl) : CMe \\ \diagdown CMe = CH \end{array}$$
,

colourless needles, m. p. 143° , is prepared from 2:4-dimethylpyrrole and chloroacetonitrile; the intermediate production of a stable ketimine is not observed. It is converted by dimethylamine in absolute alcoholic solution into 5-dimethylaminoacetyl-2:4-dimethylpyrrole, m. p. 110° . 5-Chloroacetyl-2:4-dimethylpyrrole and formaldehyde yield *bis*-5-chloroacetyl-2:4-dimethylpyrrolmethane,
$$CH_2Cl \cdot CO \cdot \overset{\overset{|}{HN \cdot CMe}}{\underset{\underset{|}{CMe}}{C}} : C \cdot CH_2 \cdot C \leq \overset{\overset{|}{CMe}}{\underset{\underset{|}{CMe}}{C}} \cdot CO \cdot CH_2Cl$$
, m. p. 258° , from

which *bis*-5-dimethylaminoacetyl-2:4-dimethylpyrrolmethane, colourless needles, m. p. 170° after previous softening, is obtained in the usual manner.

2:4-Dimethylpyrrole is converted by formic acid (90%) in the presence of perchloric acid into *bis*-2:4-dimethylpyrrolmethene perchlorate, $C_{13}H_{17}O_4N_2Cl$, reddish-brown needles which become discoloured at 200° , but do not melt below 260° ; the corresponding

base,
$$\begin{array}{l} CH \cdot CMe \\ | \quad | \\ CMe \cdot NH \end{array} > C : CH : C < \begin{array}{l} CMe : CH \\ N = CMe \end{array}$$
, crystallises in yellow needles, m. p. 117° .

Ethyl 2:4-dimethylpyrrole-5-carboxylate, m. p. 125° , is prepared by the successive addition of ethereal solutions of 2:4-dimethylpyrrole and ethyl chloroformate to magnesium ethyl bromide dissolved in ether; it is hydrolysed by potassium hydroxide solution (50%) to 2:4-dimethylpyrrole-5-carboxylic acid, m. p. 136° , which is also obtained directly by the action of carbon dioxide on the Grignard compound from 2:4-dimethylpyrrole. The ester is converted by the hydrocyanic acid method into 5-carbethoxy-

2 : 4-dimethylpyrrole-3-aldehyde, $\text{NH} \begin{smallmatrix} \text{C}(\text{CO}_2\text{Et})\text{:}\text{C Me} \\ \text{C Me} \text{---} \text{C-CHO} \end{smallmatrix}$, needles, m. p. 145°, which is hydrolysed to the corresponding acid, m. p. 230° after previous partial decomposition. The latter compound is transformed by dry distillation into 2 : 4-dimethylpyrrole-3-aldehyde, m. p. 126°, in which a second aldehyde group could not be introduced by means of hydrocyanic acid. 5-Carbethoxy-2 : 4-dimethylpyrrole-3-aldehyde gives a phenylhydrazone, m. p. 204°, an azlactone, $\text{C}_{19}\text{H}_{18}\text{O}_4\text{N}_2$, m. p. 232°, an oxime, m. p. 196—197° (which is converted into ethyl 3-cyano-2 : 4-dimethylpyrrole-5-carboxylate, m. p. 171°, by anhydrous sodium acetate and acetic anhydride), and a semicarbazone, m. p. 285° (decomp.). The latter substance is converted by alcoholic sodium ethoxide solution at 160—170° into 2 : 3 : 4-trimethylpyrrole which is identified as the picrate.

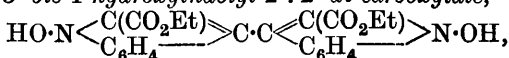
Ethyl 2 : 4-dimethylpyrrole-5-carboxylate is converted by chloroacetonitrile into ethyl 3-chloroacetyl-2 : 4-dimethylpyrrole-5-carboxylate, m. p. 163°, which is transformed by potassium cyanide into ethyl 3-cyanoacetyl-2 : 4-dimethylpyrrole-5-carboxylate, m. p. 172—173°. H. W.

Ethyl o-Nitrobenzylacetoacetate and its Transformations.

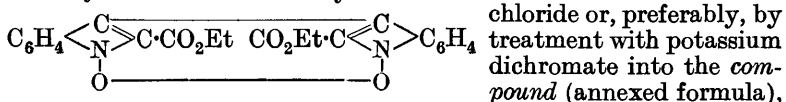
S. GABRIEL, WILH. GERHARD, and R. WOLTER (*Ber.*, 1923, **56**, [B], 1024—1036).—Ethyl o-nitrobenzylacetoacetate, a pale, brownish-yellow liquid, b. p. about 180°/1 mm., is prepared by the addition of a solution of a molecular proportion of o-nitrobenzyl chloride in alcohol to a similar solution of two molecular proportions of ethyl acetoacetate and two atomic proportions of sodium and subsequent preservation of the mixture for two days. It is readily converted by alcoholic potassium hydroxide solution into a mixture of ethyl 1-hydroxyindole-2-carboxylate, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{---CH} \\ \text{N(OH)} \end{smallmatrix} \text{C-CO}_2\text{Et}$, coarse needles, m. p. 64—65°, and 1-hydroxyindole-2-carboxylic acid, m. p. 159.5° (the potassium salt, $\text{C}_{11}\text{H}_{10}\text{O}_3\text{NK}$, lemon-yellow leaflets, and the unstable ammonium salt, lemon-yellow needles, of the ester are described). The ethyl ester is converted by sodium methoxide and methyl iodide at 100° into methyl 1-methoxyindole-2-carboxylate, needles, m. p. 63—64°, and by ethylation into ethyl 1-ethoxyindole-2-carboxylate, from which 1-ethoxyindole-2-carboxylic acid, colourless needles, m. p. 150—151°, is prepared. 1-Benzoyloxyindole-2-carboxylic acid has m. p. 168—169° (decomp.); it gives a methyl ester, pointed, flattened needles, m. p. 82—83°, and an ethyl ester, m. p. 77—78°. Ethyl 1-benzoyloxyindole-2-carboxylate forms crystals, m. p. 104—105°, whilst ethyl 1-acetoxyindole-2-carboxylate crystallises in needles, m. p. 76—77°. Chlorination of the ester in the presence of carbon tetrachloride yields a di-chloro-ester, $\text{C}_{11}\text{H}_9\text{O}_3\text{NCl}_2$, m. p. 98—99°. A tribromo-compound, $\text{C}_{11}\text{H}_8\text{O}_3\text{NBr}_3$, small needles, m. p. 138.5°, is obtained from the ester and bromine in the presence of glacial acetic acid, whereas a monobromo-derivative, rhombohedra, m. p. 82—84°, is formed when benzene is used as solvent. Ethyl 1-hydroxyindole-2-carboxylate is reduced by hydriodic acid and phosphonium iodide, or, more conveniently,

by stannous chloride in the presence of glacial acetic and fuming hydrochloric acids to *ethyl indole-2-carboxylate*, m. p. 125—126°, which is converted in the usual manner into indole-2-carboxylic acid, m. p. 203°; the latter substance is transformed by thionyl chloride into a mixture of the corresponding chloride and anhydride. Ethyl indole-2-carboxylate is converted by bromotrinitromethane into *ethyl 3-bromoindole-2-carboxylate*, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CBr} \\ \text{NH} \end{smallmatrix} \text{C} \cdot \text{CO}_2\text{Et}$, pale yellow needles, m. p. 152—153°, which is hydrolysed by potassium hydroxide solution to *3-bromoindole-2-carboxylic acid*, slender needles, m. p. 199° (decomp.). *Ethyl 3-chloroindole-2-carboxylate*, needles, m. p. 153—154°, is obtained when an intimate mixture of ethyl indole-2-carboxylate and phosphorus pentachloride is heated on the steam-bath, whereas, at a higher temperature, a *dichloro-derivative*, $\text{C}_{11}\text{H}_9\text{O}_2\text{NCl}_2$, needles, m. p. 194—195°, is produced. *3-Chloroindole-2-carboxylic acid*, m. p. 180—182° (decomp.), is transformed by thionyl chloride into the corresponding *chloride*, a greyish-yellow, crystalline mass; it is readily reduced by hydriodic acid and phosphonium iodide to indole-2-carboxylic acid.

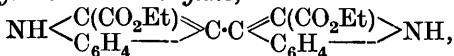
Ethyl 1-hydroxyindole-2-carboxylate is oxidised by cautious treatment with ferric chloride in the presence of acetic acid (50%) to *ethyl 3 : 3'-bis-1-hydroxyindolyl-2 : 2'-di-carboxylate*,



pale yellow, crystalline needles, m. p. 152—153° (decomp.); the corresponding *potassium salt*, the *dimethyl ether*, a colourless, crystalline powder, m. p. 129° after softening at 126°, and *3 : 3'-bis-1-hydroxyindolyl-2 : 2'-dicarboxylic acid*, microscopic rhombs, gradual decomp. 250—270°, are described. Ethyl 1-hydroxyindole-2-carboxylate is converted by more drastic oxidation with ferric



green leaflets, m. p. 189° (decomp.), which is reduced by stannous chloride in the presence of acetic and hydrochloric acids to *ethyl 3 : 3'-bis-indolyl-2 : 2'-dicarboxylate*,



colourless needles, m. p. 225—226°; the latter ester is also obtained by the reduction of ethyl 3 : 3'-bis-1-hydroxyindolyl-2 : 2'-dicarboxylate, preferably by means of stannous chloride. It is hydrolysed by potassium hydroxide solution to *3 : 3'-bis-indolyl-2 : 2'-dicarboxylic acid*, $\text{C}_{18}\text{H}_{12}\text{O}_4\text{N}_2 \cdot \text{H}_2\text{O}$, a crystalline powder, m. p. above 285°, the *potassium salt* and *ammonium salt*, rhombic leaflets, of which are described. Thionyl chloride transforms the acid into the corresponding *chloride*, a lemon-yellow, crystalline powder which becomes red at 170—180°, but does not melt below 290°, from which the ethyl ester, m. p. 225—226°, and the *methyl ester*, pale yellow prisms or plates, m. p. 318—320°, are prepared. The acid loses carbon

dioxide and water when heated in a vacuum at above 280° , and yields α -bis-3 : 3'-indolyl, $\text{NH} \langle \text{C}_6\text{H}_4 \rangle \text{C} \cdot \text{C} \langle \text{C}_6\text{H}_4 \rangle \text{NH}$, colourless rhombs, m. p. about 286 — 287° , in a sealed capillary, which is converted by hydriodic or hydrobromic acid in the presence of glacial acetic acid into the salt of the isomeric β -base (see later).

Ethyl 3 : 3'-bis-1-hydroxyindolyl-2 : 2'-dicarboxylate is converted by hydriodic and glacial acetic acids under the conditions customary in estimation of alkoxy-groups into ethyl 3 : 3'-bis-indolyl-2-carboxylate, $\text{NH} \langle \text{C}_6\text{H}_4 \rangle \text{C} \cdot \text{C} \langle \text{C}(\text{CO}_2\text{Et}) \rangle \text{C}_6\text{H}_4 \text{NH}$, short, pale-yellow prisms or plates, m. p. 172 — 173° , which gives a yellow iodide, $\text{C}_{19}\text{H}_{16}\text{O}_2\text{N}_2\text{HI}$, flattened needles, and a brown per-iodide, $\text{C}_{19}\text{H}_{16}\text{O}_2\text{N}_2\text{HI}_2$, which inhibit complete de-alkylation owing to their sparing solubility in the Zeisel mixture. The ester is hydrolysed to 3 : 3'-bis-indolyl-2-carboxylic acid, chrome-red needles, m. p. 209 — 210° . Treatment of ethyl 3 : 3'-bis-1-hydroxyindolyl-2 : 2'-dicarboxylate with colourless hydriodic and glacial acetic acids in the presence of phosphonium iodide yields β -bis-3 : 3'-indolyl, m. p. 207 — 208° ; the corresponding hydrobromide, $\text{C}_{16}\text{H}_{13}\text{N}_2\text{HBr}$, lemon-yellow needles, and hydriodide, are described.

Methyl 1-hydroxyindole-2-carboxylate, m. p. 100 — 101° , is oxidised in a similar manner by ferric chloride to methyl 3 : 3'-bis-1-hydroxyindolyl-2 : 2'-dicarboxylate, $(\text{C}_{10}\text{H}_8\text{O}_2\text{N})_2$, yellow needles, m. p. 209 — 210° (decomp.) after softening at 160° , and by potassium dichromate to the compound, $(\text{C}_{10}\text{H}_7\text{O}_2\text{N})_2$, reddish-brown crystals which appear green by reflected light. Methyl 3 : 3'-bis-1-hydroxyindolyl-2 : 2'-dicarboxylate is reduced by stannous chloride to methyl 3 : 3'-bisindolyl-2 : 2'-dicarboxylate, m. p. 318 — 320° .

H. W.

2 : 8-Diamino-5-benzyl-10-methyldihydroacridine. P. KARRER (*Helv. Chim. Acta*, 1923, 6, 409—411).—This compound is obtained by the action of benzyl-magnesium bromide on the hydrochloride of 2 : 8-diamino-10-methylacridinium chloride. 2 : 8-Diamino-5-benzyl-10-methyldihydroacridine forms white, felted needles, it is unusually stable, and only becomes yellow very slowly in air. The dihydrochloride forms colourless needles which rapidly redden in air.

E. H. R.

The Use of Rhodanine in Organic Syntheses. II. Amino-acids and Ketonic Acids. CH. GRÄNACHER, M. GERÖ, A. OFNER, A. KLOPFENSTEIN, and E. SCHLATTER (*Helv. Chim. Acta*, 1923, 6, 458—467).—Continuing previous work (A., 1922, i, 849), a number of new condensation products of rhodanine with aldehydes have been prepared and their decomposition products studied. The condensation products crystallise with unusual facility, but the α -thiolcarboxylic acids obtained by their alkaline decomposition are difficult to crystallise in the aromatic series, and in the aliphatic series are generally oily substances which cannot be distilled without decomposition.

5-Ethylidenerrhodanine, $\begin{array}{c} \text{NH}\cdot\text{CO} \\ | \\ \text{CS}-\text{S} \end{array} > \text{C}:\text{CHMe}$, obtained by condensing

rhodanine with paracetaldehyde in boiling acetic acid, forms lustrous, brownish-yellow leaflets, m. p. 143°. 5-Crotonylidenerrhodanine, from rhodanine and crotonaldehyde, crystallises in brownish-yellow needles, m. p. 189°. 5-isoValerylidenerrhodanine forms brownish-yellow leaflets, m. p. 83°. 5-Phenylethylidenerrhodanine, from phenylacetaldehyde and rhodanine, forms lustrous, yellow needles, m. p. 217°. Rhodanylidene-glyoxylic [rhodanylidene-acetic] acid, $\begin{array}{c} \text{NH}\cdot\text{CO} \\ | \\ \text{CS}-\text{S} \end{array} > \text{C}:\text{CH}\cdot\text{CO}_2\text{H}$, obtained by condensing glyoxylic

acid with rhodanine, crystallises in lustrous, brownish-red scales, decomposing without melting at 225°; its ethyl ester is a yellow, crystalline powder, and its potassium salt, which crystallises with one mol. of potassium hydroxide, is a brownish-yellow, crystalline powder.

α -Thiol-p-methoxycinnamic acid, obtained by heating anisylidenerrhodanine with 15% sodium hydroxide solution, forms golden-yellow crystals, m. p. 178°; the yield is nearly theoretical. With hydroxylamine in boiling alcohol it gives α -oximino-p-anisylpropionic acid, white needles, m. p. 159°, from which p-anisylpyruvic acid can be obtained. When reduced with sodium amalgam, the oxime gives p-anisylalanine. α -Thiolmethylenedioxycinnamic acid is obtained by the action of alkali on piperonylidenerhodanine; with hydroxylamine it gives α -oximinomethylenedioxypheylpropionic acid, lustrous, yellow leaflets, m. p. 156–158°, which is reduced by sodium amalgam and alcoholic lactic acid to methylenedioxypheylalanine, white leaflets, m. p. 250–255°. α -Thiol-p-isopropylcinnamic acid is obtained from cuminyldenerhodanine; it is a yellow, amorphous powder, which with hydroxylamine gives α -oximino-p-isopropylpheylpropionic acid, white, felted needles, m. p. 170°. Hydrolysis of the oxime gives p-isopropylpheylpyruvic acid, needles or leaflets, m. p. 140–150°, and reduction of the oxime gives p-isopropylpheylalanine, granular aggregates sintering at 230°, m. p. 255°. E. H. R.

The Preparation and Properties of 4':4''-Tetramethyldiaminoanthrafuchsone. FREDERICK ALFRED MASON (T., 1923, 123, 1546–1559).

Synthetic Experiments with the Fission Products of the Blood Pigments and the Formation of Complex Salts from Dipyrromethenes. I. HANS FISCHER and MAX SCHUBERT (Ber., 1923, 56, [B], 1202–1211).—It has been shown previously that the blood pigments contain compounds in which the pyrrole nuclei are united by carbon atoms in the α -position. The synthetic methods used hitherto in the preparation of similar substances are inadequate, since they only allow the union of two similar nuclei and it has been shown, for example, in the case of bilirubic acid, that the compound is formed from a basic hydroxypyrrole and a pyrrolecarboxylic acid. The synthesis of pyrrolealdehydes

has therefore been attempted with the ultimate object of condensing them with a second selected pyrrole component. The experiments now described are chiefly effected with cryptopyrrole (2 : 4-dimethyl-3-ethylpyrrole).

The formation of complex compounds containing copper and the dipyrlylmethene group has been investigated. Although the spectroscopic behaviour of these compounds is not completely analogous to that of the blood pigments, the authors consider that their results prove that the structure of the dipyrlylmethenes is closely related to that of the latter compounds.

Attempts to secure a better method for the preparation of cryptopyrrole are described. The *semicarbazone* of 3-acetyl-2 : 4-dimethylpyrrole, m. p. 203—204°, is crystalline and reducible by sodium ethoxide, but the yields are so poor that the method has no practical significance. In confirmation of previous experiments, the corresponding hydrazone could not be isolated by reason of its very pronounced tendency to give the ketazine. On the other hand, ethyl 3-acetyl-2 : 4-dimethylpyrrole-5-carboxylate readily yields the corresponding *hydrazone*, $\text{NH} \begin{array}{c} \text{C}(\text{CO}_2\text{Et}) \cdot \text{CMe} \\ \text{CMe} = \text{C} \cdot \text{CMe} \cdot \text{N} \cdot \text{NH}_2 \end{array}$, m. p.

137°, which is converted (without being isolated) by sodium ethoxide solution into 2 : 4-dimethyl-3-ethylpyrrole (picrate, m. p. 136°), the yield being in some cases 50% of that theoretically possible. Cryptopyrrole is transformed by chloroacetonitrile into 5-chloroacetyl-2 : 4-dimethyl-3-ethylpyrrole, colourless needles, m. p. 149°, from which 5-dimethylaminoacetyl-2 : 4-dimethyl-3-ethylpyrrole hydrochloride, colourless needles, m. p. 201—202°, is derived.

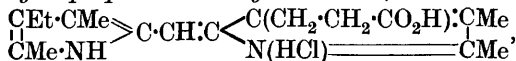
Cryptopyrrole dissolved in chloroform is converted by anhydrous hydrocyanic acid and hydrogen chloride into C-dicryptopyrlylmethylamine, m. p. 142°, which is transformed by boiling water into 2 : 4-dimethyl-3-ethylpyrrole-5-aldehyde, colourless needles, m. p. 105—106°; the corresponding *oxime*, colourless needles, m. p. 118°, and its *picrate*, m. p. 155°; the *semicarbazone*, colourless needles, m. p. 203°, and its *picrate*, m. p. 162°, are described. The semicarbazone is reduced by sodium ethoxide solution at 150—160° to phyllopyrrole, which is identified as the picrate, m. p. 104°.

2 : 4-Dimethyl-3-ethylpyrrole-5-aldehyde condenses with ethyl 2 : 4-dimethylpyrrole-3-carboxylate in the presence of concentrated hydrochloric acid to give bis-3-carbethoxy-2 : 4-dimethylpyrlylmethene, $\text{CO}_2\text{Et} \cdot \text{C} \begin{array}{c} \text{CMe} \\ \text{MeC} \cdot \text{NH} \end{array} \begin{array}{c} \text{C} \\ \text{CH} \end{array} \text{C} \begin{array}{c} \text{CMe} \cdot \text{C} \cdot \text{CO}_2\text{Et} \\ \text{N} = \text{CMe} \end{array}$, m. p. 189°; the

carbon bridge is derived from the pyrrolealdehyde, which loses its aldehydic group as formic acid. The course of the reaction is somewhat unexpected, since the aldehydic group is relatively firmly attached. Bis-2 : 4-dimethyl-3-ethylpyrlylmethene perchlorate, $\text{CEt} \cdot \text{CMe} \begin{array}{c} \text{C} \\ \text{CMe} \cdot \text{NH} \end{array} \begin{array}{c} \text{C} \\ \text{CH} \end{array} \text{C} \begin{array}{c} \text{CMe} \\ \text{N}(\text{HClO}_4) \cdot \text{CMe} \end{array} \text{CEt}$, coarse, red needles, decomp. 240° after becoming discoloured at 170°, is obtained by the condensation of 2 : 4-dimethyl-3-ethylpyrrole-5-aldehyde in alcoholic solution in the presence of perchloric acid. Molar quantities of

cryptopyrrolealdehyde and cryptopyrrolecarboxylic acid in the presence of concentrated hydrochloric acid give 2:4-dimethyl-3-ethylpyrrolmethenyl-2:4-dimethylpyrrol-3-propionic acid, hydrochloride, $\begin{array}{c} \text{CEt}\cdot\text{CMe} \\ | \\ \text{CMe}\cdot\text{NH} \end{array} > \text{C}\cdot\text{CH}:\text{C} < \begin{array}{c} \text{CMe} \\ | \\ \text{N(HCl)}\cdot\text{CMe} \end{array} = \text{C}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, brownish-

red needles, m. p. 215°, whilst the aldehyde and hæmopyrrolecarboxylic acid yields 2:4-dimethyl-3-ethylpyrrolmethenyl-2:3-dimethylpyrrol-4-propionic acid hydrochloride,



brownish-red needles, m. p. 220°.

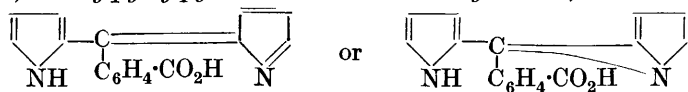
The copper salt of bis-2:4-dimethylpyrrolmethene (annexed formula) is precipitated in green needles when a solution of the methene in alcohol is treated with an ammoniacal copper solution. Copper salts are prepared in a similar manner from 2:4-dimethyl-3-ethylpyrrolmethenyl-2:4-dimethylpyrrol-3-propionic acid (reddish-brown needles), 2:4-dimethyl-3-ethylpyrrolmethenyl-2:3-dimethylpyrrol-4-propionic acid and from bis-hæmopyrrolecarboxylic ester methene.

3-Acetyl-2:4-dimethylpyrrole-5-carboxylamide, m. p. 260°, is obtained by the action of concentrated aqueous ammonia on the corresponding ethyl ester at 150–160°. H. W.

Pyrrole Group. XIV. Syntheses by Means of Magnesium-Pyrrol Halides. Pyrrolephthalein. BERNARDO ODDO and FRANCESCO TOGNACCHINI (*Gazzetta*, 1923, **53**, i, 265–270).—The action of magnesium pyrrol bromide on phthalyl chloride in ethereal solution yields the following two compounds.

(1) *Pyrrolephthalein*, $\text{CO} < \text{O} \xrightarrow{\text{C}_6\text{H}_4} \text{C} \left(\text{C} \begin{array}{c} \text{NH}\cdot\text{CH} \\ \text{CH}\cdot\text{CH} \end{array} \right)_2$, which forms white, lozenge-shaped crystals, m. p. 202°, and with silver nitrate solution and a drop of aqueous ammonia gives a white precipitate which immediately redissolves. When heated in acid solution, it undergoes resinification, with formation of phenylpyrrolpyrrolene-methane-o-carboxylic acid, pyrrolene-phthalide, and pyrrole. In freezing acetic acid, it has the normal molecular weight.

(2) *Phenylpyrrolpyrrolene-methane-o-carboxylic acid*,



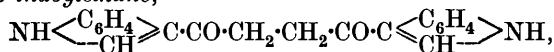
which is formed also when pyrrolephthalein is boiled with 20% sodium hydroxide solution, crystallises in almost white, silky needles, m. p. about 130°. After some time, it undergoes transformation into a compound, m. p. about 153°, owing probably to elimination of a molecule of water from the carboxyl and imino-

groups; if this product is recrystallised from water, the melting point resumes its original value.

When either of these compounds is coupled in alkaline solution with diazobenzene chloride, it yields a *compound*, which forms silky, reddish-brown crystals, m. p. 126°, and is probably benzene-bisazopyrrolephthalein. Treatment of a trace of this compound with concentrated sulphuric acid yields an ultramarine coloration changing to reddish-purple on dilution; concentrated nitric acid gives a deep violet solution, which yields a red precipitate on dilution, and concentrated hydrochloric acid gives a violet coloration, turning in a few seconds to yellow. Towards alkali, it behaves similarly to pyrrolephthalein. T. H. P.

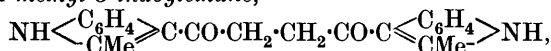
Synthesis of γ -Diketones in the Indole Group. G. SANNA (*Gazzetta*, 1923, 53, i, 177—182; cf. this vol., i, 57, 59).—In its action on magnesium derivatives of indole and 2-methylindole, succinyl chloride behaves in accordance with its symmetrical formula, the products being diketonic and not lactonic in character.

$\alpha\beta$ -Di-3-indoylethane,

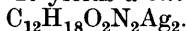


prepared by the action of succinyl chloride on magnesium indolyl bromide, forms minute, colourless prisms, m. p. 287°, exhibits normal cryoscopic behaviour in acetic acid, and dissolves in sulphuric acid, giving a yellow and then a rust-red coloration changing to green on heating. It forms a dirty white, pulverulent *silver* derivative, $\text{C}_{20}\text{H}_{14}\text{O}_2\text{N}_2\text{Ag}_2$, and, when heated in a sealed tube at 140—150° with alcoholic ammonia solution, yields a small proportion of a yellow compound, m. p. 254°, which is possibly di-indylpyrrole, $\text{C}_{20}\text{H}_{15}\text{N}_3$. It yields a *dioxime*, $\text{C}_{20}\text{H}_{18}\text{O}_2\text{N}_4$, which forms blade-like, colourless, prismatic crystals, m. p. 305° (decomp.).

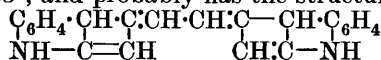
$\alpha\beta$ -Di-2-methyl-3-indoylethane,



obtained similarly from magnesium 2-methylindolyl bromide, crystallises in minute prisms, m. p. 297° (decomp.), has the normal molecular weight in freezing acetic acid, and dissolves in sulphuric acid, giving a blood-red solution, which becomes violet and then purple-red when heated. It yields a *silver* derivative,



When heated in a closed tube with alcoholic ammonia solution it yields: (1) a small proportion of a yellow, microcrystalline powder, m. p. 237°, which is probably dimethylketoylpyrrole, $\text{C}_{22}\text{H}_{13}\text{N}_3$; (2) a *compound*, $\text{C}_{22}\text{H}_{16}\text{N}_2$, which crystallises in tabular prisms, m. p. 285°, and probably has the structure



(cf. this vol., i, 59). The *dioxime* of $\alpha\beta$ -di-2-methyl-3-indoylethane, $\text{C}_{22}\text{H}_{22}\text{O}_2\text{N}_4$, crystallises in prisms, m. p. 267°. T. H. P.

Quaternary Salts of Glyoxalines. JEAN SARASIN (*Helv. Chim. Acta*, 1923, 6, 370—376).—It has been shown by Pyman

(T., 1910, 97, 1815) that 1:4- and 1:5-dimethylglyoxalines give the same methiodide, showing that the halogen is mobile between the two nitrogen atoms. The author has investigated the effect of this kind of tautomerism on the decomposition by heat of quaternary salts of 1-methylglyoxaline of the type $\begin{matrix} \text{NMe}\cdot\text{CH} \\ \text{CH}=\text{CH} \end{matrix} > \text{N} < \begin{matrix} \text{R} \\ \text{I} \end{matrix}$,

in which the radicle R has been varied. The methiodide when heated in a vacuum decomposes completely into methyl iodide and 1-methylglyoxaline. The ethiodide gives a mixture of methyl and ethyl iodides and of 1-methyl- and 1-ethyl-glyoxalines, and the isoamyl iodide behaves in a similar manner. On the other hand, 1-methylglyoxaline benzylbromide gives no trace of 1-benzylglyoxaline when heated.

When the quaternary salts of Wallach's 4(or 5)-chloro-1-methylglyoxaline are heated, they give rise to a new series of 5(or 4)-chloro-1-alkylglyoxalines, having higher boiling points than their isomerides. It can be supposed that, owing to repulsion between chlorine and iodine, the methiodide of 4(5)-chloro-1-methylglyoxaline will have the formula $\begin{matrix} \text{NMe}\cdot\text{CH} \\ \text{CH}=\text{CH} \end{matrix} > \text{NMeI}$, and that on decomposition by heat

it will lose the methyl group attached to the 1-nitrogen atom. The new product must therefore be 5-chloro-1-methylglyoxaline, and Wallach's compound can only be 4-chloro-1-methylglyoxaline.

The quaternary salts of 4-chloro-1-methylglyoxaline are stable and well crystallised; the *methiodide* has m. p. 174—175°, *ethiodide*, m. p. 156—157°, *isoamyl iodide*, m. p. 118—119°, *allylbromide*, m. p. 141—142°, *benzylbromide*, m. p. 107—109°. 5-Chloro-1-methylglyoxaline is a liquid, b. p. 250—252°; its *picrate* has m. p. 166—167°. 5-Chloro-1-ethylglyoxaline, obtained by heating 4-chloro-1-methylglyoxaline *ethiodide*, has b. p. 258—260°; its *picrate* has m. p. 146—147°. 5-chloro-1-isoamylglyoxaline, obtained by heating the above *isoamyl iodide*, has b. p. 286—288°; its *picrate* has no definite m. p. 5-Chloro-1-allylglyoxaline has b. p. 129—131°/12 mm. and decomposes when distilled at the ordinary pressure; *picrate*, m. p. 110—113°. The 5-chloro-1-alkylglyoxalines are reduced by sodium and alcohol to 1-alkylglyoxalines, but 1-allylglyoxaline cannot be obtained in this way. 4-Chloro-1-methylglyoxaline benzylbromide does not give 5-chloro-1-benzylglyoxaline when heated.

E. H. R.

New Syntheses in the Glyoxaline Group. JEAN SARASIN (*Helv. Chim. Acta*, 1923, 6, 377—385).—Attempts to obtain an allyl derivative of glyoxaline from 4-chloro-1-methylglyoxaline and allyl chloride by Fittig's reaction were unsuccessful. The 4-chlorine atom is very resistant and is not affected by a Grignard reagent, ethyl sodiomalonate, diethylamine, or potassium iodide at temperatures up to 150°. When heated with 40% formaldehyde in a sealed tube at 120°, 4-chloro-1-methylglyoxaline is transformed quantitatively into 4-chloro-1-methyl-2-hydroxymethylglyoxaline, a colourless, crystalline compound, m. p. 109—110°, forming a *picrate*, m. p. 148—150°. When reduced with hydriodic acid and red

phosphorus, this gives 1:2-dimethylglyoxaline. Chloral forms with 4-chloro-1-methylglyoxaline an unstable compound, m. p. 82—85°, b. p. 150°/15 mm.

The synthesis of 4(5)-methyl-5(4)-allylglyoxaline was effected as follows. Oximinoallylacetone, $\text{CH}_3\cdot\text{CO}\cdot\text{C}(\text{NOH})\cdot\text{C}_3\text{H}_5$, was reduced to *aminoallylacetone*, $\text{CH}_3\cdot\text{CO}\cdot\text{CH}(\text{NH}_2)\cdot\text{C}_3\text{H}_5$, the *hydrochloride* of which has m. p. 152—153° (decomp.). When this is heated with ammonium thiocyanate in aqueous solution it forms, nearly quantitatively, 2-mercapto-4(5)-methyl-5(4)-allylglyoxaline, m. p. 238—239°, which when oxidised with ferric chloride is converted into 4(5)-methyl-5(4)-allylglyoxaline, m. p. 71—72°, b. p. 180—181°/12 mm.; yield 50%, but lower when other oxidising agents such as potassium persulphate or hydrogen peroxide are used. When this methylallylglyoxaline is methylated with methyl iodide it gives a mixture of 1:4-dimethyl-5-allyl- and 1:5-dimethyl-4-allyl-glyoxalines, which were not separated.

When heated with hydrobromic acid in acetic acid solution, 4(5)-methyl-5(4)-allylglyoxaline is converted into 4(5)-methyl-5(4)- β -bromopropylglyoxaline, m. p. 109—110°, which is converted by ammonia into 4(5)-methyl-5(4)- β -aminopropylglyoxaline, b. p. 185—186°/10 mm. The *dihydrochloride*, which is very hygroscopic, has m. p. 215—217°, and the *dipicrate*, 229—230°. With diethylamine, the above bromo-compound reacts to give 4(5)-methyl-5(4)-diethylaminopropylglyoxaline, b. p. 143—144°/2 mm.; *dihydrochloride*, m. p. 199—200°; *dipicrate*, m. p. 178—179°. When 4(5)-methyl-5(4)-allylglyoxaline is treated with bromine in carbon disulphide, 4(5)-methyl-5(4)- $\beta\gamma$ -dibromopropylglyoxaline, m. p. 116—117°, is formed, and with iodine chloride, 4(5)-methyl-5(4)- $\beta\gamma$ -chloroiodopropylglyoxaline, m. p. 94—95° (decomp.). Attempts to eliminate a single atom of halogen from these dihalogen compounds with potassium hydroxide or sodium ethoxide were unsuccessful.

E. H. R.

The Isomerism of Reduced Derivatives of Quinoxaline. I. The Four Stereoisomeric 2:3-Diphenyl-1:2:3:4-Tetrahydroquinoxalines. GEORGE MACDONALD BENNETT and CHARLES STANLEY GIBSON (T., 1923, 123, 1570—1575).

Barbituric Acid. II. WALTER BOCK (*Ber.*, 1923, 56, [B], 1222—1227; cf. this vol., i, 64).—A solution of barbituric acid in water is converted by the requisite quantity of gaseous chlorine into 5-chlorobarbituric acid, long needles, m. p. 290—295° after slight previous decomposition (*ammonium* salt, prismatic crystals, m. p. 245° [decomp.] after becoming discoloured at 200°), or 5:5-dichlorobarbituric acid, colourless crystals, decomp. 209—211°. 5-Chlorobarbituric acid may also be obtained by the action of aqueous hydrochloric acid on the 5-bromo-acid; it is relatively very stable towards boiling water. Attempts to prepare 5-bromobarbituric acid from the 5-chloro-acid and hydrobromic acid were unsuccessful, probably by reason of the limited stability of the bromo-acid in boiling aqueous solution.

5:5'-Dichlorohydurilic acid is readily hydrolysed by boiling

water to 5-chlorobarbituric acid and alloxan: $C_8H_4O_6N_4Cl_2 + H_2O = C_4H_3O_3N_2Cl + C_4H_2O_4N_2 + HCl$. *Ammonium 5:5'-dichlorohydrilate* forms colourless or pale pink, hydrated crystals ($+2.5H_2O$), whereas the anhydrous compound is dark red; it has m. p. about 235° after becoming discoloured at 140° .

5:5-Dichlorobarbituric acid is transformed by the prolonged action of chlorine into trichloroacetylcarbamide; the course of the reaction appears to be somewhat complicated, since 5:5'-dichlorohydrilic is formed as by-product.

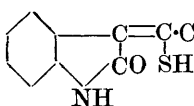
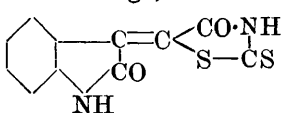
Under definite conditions, barbituric acid is converted by bromine and alkali hydroxide into tribromoacetylcarbamide, whereby potassium 5-bromobarbiturate is intermediately produced; the subsequent addition of bromine causes evolution of carbon dioxide and formation of tribromoacetylcarbamide, in accordance with the equation $C_4H_2O_3N_2BrK + HBrO + Br_2 = C_3H_3O_2N_2Br_3 + CO_2 + KBr$. Tribromoacetylcarbamide is also obtained from 5:5-dibromobarbituric acid and bromine, but the production of the dibromo-acid is not observed intermediately when barbituric acid is used as initial material.

H. W.

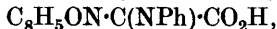
Dyes Derived from Phenanthraquinone. III. Phenanthriminazoles. ANUKUL CHANDRA SIRCAR and GOPAL CHANDRA SIRCAR (T., 1923, 123, 1559—1565).

The Use of Rhodanine in Organic Syntheses. III. Derivatives of Oxindole. CH. GRÄNACHER and A. MAHAL (*Helv. Chim. Acta*, 1923, 6, 467—482).—A number of new oxindole derivatives have been synthesised from the condensation product of isatin with rhodanine. According to Andreasch (A., 1917, i, 663), isatin condenses with rhodanine in the 2-position to give "rhodanine-2-indolindigo," but it is now shown that condensation takes place

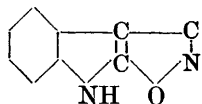
in the 3-position with formation of 3-rhodanylideneoxindole (annexed formula), which forms a pyridine additive compound, $(C_{11}H_6O_2N_2S_2)_2 \cdot C_5H_5N$, crystallising in red needles. The isomeric ψ -indoxylidene-rhodanine is obtained by condensing isatinilide with rhodanine. By warming 3-rhodanylideneoxindole in 10% sodium hydroxide solution, oxindole-3- α -thiolacetic acid (annexed formula) is obtained, which forms a bright orange powder. The thiol group is not removed by long boiling with ammonia. The isomeric ψ -indoxylidene- α -thiolacetic acid forms a reddish-brown powder which begins to decompose at 148° . When oxindole-3- α -thiolacetic acid is reduced with zinc and concentrated hydrochloric acid, oxindole-3-acetic acid is formed, colourless needles, m. p. 218 — 219° . Only traces of skatolecarboxylic acid could be obtained by further reduction with sodium and amyl alcohol. By acetic anhydride, oxindole-3-acetic acid is converted into diacetyloxindole-3-acetic acid (*N*-acetyloxindole-3-acetic acetic anhydride), lustrous leaflets, m. p. 228 — 230° . By heating with aniline, oxindole-3- α -thiolacetic acid is converted into aniline



oxindole-3- α -aniloacetate, yellow needles, m. p. 232°, sintering from 220°. The free *oxindole-3- α -aniloacetic acid*,

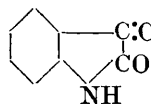


forms a yellow, crystalline powder, m. p. 232°. The *silver salt*, which forms bunches of needles, is decomposed by water. *Oxindole-3-glyoxylic acid* is obtained by hydrolysis of the above aniline salt in boiling acetic acid solution, and crystallises in orange leaflets, decomposing at 265—270°. Its ammoniacal solution reduces a solution of a silver salt. By the action of hydroxylamine on *oxindole-3- α -thiolacetic acid* there is formed, not the expected oximino-compound, but *indoisooxazole- γ -carboxylic acid* (annexed formula) by the closure of an isooxazole ring. The compound crystallises in yellow cubes or lustrous, yellow leaflets, m. p. 251°. When the ammonium

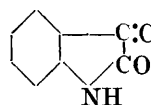


salt of this acid reacts with silver nitrate, the *silver oxindole-3- α -oximinoacetate* is formed, crystallising in yellowish-white needles.

N-Methylisatin condenses with rhodanine to form *3-rhodanylidene-N-methyloxindole*, crystallising in red needles. By alkali, it is converted into the corresponding α -thiolacetic acid.



The oxindole-3-aldehyde described by Friedländer (A., 1910, i, 592) does not condense with rhodanine, probably because it is not a true aldehyde, but has the tautomeric acid-structure (annexed formula). This is confirmed



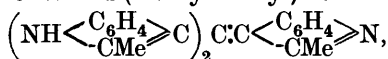
by the strongly acid properties of the aldehyde. With benzenesulphonyl chloride, it forms a *phenylsulphonoxindole-3-aldehyde*, (annexed formula) brownish-yellow needles, m. p. 155—160° (decomp.); and with benzoyl chloride it gives *benzoyloxindole-3-aldehyde*, yellow needles, m. p. 192°.

E. H. R.

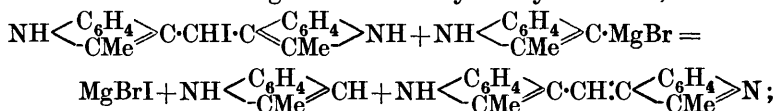
The Action of Potassium Hydroxide on Chloroacetyl-*p*-anisidine. FRÉDÉRIC REVERDIN (*Helv. Chim. Acta*, 1923, 6, 424—428).—Although nitro-derivatives of chloroacetyl-*p*-anisidine are readily hydrolysed by dilute alkali hydroxides, in the case of chloroacetyl-*p*-anisidine itself very little *p*-anisidine is formed, but condensation products arise, differing according to the solvent used. With aqueous 4% potassium hydroxide on the water-bath, a compound is formed, m. p. 185—186°, crystallising in white needles, having the composition $\text{C}_{25}\text{H}_{26}\text{O}_5\text{N}_3$ or $\text{C}_{25}\text{H}_{27}\text{O}_5\text{N}_3$, and a second compound, m. p. 133°. The first compound gives with lead peroxide in acetic acid solution a blue coloration, changing through violet to brown; it can be sulphonated, and with nitrous acid forms a derivative, yellow needles, m. p. 168°, which may be a nitro-derivative. With alcoholic potassium hydroxide, chloroacetyl-*p*-anisidine gives a crystalline product, m. p. 257—258°, needles, which does not give a coloration with lead peroxide, and appears to be 2:5-diketo-1:4-di-*p*-anisylpiperazine. It forms a tetranitro-derivative, m. p. 282—283° (decomp.).

E. H. R.

Syntheses in the Indole Group. IX. Indyl Colouring Matters derived from Methane. BERNARDO ODDO and FRANCESCO TOGNACCHINI (*Gazzetta*, 1923, 53, i, 271—275).—The action of magnesium 2-methylindolyl bromide on iodoform yields an orange-yellow compound, m. p. 231—232°, which imparts its colour to wool and silk and yields a leuco-base on reduction. According to the simplest interpretation of the reaction, this leuco-base would have the formula $(\text{NH} \langle \text{C}_6\text{H}_4 \rangle_{\text{CMe}} \text{C})_3\text{CH}$, and would give on oxidation 2-methylindolenine-di(methylindolyl)methane,



which would be identical with the compound obtained by Ellinger and Flamand (A., 1909, i, 846; 1911, i, 329). Since, however, the interaction of iodoform and magnesium phenyl bromide yields principally tetraphenylethane (cf. Oddo and Binaghi, A., 1922, i, 313), it is probable that the first product of the above reaction is 2-iododi-methylindolyl-methane, and that this then reacts with a further molecule of magnesium 2-methylindolyl bromide, thus:



the final product would then be 2-methylindolyl-2-methylindolidene-methane. Alternatively, the latter might be formed by auto-oxidation of tetra-2-methylindolylethane, which possibly constitutes the first product of the reaction.

The *tartrate* of the orange-yellow base, $\text{C}_{19}\text{H}_{16}\text{N}_2 \cdot \text{C}_4\text{H}_6\text{O}_6$, m. p. 167°, and the sulphate (cf. Ellinger and Flamand, *loc. cit.*) were analysed.

T. H. P.

Preparation of certain Azo-derivatives. DINO BIGIARI and GINO CARRARA (*Gazzetta*, 1923, 53, i, 285—290; cf. A., 1922, i, 878).—The authors have prepared various azoxyphenols by the action of acetic acid and hydrogen peroxide on the corresponding azo-derivative, and various nitro-derivatives of azo-compounds by treating the latter with nitrous acid. When the residue $\text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$ is present, this reagent, even in marked excess, yields a mono-nitro-derivative with the nitro-group in the ortho-position to the hydroxyl, whereas the radicals NPh , $\text{NO} \cdot \text{Ph}$, and $\text{NO} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$ are inert towards nitrous acid. In this way, it is therefore possible to establish the position of the azo-oxygen in the azoxyphenols, α -azoxyphenol yielding a nitro-derivative, and β -azoxyphenol remaining unchanged, when treated with nitrous acid. A quantitative yield of nitro-derivative is obtained with the azoxyphenols but not with the azophenols. *p*-Azophenol is partly oxidised to *p*-nitrophenol by the action of nitrous acid, this reaction being analogous to the oxidation of hyponitrous acid to nitric acid by the action of permanganate in alkaline solution.

The yield of *p*-azophenol may be raised from 36—42% to 60—

c c* 2

70% by varying the procedure given by Willstätter and Benz (A., 1906, i, 990).

p-Azoxyphenol forms lustrous, reddish-yellow needles, m. p. 224° (decomp.), a molecule of water of crystallisation being lost at 100°; Fischer and Wacker's preparation (A., 1888, 1286) was impure.

Diacetyl-*p*-azoxyphenol has m. p. 163° (Wohl and Goldenberg, A., 1904, i, 210, gave m. p. 165°).

α -m-Nitro-*p*-hydroxyazoxybenzene, $\text{C}_6\text{H}_5\cdot\text{NO}\cdot\text{N}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{NO}_2$, forms transparent, greenish-yellow, tabular crystals, m. p. 125°.

m-Nitro-*p* : *p'*-dihydroxyazoxybenzene,
 $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}\cdot\text{N}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{NO}_2$,
 crystallises in reddish-yellow chips, m. p. 193° (decomp.).

When treated with nitrous acid, *p*-azophenol yields the *m* : *m'*-dinitro-derivative (Robertson, T., 1913, 103, 1473), together with *p*-nitrophenol and a black, pulverulent compound, m. p. 174° (decomp.), corresponding in composition with Willstätter and Benz's azoquinhydrone (*loc. cit.*). T. H. P.

Hydrochlorides of *p*-Aminoazo-compounds. D. VORLÄNDER and ERNST WOLFERTS (*Ber.*, 1923, 56, [B], 1229—1239).—The addition of hydrogen chloride to a number of *p*-aminoazo-compounds under widely varied conditions has been examined. The observations are not readily explicable by the hypothesis that quinonoid compounds are produced.

The following salts of *p*-dimethylaminoazobenzene are described : the anhydrous *monohydrochloride*, from equivalent quantities of base and hydrogen chloride in anhydrous ether, dark, reddish-violet crystals, m. p. 168—174°, or black to brownish-red crystals, m. p. 162—167°, decomp. about 173°, prepared by passing dry air over the hydrated monohydrochloride or the dihydrochloride : the anhydrous *dihydrochloride*, m. p. about 162°, decomp. about 173°, a pale red or red, crystalline powder obtained by passing dry hydrogen chloride over the anhydrous monohydrochloride at the atmospheric temperature ; a mixture of the two hydrochlorides (or a compound of a molar proportion of base with one and a half molar proportions of acid), clusters of red needles, m. p. about 172°, from solutions of the base in anhydrous ether or light petroleum saturated with hydrogen chloride ; the monohydrated monohydrochloride, purple-red needles with bluish-violet glance, m. p. 95—105°, decomp. about 115°, from dilute hydrochloric acid ; the *compound*, probably $\text{C}_{14}\text{H}_{15}\text{N}_3\cdot 2\text{HCl}\cdot 4\text{H}_2\text{O}$, dark red leaflets, m. p. about 60°, decomp. about 90°, from solutions of the base in hydrochloric acid (*d* 1.1) ; the *monohydrochloride* (+ C_6H_6), lustrous, red leaflets, m. p. about 165° (decomp.), prepared from the base and hydrogen chloride in the presence of benzene ; the *monohydrochloride* (+ CHCl_3), lustrous, red needles, m. p. about 166°, decomp. about 175°, from the base and hydrogen chloride in chloroform solution. (The melting and decomposing points depend greatly on the previous history of the specimens and the manner of heating.)

p-Aminoazobenzene hydrochloride does not show any tendency

to combine with benzene, chloroform, or ether when formed in the presence of these media. It shows little ability to combine with a further molecule of hydrogen chloride.

The alteration in colour caused by the transformation of the mono- to the di-hydrochloride is more pronounced in the case of *p*-dimethylamino-*p*'-methoxyazobenzene, m. p. 161—163°. The *monohydrochloride* is blue or bluish-violet, whereas the *dihydrochloride* is yellowish-red. The transformation can be effected readily in aqueous hydrochloric acid solutions of suitable concentration and reversed by diluting on warming the solution. The hydrogen chloride is less firmly retained than in the case of the corresponding non-methoxylated compound.

pp'-Tetramethyldiaminoazobenzene behaves very similarly to *p*-dimethylamino-*p*'-methoxyazobenzene. It gives a blue *monohydrochloride*, m. p. about 220°, and a red *dihydrochloride*, m. p. about 190°, which do not contain solvent of crystallisation. Both compounds readily lose hydrogen chloride with the formation of the free base. At the atmospheric temperature, the red dihydrochloride combines further with hydrogen chloride, whereby its colour becomes only slightly paler. H. W.

A Drop Method for the Study of the Coagulation of Proteins.

JAN BEČKA (*Biochem. Z.*, 1923, 137, 456—464).—To save time, labour, and material involved in making large numbers of dilutions in test-tubes of reagents and proteins, the author uses a glass plate with black undersurface. By means of a capillary tube drops of the previously prepared dilutions can be placed rapidly and systematically on the plate and mixed with drops of the suitably diluted precipitant. A glance shows the limits of coagulation at the different dilutions. H. K.

The Structure of Proteins. EMIL ABDERHALDEN (*Z. physiol. Chem.*, 1923, 128, 119—128).—Diketopiperazine compounds have been isolated from the hydrolysis of protein. Silk fibrin when hydrolysed with 70% sulphuric acid yields *glycylalanine anhydride*, $C_5H_8O_2N_2$, m. p. 247°, $[\alpha]_D^{20} -4.7^\circ$ (2% solution in water). Casein yields *l-leucyl-d-valine anhydride*, $C_{11}H_{20}O_2N_2$, $[\alpha]_D^{20} -45.9^\circ$ (in acetic acid), and also *l-phenylalanyl-d-alanine anhydride*. From gliadin, in the same way, *l-prolyl-l-leucine anhydride*, m. p. 160°, $[\alpha]_D^{20}$ about -120° (in alcohol), and *l-prolyl-glycine anhydride*, m. p. 209°, $[\alpha]_D^{20} -206.5^\circ$ (in water), were obtained. The structure of proteins is discussed in the light of these findings, particularly with regard to the possibility of the existence of such diketopiperazine rings in the protein molecule. W. O. K.

Protein Chemistry. III. Iodination of Proteins with Nitrogen Iodide. F. BLUM and E. STRAUSS (*Z. physiol. Chem.*, 1923, 127, 199—207).—By the action of iodine in ammoniacal solution in the cold on proteins, iodoproteins are obtained which give the biuret reaction and are more closely allied to the original protein than iodoproteins previously obtained. That from serum globulin contains 6.6% of iodine, that from ovalbumin 5.2%, and that from thyreoglobulin 4.8%. W. O. K.

Partial Decomposition of Protein. EMIL ABDERHALDEN and HIDEKI SUZUKI (*Z. physiol. Chem.*, 1923, **127**, 281—290).—Goose feathers were allowed to remain five days at room temperature with ten times their weight of 70% sulphuric acid, and the mixture then poured into water. The products of hydrolysis were fractionated. A product, $C_{17}H_{26}O_5N_4$, has been isolated which is apparently prolylprolylglycylprolyl, $[\alpha] -147.5^\circ$.

W. O. K.

The Rotation and Molecular Weight of Casein. J. ZAYKOWSKY (*Biochem. Z.*, 1923, **137**, 562—569).—The rotation of pure casein prepared by avoiding the action of hydroxyl-ions has been examined under a variety of conditions. A 1% solution in 10% potassium acetate has $[\alpha]_D^{18} +81.55^\circ$; somewhat higher values are found in sodium acetate and sodium salicylate solutions, and also with increasing concentration of the casein. Warming in neutral solution has no influence on the rotation. In alkaline solutions, the rotation falls off and especially rapidly on warming at 80° . Various concentrations of borax have no influence on the rotation of 2% casein solution ($[\alpha]_D^{18} +95.3^\circ$). In *N*/10-hydrochloric acid the rotation was 88.97° . When increasing volumes of *N*/10-sodium, potassium, calcium, or barium hydroxides are added to casein, the rotation increases to a maximum at 8.0 c.c. per 0.25 g. of casein. This corresponds with 0.0032 g. equivalents of alkali per g. of casein, whereas 1 g. of casein requires 0.0008 g. equivalent of alkali to render it neutral to phenolphthalein. If the latter point corresponds with a bi-metallic salt, then casein is an octabasic acid and has a molecular weight of about 20,000.

H. K.

Hæmatoidin. HANS FISCHER and FRITZ REINDEL (*Z. physiol. Chem.*, 1923, **127**, 299—316).—From a study of the crystallographic and general properties of hæmatoidin, $C_{33}H_{36}O_6N_4$, it is concluded that it is identical with bilirubin. Both give similar compounds on coupling with diazo-salts.

W. O. K.

Bile Pigments. VII. HANS FISCHER and GEORG NIEMANN (*Z. physiol. Chem.*, 1923, **127**, 317—328).—If bilirubin is reduced with hydrogen and palladium, mesobilirubin is obtained (cf. A., 1914, i, 1135; 1915, i, 148) of which the *dimethyl ester*, *hydrochloride*, $C_{34}H_{44}O_6N_4 \cdot 2HCl$, lustrous, green leaflets, red by transparent light, m. p. 190° , is now described. On further reduction, mesobilirubin yields mesobilirubinogen, m. p. 202° . A colloidal solution of mesobilirubin is formed when a mixture of mesobilirubin (0.1 g.) and taurocholic acid (0.1 g.) is dissolved in alkali and precipitated with acid. This colloidal solution fluoresces strongly. Mesobilirubin, when treated with concentrated nitric acid, yields methylethylmaleimide.

W. O. K.

Synthetic Researches on the Constitution of Bile Pigments. I. HANS FISCHER and ERNST LOY (*Z. physiol. Chem.*, 1923, **128**, 59—84).—From ethyl 4-hydroxy-2-methylpyrrole-3-carboxylate, on treatment with anhydrous hydrocyanic acid and hydrochloric acid in chloroform solution, is formed the corresponding *aldimine*,

$C_9H_{12}O_3N_2$, brown needles, m. p. 235° , which is hydrolysed with dilute sodium hydroxide solution to yield *ethyl 4-hydroxy-2-aldehydo-2-methylpyrrole-4-carboxylate*, pale yellow needles, m. p. 187° (*semicarbazone*, yellow leaflets, decomp. 243° ; *oxime*, colourless needles, m. p. 202° ; *acetyl* derivative of the oxime, $C_{11}H_{14}O_5N_2$, yellow needles, m. p. 115°). If the aldimine or the free aldehyde is heated on the water-bath with dilute acid, condensation takes place and *bis-(4-hydroxy-3-carbethoxy-2-methylpyrrol)methene*, $C_{17}H_{20}O_6N_2$, is formed, yellow needles, decomp. $240-275^\circ$. The aldehyde also condenses with ethyl 2:4-dimethylpyrrole-3-carboxylate to yield *(4-hydroxy-3-carbethoxy-2-methylpyrrol-2:4-dimethyl-3-carbethoxypyrrolidyl)methene*, $C_{18}H_{22}O_5N_2$, thin, yellow needles, decomp. 245° , which is reduced with hydrogen in presence of platinum black to form *(4-hydroxy-3-carbethoxy-2-methylpyrrol-2:4-dimethyl-3-carbethoxypyrryl)methane*, pale yellow needles, m. p. 191° . Acetic acid-hydrogen iodide acts on ethyl 4-hydroxy-2-methylpyrrole-3-carboxylate to yield a compound, $C_{16}H_{20}O_5N$, colourless leaflets, m. p. 158° , described by Benary and Silbermann (A., 1913, i, 651) and the same compound is formed in attempting to condense the hydroxypyrrrole with acetonitrile in chloroform solution in presence of hydrogen chloride. It is apparently *5-(3-carbethoxy-2-methyl-4-pyrrol)-4-hydroxy-3-carbethoxy-2-methylpyrrole*.

Condensation of ethyl 4-hydroxy-2-methylpyrrole-3-carboxylate with formic acid yields the above-mentioned *bis-(4-hydroxy-3-carbethoxy-2-methylpyrrol)methene*, decomp. $240-275^\circ$, and also *bis-(2-methyl-3-carbethoxypyrryl)furan*, yellow needles, decomp. 282° . The latter compound is also formed on heating ethyl 4-hydroxy-2-methylpyrrole-3-carboxylate with oxalic acid, and also there is formed in the reaction *bis-(4-hydroxy-3-carbethoxy-2-methylpyrrol)diketone*, yellow needles, m. p. $245-250^\circ$. Ethyl oxalate condenses with ethyl 4-hydroxy-2-methylpyrrole-3-carboxylate in presence of sodium ethoxide, and a compound, $C_{10}H_{11}O_6N$, fine white needles, decomp. 201° , which is apparently *4-hydroxy-3-carbethoxy-2-methylpyrrol-5-pyruvic acid*, is obtained. Ethyl 4-hydroxy-2-methylpyrrole-3-carboxylate and chloroacetonitrile condense in ethereal solution in presence of hydrogen chloride to form *ethyl 4-hydroxy-5-chloroacetyl-2-methylpyrrole-3-carboxylate*, thin white needles, decomp. 243° .

The compound formed by the condensation of ethyl 5-aldehydo-2:4-dimethylpyrrole-3-carboxylate with ethyl 4-hydroxy-2-methylpyrrole-3-carboxylate, is *(3-carbethoxy-2:4-dimethylpyrrol-4-hydroxy-3-carbethoxy-2-methylpyrrolidyl)methene*, which forms orange-yellow leaflets from alcohol, which decompose at 244° (*hydrochloride*, orange-red needles, m. p. 207°). This compound, on reduction with hydrogen in presence of platinum, yields *4-hydroxy-3-carbethoxy-2-methylpyrrol-3-carbethoxy-2:4-dimethylpyrrylmethane*, already mentioned as being formed by the reduction of the isomeric methene compound. Ethyl 4-hydroxy-2-methylpyrrole-3-carboxylate similarly condenses with (a) ethyl 4-aldehydo-1-*p*-tolyl-2:5-dimethylpyrrole-3-carboxylate to yield a compound,

$C_{25}H_{28}O_5N_2$, yellow leaflets, m. p. 211° , which is again decomposed on coupling with diazobenzene sulphonic acid, (b) ethyl 4-aldehydo-2:5-dimethylpyrrole-3-carboxylate to yield a *compound*, yellow, glistening leaflets, m. p. 240° , and (c) with ethyl 4-aldehydo-1-phenyl-2:5-dimethylpyrrole-3-carboxylate to yield a *compound*, microscopic needles, decomp. 210° .
W. O. K.

I. Nucleotides Formed by the Action of Boiled Pancreas on Yeast-nucleic Acid. II. Formation of Nucleotides from Yeast-nucleic Acid by the Action of Sodium Hydroxide at Room Temperature. WALTER JONES and M. E. PERKINS (*J. Biol. Chem.*, 1923, **55**, 557—565, 567—568).—The authors have now isolated the four nucleotides from the product of the action of boiled pancreas extract on yeast-nucleic acid (cf. A., 1920, i, 687; 1922, i, 479; Levene, A., 1921, i, 821); incidentally, the acid brucine salt of guanine nucleotide has been obtained in a crystalline form, and a crystalline compound which is probably the lead ammonium salt of cytosine nucleotide has been isolated. The decomposition of the nucleic acid into its constituent nucleotides is, however, by no means complete; intermediate substances are present in the final product. It is considered that only nucleotide linkings are ruptured by the action of the thermostable agent from pig's pancreas, and, since there is no increase in the titratable acidity of the mixture during the process, the conclusion is drawn that at least one nucleotide linking is of the ether type between the carbohydrate groups. Conditions have, however, been devised whereby yeast-nucleic acid is apparently quantitatively decomposed into its mononucleotides by the action of 1% sodium hydroxide at the ordinary temperature, and in this case the alkalinity of the solution has been observed to diminish progressively as the decomposition proceeds, thus indicating the liberation of weak acids during the formation of the nucleotides. From this result it is concluded that one or more of the nucleotide linkings in nucleic acid are between a phosphoric acid and a carbohydrate group. A new formula is consequently proposed for yeast-nucleic acid in which two such linkings are present, the third being of the ether type mentioned above.
E. S.

The Action of Alkali on Thymus-nucleic Acid and Yeast-nucleic Acid. H. STEUDEL and S. NAKAGAWA (*Z. physiol. Chem.*, 1923, **128**, 129—134).—The rotatory power of thymus-nucleic acid obtained from herring sperm or from spleen is not influenced by remaining several days with alkali, whereas that of yeast-nucleic acid changes from dextro to lævo. Natural or synthetical clupein nucleate, when left with alkali shows only a small decrease in its lævorotation. This small change is probably to be ascribed to the protein portion. Sodium guanylate undergoes a small change in rotation when left in contact with hydrochloric acid.
W. O. K.

Yeast-nucleic Acids. IV. A Simple Method of Isolating Adenylic Acid. H. STEUDEL and E. PEISER (*Z. physiol. Chem.*, 1923, **127**, 262—267).—After separation of guanylic acid as the

sodium salt (A., 1922, i, 279), adenylic acid may be isolated from yeast by precipitation as the lead salt. Adenylic acid, m. p. 195° , $[\alpha]_D^{20} = 41.78^{\circ}$, has the formula $C_{10}H_{14}O_7N_5P, H_2O$. W. O. K.

Fission of Proteins by Formic Acid. N. D. ZELINSKY and V. S. SADIKOV (*Biochem. Z.*, 1923, **137**, 397—400).—Formic acid of various strengths proved unsuitable for the hydrolysis of proteins even using an autoclave at 180° . Examination of the products of the action of 10% formic acid on gelatin only gave one amino-acid, glycine. Even after hydrolysis with hydrochloric acid, the products are very complex. Formic acid appears to effect condensation. H. K.

Relation between the Fermentative and Catalytic Fission of Proteins. VLADIMIR SERGIEVITSCH SADIKOV and N. D. ZELINSKY (*Biochem. Z.*, 1923, **137**, 401—404).—There is a rough parallelism between the proportion of ether, chloroform, and ethyl acetate soluble extracts from the catalytic fission (1% phosphoric acid at 180°) and from the fermentative fission (pepsin, trypsin, and erepsin) of gelatin and casein indicating similarity of the chemical processes involved. H. K.

The Specificity of Enzymes. III. The Affinity of Enzymes for Stereoisomeric Sugars. RICHARD WILLSTÄTTER and RICHARD KUHN (*Z. physiol. Chem.*, 1923, **127**, 234—242).—The effect of α - and β -glucose on the rate of inversion of sucrose by invertase has been compared. α -Glucose causes no change in k , the velocity constant of the reaction, but β -glucose causes a decrease from 158.5 to 137.5. A similar difference between the effects of α - and β -glucose is observed in the case of the hydrolysis of raffinose by invertase. In the case of maltase, however, acting on maltose, both α - and β -glucose have approximately the same effect, β -glucose being at most only slightly more effective than α -glucose. The enzymes of the emulsin complex in their action on salicin and helicin, are, like invertase, inhibited to a greater degree by the addition of β -glucose than of α -glucose. W. O. K.

Saccharase. II. H. VON EULER and K. JOSEPHSON (*Ber.*, 1923, **56**, [B], 1097—1103).—The purest saccharase preparations which have been obtained resemble closely the natural proteins in their chemical nature. The nitrogen content, which increases with increasing purity of the enzyme, is of the same order of magnitude as the mean value found for the proteins, and it is probable than an eventual, not very considerable, increase in the purity of the enzyme would cause the disappearance of the observed difference. The amino-nitrogen is only a small fraction of the total nitrogen. Hydrolysis of saccharase with concentrated acids increases the number of free amino-groups in the same manner as in the case of the natural proteins. It appears highly probable that purified saccharase preparations have a sulphur content which is proportional to their activity; the order of magnitude is identical with that exhibited by the proteins. The preparations of saccharase ($f = 100$ —230), therefore, appear to consist largely of substances which

are closely allied to the proteins. This hypothesis is in harmony with their change in thermostability with temperature. H. W.

Emulsin. II. BURCKHARDT HELFERICH, PAUL ELIAS SPEIDEL, and WALTER TOELDTE (*Z. physiol. Chem.*, 1923, **128**, 99—108).—The activity of emulsin is reduced by the action on it of pepsin or by keeping it under methyl alcohol. Ultra-filtration under pressure does not cause much decrease in its activity. Methylation with diazomethane or acetylation with acetyl chloride inactivates it.

W. O. K.

The Action of Emulsin on the System Hydrocyanic Acid-Benzaldehyde-Benzaldehydecyanohydrin. E. NORDEFELDT (*Biochem. Z.*, 1923, **137**, 489—495).—The velocity of fission of benzaldehydecyanohydrin is independent of the presence of emulsin and depends solely on the acidity of the solution. The *d*-cyanohydrin is formed (shown previously) in the presence of emulsin more rapidly than the *lævo*-form and is now found to undergo fission more rapidly, resulting in a preponderance of the cyanohydrin.

H. K.

Reversibility of the Action of Urease of Soja Bean. HERBERT DAVENPORT KAY (*Biochem. J.*, 1923, **17**, 277—285).—Carbamide is produced in very small quantities during the action of urease on a mixture of ammonium carbonate and carbamate in strong solution in water at room temperatures under conditions which preclude its formation by any other means than enzymic synthesis. The action of urease is therefore reversible. The methods used for the estimation of the synthesised carbamide were the hydrolysis of the compound with urease and consequent estimation of the hydrogen-ion concentration, and the xanthhydrol method. S. S. Z.

Histozyyme. I. I. A. SMORODINCEV (*J. Russ. Phys. Chem. Soc.*, 1920, **51**, 156—177).—Histozyyme is found in the greatest quantities in the kidneys of pigs and the skeletal muscles of dogs. All the organs of dogs examined, namely, the liver, kidneys, spleen, lungs, and cardiac and skeletal muscles, have the property of hydrolysing hippuric acid with the production of benzoic acid and glycine; the histozyyme content being smallest in the liver. This enzyme is also found in the kidneys of calves and horses. The best sterilisers for histozyyme are sodium fluoride or toluene. A number of experiments carried out with this enzyme on the hydrolysis of hippuric and other substituted amino-acids show that it is almost insoluble in water or aqueous glycerol, and must therefore be considered as an endo-ferment. Its activity is not very pronounced, being greatest for hippuric acid with a 4% emulsion, the rate of hydrolysis being greatest at the beginning of the reaction, and then slowly decreasing. With more dilute solutions of hippuric acid the percentage hydrolysis is greater than for more concentrated solutions. Chloroform, phosphates, physiological salt solution, and alkalis have a retarding influence on the hydrolysis, the presence of only 0.004% of sodium hydroxide having a marked effect. Sulphuric acid, on the other hand, accelerates the reaction. At 8°, histozyyme exhibits

a feeble hydrolytic action on hippuric acid, whilst at 37° its action is four times as great as at 15°. It has no action on β -alanine, *dl*- β -benzamido-butyric, benzamidoisobutyric, and *l*- α -benzamido-butyric acids, but is capable of hydrolysing *d*- α -benzamido-butyric acid, and *l*-leucine, with the liberation of benzoic acid, and glycocholic and taurocholic acids with the liberation of cholic acid. Histozyyme is also probably the ferment responsible for the hydrolysis of laurylglycine, laurylalanine, laurylalanylglycine, butyrylglycine, and butyrylalanine with the production of the corresponding fatty acids. In view of the above reactions, it is thought desirable that histozyyme should be renamed "aminoacylase," in order to bring its name into line with those of other ferments. R. T.

Histozyyme. II. I. A. SMORODINCEV (*J. Russ. Phys. Chem. Soc.*, 1920, **51**, 178—182).—A preparation of histozyyme from the kidneys of dogs has only half the hydrolytic power of the juice expressible from them, whilst from the liver, the latter is six times less active than a preparation made from the organ itself. More of the ferment is contained in the kidneys of dogs than in those of oxen, or than in the liver of dogs. The precipitation of histozyyme from the expressed juice by means of acetone slightly reduces its activity, as does the prolonged action of ether. Autolysis greatly reduces the hydrolytic power of the juice, and to a lesser extent that of the preparation of histozyyme obtained from the latter by precipitation with acetone. R. T.

Oxidising Enzymes. VI. Tyrosinase. MURIEL WHELDALÉ ONSLOW (*Biochem. J.*, 1923, **17**, 216—219).—In corroboration and extension of Bach's hypothesis that tyrosinase consists of at least two enzymes (A., 1914, i, 445) the author puts forward a suggestion that this enzyme is a mixture of a water-splitting enzyme (reductase or deaminase), a carboxylase, and an oxydase. S. S. Z.

The Influence of Thorium-X on the Catalase of Liver. ALFRED MAUBERT, LÉON JALoustRE, and PIERRE LEMAY (*Compt. rend.*, 1923, **176**, 1502—1505).—The presence of thorium-X affects the action of the catalase of liver on hydrogen peroxide, activating it when present in small quantities, but inhibiting it if the quantities are increased beyond a certain point. This is apparently due to the α -radiation, as thorium emanation has a similar effect. H. J. E.

Enzymic Fat Synthesis. II. L. SPIEGEL (*Z. physiol. Chem.*, 1923, **127**, 208—209; cf. A., 1922, i, 694).—The addition of calcium chloride increases the yield of fat obtained from glycerol and fatty acids by the action of an enzyme emulsion prepared from fresh sunflower seeds. W. O. K.

The Sulphur Content of Arsphenamine [Salvarsan] and its Relation to the Mode of Synthesis and the Toxicity. IV. WALTER G. CHRISTIANSEN (*J. Amer. Chem. Soc.*, 1923, **45**, 1316—1321).—Conclusions previously drawn respecting the distribution of sulphur in salvarsan (A., 1922, i, 601) have been substantiated.

The use of pure instead of commercial sodium hyposulphite for the reduction of 3-nitro-4-hydroxyphenylarsinic acid or the corresponding amino-acid results in a greater rate of reduction, a larger yield, and a higher sulphur content. These factors are controlled by the acidity of the reduction mixture, and the addition of sodium carbonate to pure sodium hyposulphite slows down the rate of reduction, decreases the yield, and lowers the sulphur content. The use of acetic acid with commercial hyposulphite has the opposite effect. Specimens of salvarsan prepared by means of pure hyposulphite are more soluble in water than if commercial hyposulphite is used.

W. S. N.

Arsenated Derivatives of Diketophenylpyrrolidine. JOHN R. JOHNSON and ROGER ADAMS (*J. Amer. Chem. Soc.*, 1923, 45, 1307—1315).—Details are given of the preparation of nitrophenylarsinic acids by the diazotisation of the corresponding amine and treatment of the diazo-derivative with sodium arsenite solution. *o*-Methoxyphenylarsinic acid, white needles, m. p. 193—194°, is obtained by the use of *o*-anisidine; similarly, *p*-anisidine gives *p*-methoxyphenylarsinic acid. *p*-Nitro-*o*-methoxyphenylarsinic acid, pale yellow needles, m. p. above 250°, is prepared from *o*-methoxy-*p*-nitroaniline, which is formed in 60% yield, together with 5-nitro-2-methoxyaniline (32%), by the action of ice-cold nitric acid on *o*-acetanisidine in acetic acid-acetic anhydride solution. *o*-Arsanilic acid, 3-amino-*o*-tolylarsinic acid, 5-amino-*o*-tolylarsinic acid, and *p*-amino-*o*-methoxyphenylarsinic acid, white needles, m. p. 203—204° (208—209°, if heated rapidly), are prepared by the reduction of the corresponding nitro-compounds by means of ferrous chloride. Arsenated derivatives of diketophenylpyrrolidine are produced by boiling pyruvic acid with an alcoholic solution of an aminoarylarsinic acid and an aromatic aldehyde, but aminoarylarsinic acids having a substituent in the *ortho*-position to the amino-group form benzylidene derivatives which do not react with pyruvic acid. The reaction is not applicable to the simple aliphatic aldehydes. Benzaldehyde, *p*-arsanilic acid, and pyruvic acid (or ethyl pyruvate) give 4 : 5-diketo-2-phenylpyrrolidine-1-*p*-phenylarsinic acid, $\text{CO}-\text{CO} \rightarrow \text{CH}_2 \cdot \text{CHPh} \rightarrow \text{N} \rightarrow \text{AsO}_3\text{H}_2$ previously described as 4-carboxy-2-phenylquinoline-6-arsinic acid (A., 1922, i, 187). The quinoline structure was originally assigned to this compound because it loses carbon dioxide on heating. It is now found, however, that 4 : 5-diketo-2-phenyl-1-*p*-nitrophenylpyrrolidine also loses carbon dioxide when boiled with ethyl benzoate, particularly in the presence of an equal quantity of *o*-nitrophenylarsinic acid. Moreover, when the compound is subjected to alkaline fusion, aniline is the chief nitrogenous product. It is held, therefore, that the pyrrolidine structure is firmly established for this compound. Benzylidene-*p*-arsanilic acid, heavy, white, granular crystals, m. p. 225° (decomp.), is formed in small quantities during the preparation. By using *o*-methoxybenzaldehyde in place of benzaldehyde, 4 : 5-diketo-2-*o*-anisylpyrrolidine-1-*p*-phenylarsinic acid is obtained as a pale

yellow powder, m. p. 173—176° (decomp.). Anisaldehyde condenses with arsanilic acid and pyruvic acid to give 4:5-diketo-2-*p*-anisylpyrrolidine-1-*p*-phenylarsinic acid, white crystals, m. p. 164—165° (decomp.). 4:5-Diketo-2-*mp*-methylenedioxyphenylpyrrolidine-1-phenylarsinic acid, light yellow powder, m. p. 176—178° (decomp.), is formed from arsanilic acid, piperonal, and pyruvic acid, whilst the use of *p*-chlorobenzaldehyde leads to the formation of 4:5-diketo-2-*p*-chlorophenylpyrrolidine-1-*p*-phenylarsinic acid, white powder, m. p. 163—165° (decomp.). Condensation products are also formed from salicylaldehyde, *p*-dimethylaminobenzaldehyde, or cinnamaldehyde, but not from paracetaldehyde or *n*-butaldehyde. 4:5-Diketo-2-phenylpyrrolidine-1-*m*-tolyl-6-arsinic acid, cream-coloured powder, m. p. 180—186° (decomp.), is made from 6-amino-*o*-tolylarsinic acid, pyruvic acid, and benzaldehyde; benzaldehyde, pyruvic acid, and *p*-amino-*o*-anisylarsinic acid give 4:5-diketo-2-phenylpyrrolidine-1-*m*-anisyl-4-arsinic acid, yellow powder, m. p. 175—176°. Benzaldehyde condenses in alcoholic solution with *o*-arsanilic acid to give benzylidene-*o*-arsanilic acid, m. p. 228—230° (decomp.), and with *m*-methyl-6-amino *m*-tolylarsinic acid with formation of 6-benzylideneamino-*m*-tolylarsinic acid, cream-coloured solid, m. p. 202—205° (decomp.). *p*-Chlorobenzaldehyde and 6-amino-*m*-tolylarsinic acid give 6-*p'*-chlorobenzylideneamino-*m*-tolylarsinic acid, pale yellow powder, m. p. 255—260° (decomp.). The same benzylidene derivatives are produced in the presence of pyruvic acid.

W. S. N.

Mercury Compounds of the Phenyl Halides. MARTIN E. HANKE (*J. Amer. Chem. Soc.*, 1923, 45, 1321—1330).—Halogenated phenylsulphinic acids, prepared by a modification of Gattermann's method (A., 1899, i, 516), react with mercuric acetate in glacial acetic acid solution with formation of halogen derivatives of phenylmercuric acetate, which are converted by means of aqueous alcoholic sodium chloride into derivatives of phenylmercuric chloride. By the action of bromine in an aqueous suspension containing potassium bromide, or, perhaps better, by means of bromine in acetic acid solution, the mercuric acetate grouping is replaceable by bromine.

The following compounds are described: *p*-Chlorophenylmercuric acetate, m. p. 193°, is prepared from *p*-chlorobenzenesulphinic acid; the corresponding chloride has m. p. 225°. *m*-Chlorobenzenesulphinic acid, long, white needles, m. p. 81°. *m*-Chlorophenylmercuric acetate has m. p. 133°; the chloride, m. p. 210°. *o*-Chlorobenzenesulphinic acid is a white, crystalline solid, m. p. 120°. *o*-Chlorophenylmercuric acetate has m. p. 115°; the chloride, m. p. 145°. *p*-Bromophenylmercuric acetate has m. p. 196°; the chloride, m. p. 250°. *m*-Bromobenzenesulphinic acid, m. p. 88°. *m*-Bromophenylmercuric acetate, m. p. 160°, and the chloride, m. p. 198°. *o*-Bromobenzenesulphinic acid, m. p. 130°. *o*-Bromophenylmercuric acetate, m. p. 124°, and the chloride, long, white needles, m. p. 155°. *p*-Iodophenylmercuric acetate, m. p. 191°. All these mercury compounds are white, crystalline solids. The action of

warm 68% nitric acid on *p*- or *o*-chloro-, or *p*- or *o*-bromo-phenyl-mercuric acetate leads to the replacement of the mercuric acetate group by the nitro-group, with formation of known products, but this reaction does not proceed smoothly with the meta-substituted derivatives. Direct mercuration of phenyl halides may be effected by heating mercuric acetate with a large excess of a phenyl halide at 140° during one and a half to two and a half hours, after which the excess of phenyl halide is removed by distillation in steam. It is shown that in this way *p*-chloro- and *p*-iodo-phenyl-mercuric acetates and *o*-, *m*-, and *p*-bromophenylmercuric acetates are produced (cf. Dimroth, A., 1902, i, 656; Kharasch and Jacobsohn, A., 1922, i, 189). W. S. N.

Mercury Derivatives of Salicylaldehyde and the Nitro-salicylaldehydes. FRANK C. WHITMORE and EDMUND BURRUS MIDDLETON (*J. Amer. Chem. Soc.*, 1923, **45**, 1330—1334).—The direct mercuration of salicylaldehyde (cf. Henry and Sharp, T., 1922, **121**, 1055) is accomplished by boiling with mercuric acetate and a small amount of acetic acid in 50% alcoholic solution, and leads to the formation of 3:5-diacetoxymercurisalicylaldehyde, needles, m. p. 234° (decomp.). This diacetate is soluble in aqueous sodium hydroxide solution; the action of boiling alcoholic potassium iodide removes all the mercury as potassium mercuric iodide, forming salicylaldehyde and potassium hydroxide. The diacetate reacts with hydroxylamine and with phenylhydrazine as an oxidising agent, forming metallic mercury. The action of aqueous sodium chloride gives 3:5-dichloromercurisalicylaldehyde, m. p. above 270°. The same diacetate is also formed in aqueous solution, together with monomercured products; addition of sodium chloride to the filtered product gives 3(?)-chloromercurisalicylaldehyde, m. p. 189—190°, which reacts with iodine in chloroform solution, giving (?)3-iodosalicylaldehyde. 5-Chloromercurisalicylaldehyde is also probably formed. The mercuration of 5-nitrosalicylaldehyde gives 5-nitro-3-acetoxymercurisalicylaldehyde, pale yellow crystals, m. p. above 260°, which dissolves in aqueous sodium hydroxide, giving a solution from which 5-nitro-3-chloromercurisalicylaldehyde, m. p. above 260°, is precipitated by addition of hydrochloric acid. 3-Nitro-5-acetoxymercurisalicylaldehyde, m. p. above 260°, is produced by the mercuration of 3-nitrosalicylaldehyde. Schiff bases are obtained by heating the mercured salicylaldehydes with an excess of aniline or *p*-toluidine; similar compounds are obtained from the aminobenzoic acids in alcoholic or acetic acid solution. 3:5-Diacetoxymercurisalicylalaniline is a brick-red, amorphous, insoluble, infusible product. 3:5-Diacetoxymercurisalicylal-*p*-toluidine, 3:5-diacetoxymercurisalicylal-*p*-aminobenzoic acid, and 3:5-diacetoxymercurisalicylal-*o*-aminobenzoic acid are similar to the aniline compound. 3(?) -Chloromercurisalicylal-aniline forms flat, yellow, insoluble plates, m. p. 182—184°. The action of aniline on 5-nitrosalicylaldehyde-3-mercuric acetate gives the anhydride of 3-hydroxymercuri-5-nitrosalicylalaniline as a dark red, amorphous, infusible product, insoluble in organic solvents,

but soluble in aqueous alkali. In the formation of this compound, one molecule of acetic acid is eliminated, probably between the acinitro- and acetoxymercuri-groups. A similar product is obtained from aniline and 3-nitrosalicylaldehyde-5-mercuric acetate. *5-Nitro-3-chloromercurisalicylalaniline* is an insoluble, infusible, orange-red product.

W. S. N.

Physiological Chemistry.

Respiratory Exchange in Fresh-water Fish. VI. Pike (*Esox lucius*). JOHN ADDYMAN GARDNER and GEORGE KING (*Biochem. J.*, 1923, 17, 170—173).—The oxygen consumed by the pike is approximately proportional to the rise in temperature. This fish can exist at a tension of dissolved oxygen (0.96% of an atmosphere) considerably below normal. When the temperature of water in which the pike is kept is raised, no signs of discomfort are observed until the temperature reaches 27°, when the respirations become markedly deeper, and the fish becomes more active. At about 30°, the movements of the fish become slightly convulsive and it turns over. On return to the outside tank, the pike quickly revives without manifesting any ill effects. S. S. Z.

The Immediate Effect of Heavy Exercise (Stair-running) on some Phases of Circulation and Respiration in Normal Individuals. III. Effect of Varying the Amount and Kind of Exercise. CHRISTEN LUNDGAARD and EGGERT MÖLLER (*J. Biol. Chem.*, 1923, 55, 599—603).—The decreased oxygen content of blood from the cubital vein, caused by fast stair-running (this vol., i, 502, 623), is not produced by the following types of exercise: (a) walking up and down stairs, (b) riding a bicycle for about two minutes, (c) weight lifting. E. S.

The Action of Acetylene. II. Solubility of Acetylene in Water and Blood. RUDOLF SCHOEN (*Z. physiol. Chem.*, 1923, 127, 243—259).—Acetylene dissolves in the blood according to Henry's law, and its presence in the blood does not influence the solution of oxygen any more than does the presence of nitrogen. The solubility in blood is 98.8% that in water, and the solution appears to be purely physical in nature. W. O. K.

Effect of Insulin on Blood-sugar Concentration. L. B. WINTER and W. SMITH (*Nature*, 1923, 111, 810—811).—The blood of rabbits which have received insulin injections and have been killed when the blood-sugar concentration, as estimated by Bang's method, reaches 0.05%, contains a dextrorotatory carbohydrate which is without copper-reducing power. The liver and muscles yield a substance similar to that present in blood. It is suggested that the carbohydrate content of the animal body may not be appreciably diminished after large doses of insulin, and that the

sugar stored as glycogen is converted into this peculiar form, which may possibly be the "intermediate carbohydrate" postulated by Laquer. A. A. E.

Effect of Plant Extracts on Blood-sugar. J. B. COLLIP (*Nature*, 1923, 111, 571).—A test of the prediction that whenever glycogen occurs in nature a substance similar to "insulin" would also be found, has given positive results in the case of clam-tissue and yeast. Extracts of onion tops, onion roots, barley roots, and sprouted grain, green wheat leaves, bean tops, and lettuce were found to produce hyperglycaemia in rabbits. In the case of yeast, coincident priority is claimed with Winter and Smith. A. A. E.

Forms of Uric Acid in the Blood. M. P. WEIL and GUILLAUMIN (*Paris Medical*, 1922, 12, 588; *J. Amer. Med. Assoc.*, 1923, 80, 729).—In addition to the free uric acid and urates estimated by the usual methods, more or less complete remnants of nucleotides are present. Free uric acid is present in both plasma and corpuscles; the latter also contain the combined form. A method of estimation is described. CHEMICAL ABSTRACTS.

Distribution of Ions in Serum. P. RONA and H. PETOW (*Biochem. Z.*, 1923, 137, 356—363).—When serum is dialysed at different hydrogen-ion concentrations the sodium-, chlorine-, and calcium-ions become distributed according to Donnan's theory. The potassium-ion is anomalous and this is attributed to the formation of a non-ionisable complex with the protein. H. K.

A Possible Factor Influencing the Assimilation of Calcium. CHARLES H. HUNT, A. R. WINTER, and R. C. MILLER (*J. Biol. Chem.*, 1923, 55, 739—742).—Two lactating goats maintained a positive calcium balance in five out of six periods investigated when fed on a ration consisting of grain, dry hay, and a starch paste in which calcium phosphate had been precipitated. Calcium assimilation was probably favoured by the fine state of division of the calcium phosphate. The magnesium balance was negative in each case. These results suggest that the different effects on the calcium balance of diets containing green and dry hay (Hart, Steenbock, and Hoppert, A., 1921, i, 829) is in part due to differences in the states of aggregation of the cell contents of the two feeding-stuffs. E. S.

The Effect of Air which has been Exposed to the Radiations of the Mercury-vapour Quartz Lamp in Promoting the Growth of Rats, fed on a Diet Deficient in Fat-soluble Vitamins. ELEANOR MARGARET HUME and HANNAH HENDERSON SMITH (*Biochem. J.*, 1923, 17, 364—372).—Rats fed on a diet deficient in fat-soluble vitamins showed a prolongation of normal growth when kept in glass jars which have been exposed to the mercury-vapour quartz lamp for ten minutes every second day. When the animals were kept in jars from which the irradiated air was displaced no prolongation of growth was observed. Evidence is produced that the ozone generated by the lamp is not responsible for this phenomenon. S. S. Z.

The Action of Sodium Chloride on the Constituents of the Cell Nucleus. MARIO GARCÍA BANUŠ (*Z. physiol. Chem.*, 1923, 128, 135—140).—Treatment of cells with sodium chloride solution reduces the fraction of the nucleoprotein of which the protein can be extracted by acid. This is demonstrated directly, and also by a study of the staining properties of such cells. W. O. K.

The Composition of Herring Ova. I. Ichthulin. H. STEUDEL and E. TAKAHASHI (*Z. physiol. Chem.*, 1923, 127, 210—219).—Ichthulin obtained from herring ova by extraction first with sodium chloride solution and then with a dilute solution of sodium hydroxide yielded the following results on analysis: C, 52.3%; H, 7.6%; N, 14.1%; P, 0.014%; S, 0.895%; Fe, 0%. The presence of 1.28% of histidine, 6.33% of arginine, and 4.81% of lysine was shown by analysis by the method of Kossel and Kutscher. W. O. K.

The Composition of Herring Ova. II. The Skin of the Ova. H. STEUDEL and S. OSATO (*Z. physiol. Chem.*, 1923, 127, 220—223).—If the ova of the herring are extracted repeatedly with dilute alkali the skin is left. This has the following composition: C, 51.5%; H, 7.8%; N, 14.1%; P, 0.07%; S, 0.55%; histidine, 2.1%; arginine, 6.3%; lysine, 5.5%. The relation to ichthulin is very close, and it is suggested that the skins may be composed of an insoluble modification of ichthulin. W. O. K.

Total Non-protein Nitrogen Content of the Hen's Egg. J. S. HEPBURN (*J. Amer. Inst. Homeopathy*, 1922, 15, 409—412).—The protein-free filtrate, obtained by dilution of white, yolk, or whole egg with water and treatment with 10% sodium tungstate solution and 0.67*N*-sulphuric acid, may be used for the estimation of total non-protein nitrogen by Kjeldahl's method. From estimations made on thirty-six samples from various sources, the conclusion is drawn that the total non-protein nitrogen of white, yolk, and whole egg may vary within wide limits, and may not be taken as the sole criterion of edibility; some edible eggs showed a high value for total non-protein nitrogen, and some inedible eggs a low value for that constituent. Several % of the total nitrogen of fresh eggs may be present in the non-protein form.

CHEMICAL ABSTRACTS.

Can the Animal Organism Synthesise Cholesterol? S. J. THANNHAUSER and HANS SCHABER (*Z. physiol. Chem.*, 1923, 127, 278—280).—By comparison of the cholesterol content of incubated and unincubated eggs, it is shown that the total cholesterol content decreases by an average amount of about 11% in twenty-one days. The free cholesterol suffers a decrease of about 26%, whilst cholesterol esters increase 128%. Apparently no synthesis of cholesterol takes place during incubation. W. O. K.

Decomposition of Arginine in the Liver. K. FELIX and M. TOMITA (*Z. physiol. Chem.*, 1923, 128, 40—52).—The liver of cats decomposes arginine into urea and ornithine. 90% of the theoretical quantity of urea may be obtained after perfusion of the

liver. The liver of geese, on the other hand, is without influence on arginine. W. O. K.

The Significance of the Kidney in the Synthesis of Hippuric Acid in Man, Dog, Pig, and Sheep. I. SNAPPER, A. GRÜNBAUM, and J. NEUBERG (*N. T. v. Gen.*, 1923, **67**, 1, 5, 426; from *Physiol. Abstr.*, 1923, **8**, 107).—The surviving kidney of the dog, pig, sheep, or man was shown to be capable of forming hippuric acid from sodium benzoate and glycine, whereas after double nephrectomy the dog cannot synthesise hippuric acid. Synthesis and excretion of hippuric acids are separate functions. When the perfusion pressure is so low that no ureteral filtrate is formed there is still hippuric acid formation; the rate of formation of hippuric acid cannot therefore be used as a test of renal function in man. W. O. K.

The Possible Significance of Hexosephosphoric Esters in Ossification. ROBERT ROBISON (*Biochem. J.*, 1923, **17**, 286—293).—An enzyme is established in the ossifying cartilage of young rats and rabbits which rapidly hydrolyses hexosemonophosphoric acid, yielding free phosphoric acid. Non-ossifying cartilage shows less than one-tenth of the hydrolytic power of ossifying cartilage. This hydrolytic action is also manifested by the kidney, but the activity is only about 50% of that of an equal weight of epiphyseal cartilage. Other tissues contain the enzyme in a very much lower degree, muscle and blood being almost inactive. Glycerophosphoric acid is hydrolysed by the same tissues in approximately the same order. One of the two phosphoric acid groups of hexosediphosphoric acid is very readily hydrolysed by almost all tissues, including muscle and non-ossifying cartilage, except blood. The possible significance of this enzyme in the process of ossification in the animal body is discussed. S. S. Z.

The Serum Proteins of Milk. W. GRIMMER, C. KURTENACKER, and R. BERG (*Biochem. Z.*, 1923, **137**, 465—483).—The serum proteins of milk are as a rule incompletely precipitated by heat, acids, or salts. Calcium chloride is used on the large scale for coagulating the protein of whey. The residual nitrogen content of serum after precipitation of proteins by phosphotungstic acid is 0.027% or after tannin 0.028%. This proportion is sensibly constant and is unaffected by heating the milk or the serum. Heating serum lessens the digestibility of the proteins and rennin-whey protein is more difficultly digestible than casein. Brief action of rennin produces a greater proportion of heat-coagulable protein than is found after protracted action of rennin. In the latter case, products are formed which are not heat-coagulable. The tryptophan content of milk-serum lies between 0.012 and 0.021%. The heat-coagulable proteins and uncoagulable protein have the same tryptophan content, 3.1%. In the mother-liquor, tryptophan is not detectable. H. K.

Sugar Elimination after the Subcutaneous Injection of Dextrose in the Dog. STANLEY R. BENEDICT and EMIL OSTERBERG (*J. Biol. Chem.*, 1923, **55**, 769—794).—Experiments have been

made on the tolerance of the dog for dextrose when injected subcutaneously immediately after a meal. Following doses of 0.4 g. per kg. of body-weight, there was an increased excretion of "total" sugar, but not of fermentable sugar or of di- or poly-saccharides, which persisted during the greater part of the day of the experiment; with doses of 4 g. per kg., the urinary sugar remained above the normal for more than twenty-four hours; with still larger doses (6, 7, and 8 g. per kg.) there was an increased excretion, extending into the second day after the injection, of all forms of sugar in the urine. In one experiment, the content of sugar in the urine, following the injection of 7 g. per kg. of body-weight, was 1.21% at a time when that of the blood was only 0.12%. This is interpreted as indicating that the sugar excreted in the urine does not represent the diffusion through the kidney of an excess of dextrose, but is due rather to the excretion of some waste sugar, possibly one of the isomeric α - and β -glucoses, which is not readily utilised by the organism. The lag in the excretion of sugar can also be explained on the same lines.

The greater part of the paper is devoted to a criticism of a recent publication of Folin and Berglund (A., 1922, i, 487). It is pointed out that, with the excessive doses (200 g.) of sugar employed by these authors, the absorptive and eliminative processes would not be normal, and hence the results from their experiments are not comparable with those obtained by others (cf., for example, A., 1918, i, 322) using smaller amounts of sugar. Further, the postulation of an "emotional hyperglycæmia," due to the pain produced by drawing blood, is considered unwarranted (cf. Foster, this vol., i, 503). But the main criticism is directed towards the interpretation of the results, some of which are discussed in detail. It is maintained that Folin and Berglund have consistently misinterpreted their results, which, so far from supporting the conception of a definite glucose threshold for normal human beings, are in agreement with the view that the organism has no absolute tolerance for sugar during digestion. The criticism is extended to many other points.

E. S.

Rate of Excretion of Urea. VII. Effect of Various Other Factors than Blood Urea Concentration on the Rate of Excretion of Urea. VIII. Effect of Changes in Urine Volume on the Rate of Excretion of Urea. T. ADDIS and D. R. DRURY (*J. Biol. Chem.*, 1923, 55, 629—638, 639—651).—VII. Increased rates of excretion of urea are produced by the ingestion of milk, caffeine, or glutamic acid, and decreased rates by exercise or by the injection of pituitrin or of large amounts of adrenaline. At the same time, the proportionality between the rate of excretion of urea and its concentration in the blood (this vol., i, 511) is disturbed, thus indicating that the above changes take place independently of changes in the concentration of urea in the blood. VIII. Under otherwise constant conditions, the rate of excretion of urea is not influenced by changes in the volume of the urine.

E. S.

Creatinine Excretion in Urine. Criticism of Ambard's Theory. WILHELM LAUFBERGER (*Biochem. Z.*, 1923, **137**, 531—535).—Ambard's theory is shown experimentally to be untenable, and so likewise any amplification or extension of it. H. K.

Effect of some Organic Acids on the Uric Acid Excretion of Man. H. V. GIBSON and EDWARD A. DOISY (*J. Biol. Chem.*, 1923, **55**, 605—610).—Ingestion of the sodium salt of pyruvic acid produced an increased excretion of uric acid. Sodium lactate, on the other hand, caused a decreased excretion. The latter effect was probably due to an increased threshold of the kidney for uric acid, since a slight rise in the uric acid content of the plasma was observed (cf. Lewis, Dunn, and Doisy, A., 1918, i, 277). E. S.

The Purine Bases in the Urine on a Diet Poor in Purines. (The Question of the Origin and Treatment of Gout.) H. STEUDEL and J. ELLINGHAUS (*Z. physiol. Chem.*, 1923, **127**, 291—298).—The purine bases in the combined urines of two persons on diets poor in purines were found to consist of 71 mg. sodium heteroxanthine, 43 mg. of paraxanthine, and 56 mg. of methylxanthine (from 28.6 litres of urine).

The metabolism of nucleic acids depends very much on the bacterial decompositions proceeding in the intestines (cf. this vol., i, 270). This is of importance in connexion with gout. W. O. K.

The Porphyrin of Human Fæces. A. PAPENDIECK (*Z. physiol. Chem.*, 1923, **128**, 109—118).—The porphyrin excreted in the fæces appears to depend on the diet and to be largely exogenous in nature. Chiefly from a study of the adsorption spectra, it is concluded that the porphyrin in the fæces is not a single individual, and that it is not the same as the porphyrin of urine.

W. O. K.

Cholesterol in Beri-Beri in Pigeons. II. KAZUO HOTTA (*Z. physiol. Chem.*, 1923, **128**, 85—99; cf. this vol., i, 512).—The blood, stomach, and brains of pigeons suffering from avian beri-beri show very early an increase of cholesterol as compared with those from normal animals. Breast-muscles, spleen, heart, liver, and pancreas show increases only in the later stages of the disease. The kidney and testicles do not show any increase. W. O. K.

The Balance of Anions and Kations in the Plasma in Nephritis. JOHN MARRACK (*Biochem. J.*, 1923, **17**, 240—259).— $[\text{HPO}_4]''$ -ions were found to be increased in the majority of cases with high blood urea, whilst no increase was observed in sodium-ions. A very low figure for chlorine-ions in plasma was recorded in severe cases of nephritis. Evidence of a disturbance in the distribution of chlorine-ions between the plasma, on the one hand, and cerebrospinal fluid and tissues, on the other, is produced. The excess of kations in normal plasma unaccounted for by $[\text{HCO}_3]'$, Cl' , and $[\text{HPO}_4]''$ is combined mainly with protein. In many cases of nephritis with much urea retention, an excess of kations over the above combinations has been established. These were

combined with undetermined anions. In most cases of acidosis in nephritis the reduction of plasma $[\text{HCO}_3]'$ was due to accumulated $[\text{HPO}_4]'$ -ions and undetermined anions. The $[\text{HCO}_3]'$ of cerebrospinal fluid is the same as that of the plasma. Reduction of $[\text{HCO}_3]'$ in cerebrospinal fluid is caused by excess of chlorine-ions.
S. S. Z.

Inorganic Salt Metabolism. II. Inorganic-ion Ratio after Administration of Oxalates and Citrates. E. G. GROSS (*J. Biol. Chem.*, 1923, 55, 729—738; cf. A., 1922, i, 1210).—The subcutaneous injection of sodium oxalate produces tetany in dogs. At the same time there is a decrease in the sodium, chlorine, and calcium, and an increase in the potassium and total phosphorus content of the blood; that of magnesium, however, remains constant. Sodium and chlorine decrease in approximately the same proportion; a similar relation holds for the increase in potassium and phosphorus. Neither tetany nor a disturbance in the salt-content of the blood is produced by injection of sodium citrate.

E. S.

The Influence of Benzene on certain Aspects of Metabolism. F. P. UNDERHILL and B. R. HARRIS (*J. Ind. Hyg.*, 1923, 4, 491—500).—Benzene not only acts on the blood elements but also exerts a catabolic influence on body-tissues as a whole, as manifested by a sharp rise in creatinine and total nitrogen, within a very short period after its subcutaneous injections into rabbits, far in excess of that found in rabbits under similar conditions under ordinary starvation.
CHEMICAL ABSTRACTS.

Action of Cyanamide. III. Quantitative Estimation of Cyanamide in the Cell. H. RAIDA (*Zeit. ges. exp. Med.*, 1923, 31, 215—220; from *Physiol. Abstr.*, 1923, 8, 107).—Cyanamide is converted into urea in the body. Sub-lethal doses of cyanamide have the capacity to promote oxidation of sugar in the animal body. Pulp of liver only has the capacity of converting cyanamide into urea. The conversion of cyanamide could not be produced in vitro by any means.
W. O. K.

Can Fasting Fowls Synthesise Glycine or Ornithine? J. G. M. BULLOWA and C. P. SHERWIN (*Proc. Soc. Exp. Biol. Med.*, 1922, 20, 125—128; from *Physiol. Abstr.*, 1923, 8, 107).—Starving hens furnish a very small amount of ornithine when this is necessary for the detoxication of benzoic acid. No hippuric acid was found in the urine of well-fed birds after feeding with benzoic acid but only benzoyl-ornithine or free benzoic acid. Birds are unable to furnish glycine for detoxication purposes, and even unable to make use of it, if it is supplied to them from exogenous sources.
W. O. K.

Pharmacology of some Phenylenediamines. P. J. HANZLIK (*J. Ind. Hygiene*, 1923, 4, 386—409, 448—462).—The pharmacology of *m*- and *p*-phenylenediamines and their dimethyl and diethyl derivatives is studied. Because of their lipid solubility, these compounds may be absorbed through the skin to give toxic effects.

Stimulation of circulation, and respiration, fall of body temperature, tremors, convulsions, coma, and death follow the subcutaneous injection of the compounds into mammals. The injection of *p*-phenylenediamine into rabbits produces a characteristic oedema of the face, tongue, and nose.

CHEMICAL ABSTRACTS.

Poisoning by Pure Methyl Alcohol. G. REIF (*Z. angew. Chem.*, 1923, **36**, 276).—It had been previously stated by Theiler (*ibid.*, 148) that poisoning by methyl alcohol is due to the presence of impurities. More recently, however, the consumption of methyl alcohol, subsequently found to be chemically pure, has proved fatal in several cases.

J. B. F.

Rate of Liberation of Acid by $\beta\beta'$ -Dichlorodiethyl Sulphide and its Analogues in its Relation to the "Acid." Theory of Skin Vesication. RUDOLPH ALBERT PETERS and ERNEST WALKER (*Biochem. J.*, 1923, **17**, 260—276).—The theory that the intracellular liberation of acid is responsible for the vesicant action of dichlorodiethyl sulphide is not supported by experimental evidence, as the vesicant action and the rate of acid liberation do not run parallel. Thus the comparative rates of acid liberation in a 5% alcoholic solution were found to be as follows: $\beta\beta'$ -Dichloroethyl sulphide, 100 (vesicant); $\alpha\alpha'$ -dichlorodimethyl sulphide, 500 (non-vesicant); $\alpha\beta\beta'$ -trichlorodiethyl sulphide, nil (non-vesicant); $\alpha\beta\beta\beta'$ -tetrachlorodiethyl sulphide, 4 (non-vesicant); $\alpha\alpha\beta\beta\beta\beta'$ -hexachlorodiethyl sulphide, 1 (non-vesicant); $\beta\beta'$ -dichlorodiethylsulphone, 1 (vesicant). In the case of $\beta\beta'$ -dichlorodiethyl sulphide, the liberation of acid at constant temperature is decreased by increasing concentrations of alcohol and sodium chloride. The presence of sodium chloride does not inhibit the liberation of acid in dichlorodimethyl sulphide. One % sodium nitrate does not influence the rate of acid liberation by dichlorodiethyl sulphide. Sodium sulphate and magnesium sulphate inhibit the rate strongly in the later stages of the reaction. The velocity constant of the reaction calculated from the unimolecular formula showed a steady, small rise from 30—80% hydrolysis, and this rise was influenced by different experimental conditions, from which the authors conclude that the reaction is a two-stage reaction. Between 15° and 38°, the temperature coefficient of the reaction is 3.3 per 10° rise in temperature.

S. S. Z.

Chemistry of Vegetable Physiology and Agriculture.

Certain Phases of Nitrogenous Metabolism in Bacterial Cultures. G. C. DE BORD (*J. Bact.*, 1923, **8**, 7—45).—The presence of dextrose in peptone media increases the rate of production of amino-nitrogen in growing cultures of *Bacillus coli*, *Ps. pyocyanea*, *B. subtilis*, *C. botulinum*, and *C. sporogenes*. The amino-nitrogen in bacterial cultures is an approximate index

under certain conditions of proteolysis. Folin's method for the estimation of amino-nitrogen is applicable to peptone media. The ammonia found in bacterial cultures is not a trustworthy index of bacterial proteolysis. The presence of fermentable carbohydrate in bacterial cultures affects the nitrogenous metabolism. Some bacteria destroy dextrose without a marked increase in hydrogen-ion concentration. Hence the p_H is not an index of the destruction of dextrose.

CHEMICAL ABSTRACTS.

The Effect of Small and of Large Quantities of Humus on the Fixation of Nitrogen by *Azotobacter chroococcum*. J. VOICU (*Compt. rend.*, 1923, 176, 1421—1423).—The author has studied the fixation of nitrogen both absolutely and relatively to the amount of sugar consumed. For the smaller quantities of humus, the amount of nitrogen fixed increases approximately in proportion, the ratio of nitrogen fixed to sugar consumed remaining constant. For the larger additions of humus, the amount of nitrogen fixed increases but at a smaller rate; the nitrogen-sugar ratio, however, shows a very marked increase. The suggestion is made that a substance, present in traces only, intensifies the fixation without increasing the yield whilst in larger amounts it increases both intensity of fixation and yield (cf. Bertrand, A., 1912, ii, 377).

H. J. E.

Oxidation of Selenium by a New Group of Autotrophic Micro-organisms. JACOB G. LIPMAN and SELMAN A. WAKSMAN (*Science*, 1923, 57, 60).—In addition to *Thiobacillus thio-oxidans* (cf. A., 1922, i, 303), a group of bacteria able to derive their energy from the oxidation of selenium to selenic acid must also be classified among the strictly (obligate) autotrophic bacteria.

A. A. E.

The Viscosin of Fungi. NICOLAUS N. IVANOV (*Biochem. Z.*, 1923, 137, 320—330).—The unripe fruits of *Lycoperdon piriforme* contain between 11 and 25.8% of the mucin, viscosin. This contains 6.1—6.5% of nitrogen and 0.98—1.14% of phosphorus, and after hydrolysis 92% of the total nitrogen is present as amino-groups. The main products of hydrolysis are glucosamine and phosphoric acid. In ripe fruits, substances of the chitosan type were isolated containing 5.37—6.7% of nitrogen and 0.9—3.9% of phosphorus, and yielding glucosamine on hydrolysis.

H. K.

The Nature of the Protein of Fungi. NICOLAUS N. IVANOV (*Biochem. Z.*, 1923, 137, 331—340).—By hydrolysis of the powder of the ripe fruits of *Lycoperdon piriforme* by means of 2% sulphuric acid, pepsin, or brief warming with concentrated hydrochloric acid, two substances were isolated: (1) a peptone-like substance with 16.6% of nitrogen, soluble in 80% alcohol, and on complete hydrolysis yielding 58% of nitrogen precipitable by phosphotungstic acid. (2) An alcohol insoluble substance—a chitosan containing 6.4% of nitrogen and a variable content of phosphorus. On hydrolysis, it gave glucosamine. On one occasion, the parent protein of the fungus was isolated and on partial hydrolysis it gave the two fragments mentioned.

H. K.

The Fermentation of Dextrose and Lævulose by Dried Yeast in the Simultaneous Presence of Phosphate and Sulphite.

FUMIWO HEMMI (*Biochem. J.*, 1923, 17, 327—333).—Acetaldehyde is produced to about the same extent when dextrose and lævulose are fermented by dried yeast in the presence of phosphate. The acetaldehyde formed in the process of fermentation was fixed by sodium sulphite. The fermentation of potassium hexosephosphate also yields acetaldehyde in the presence of sodium sulphite.

S. S. Z.

The Specific Action of Carbohydrates on Embryos. F.

BOAS and F. MERKENSCHLAGER (*Biochem. Z.*, 1923, 137, 300—311).—In presence of galactose in preference to any other carbohydrate examined, calcium nitrate and chloride, although inimical to the growth and sprouting of lupin seeds, are tolerated. Seeds containing little fats are more sensitive to calcium-ions than seeds rich in fats. Unexpectedly, digitonin stimulated sprouting.

H. K.

The Glycerylphosphatase of Plant Seeds. I. ANTONIN

NĚMEC (*Biochem. Z.*, 1923, 137, 570—575).—The properties of the glycerylphosphatase of various seeds have been studied in relation to the substrate sodium glycerylphosphate. The course of the reaction follows Schütz's rule, the amount of glycerylphosphate decomposed being proportional to the square root of the time. A state of equilibrium is finally attained. As the quantity of enzyme is increased, the amount of hydrolysis is not proportional, but somewhat less. The amount of phosphate set free by autolysis is, however, proportional to the amount of enzyme used. With increasing initial amounts of glycerylphosphate, the amount of enzymatic hydrolysis is proportional to the square root of the original glycerylphosphate concentration, if the concentration be between 0.05 and 1%. Glycerol has an inhibiting influence in concentrations above 5%. The optimum temperature for glycerylphosphatase action is 35°, the amount of hydrolysis being proportional to the square root of the temperature. The seeds used were yellow and white mustard seeds and soja beans.

H. K.

The Investigation of Humic and Fatty Matter in Soil by means of Pyridine. MAURICE PIETTRE (*Compt. rend.*, 1923,

176, 1329—1331).—A mixture of equal proportions of pyridine and water is the most suitable solvent for the extraction of humus from soils. Free humus is extracted directly; combined humus from the residue after acidification with hydrochloric acid. Alternatively, total and free humus may be investigated, the proportion combined being found by difference. Pyridine also extracts other substances of a fatty nature from the soil, and methods are indicated for the separation of such substances from the dry pyridine extract.

H. J. E.

Organic Chemistry.

A Method for the Naming of All Organic Compounds. T. SHERLOCK WHEELER (*Chem. News*, 1923, **126**, 113—115).—A system of nomenclature based on the author's linear system of representing the structure of organic compounds (cf. this vol., i, 173). The original must be consulted, as the paper does not lend itself to abstraction.

The Foundation of an Electronic Theory of Organic Compounds. A. L. MARKMAN (*J. Russ. Phys. Chem. Soc.*, 1918, **50**, 144—153).—Berkenheim's theory (this vol., i, 525) is adversely criticised; it is regarded as useless even as a working hypothesis.

R. T.

Petroleum. W. RAMSAY (*J. Soc. Chem. Ind.*, 1923, **42**, 287—288r).—A large number of samples of mineral oils and asphalts from different parts of the world are found to contain nickel, held in solution or colloidal suspension, in amounts varying from 1 to more than 200 parts per million. This observation lends support to the theory of Sabatier and Senderens that petroleum is formed by catalytic hydrogenation of natural gas.

E. H. R.

Reduction of Carbon Monoxide to Methane in Presence of Iron under Increased Pressures. F. FISCHER and H. TROPSCH (*Brennstoff-Chem.*, 1923, **4**, 193—197; cf. following abstract).—In contact with iron filings at a temperature of about 400°, carbon monoxide is reduced to methane, but only in small amounts unless the pressure be increased to about 40 atmospheres. Freshly used iron does not catalyse the reaction; the metal must be in contact with the gases for some time before it becomes activated. Once formed, however, the catalyst retains its activity in presence of pure gases for a considerable time, but a gas contaminated with sulphur compounds rapidly renders it useless. With time, the filings gradually lose their structure and form a powder of iron, iron carbide, and carbon—the carbon is produced from the carbon monoxide with simultaneous formation of carbon dioxide. The main reaction occurring is the formation of carbon dioxide and methane in equal volumes from two volumes of carbon monoxide and two of hydrogen. The best result obtained was from a gas containing 40% of carbon monoxide and 50% of hydrogen at 420° and 40 atmospheres; there was 33·5% of methane in the issuing gas. A certain amount of ethane was also produced.

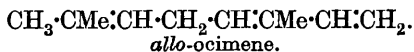
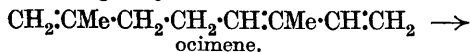
T. S. W.

Reduction of Carbon Monoxide to Methane in Presence of Iron at Ordinary Pressures. F. FISCHER, H. TROPSCH, and W. MOHR (*Brennstoff-Chem.*, 1923, **4**, 197; cf. preceding abstract).—At 400°, little methane is produced from a mixture of carbon

monoxide and hydrogen in contact with iron at the ordinary pressure. Even a catalyst which had been activated by the formation of iron carbide by exposure to a mixture of carbon monoxide and hydrogen at increased pressures gave a gas containing only 1.9% of methane from an approximately equimolecular mixture of the gases under test. The main reaction is formation of carbon and carbon dioxide.

T. S. W.

$\Delta^{4,6}$ -Heptatriene and certain Related Substances. C. J. ENKLAAR (*Rec. trav. chim.*, 1923, 42, 524—527).—The paper deals chiefly with the question of the structure of $\Delta^{4,6}$ -heptatriene, previously obtained by heating $\alpha\epsilon$ -heptadiene- δ -ol with potassium hydrogen sulphate (A., 1913, i, 244, 330), based on an investigation of its optical properties. The refraction and dispersion were found to be abnormal, which was attributed, in part, to polymerisation. Some of the hydrocarbon was fractionated from sodium; the middle portion boiling at 110—112° at 758 mm., had d_4^{17} 0.755 and its analysis agreed with the formula C_7H_{10} . After keeping in a sealed tube for three weeks, it had d_4^{17} 0.7577, and after three months it had risen to d_4^{17} 0.765 so that some polymerisation must have occurred, but this would not account fully for the optical abnormalities exhibited. The author therefore suggests that heptatriene (and hexatriene) prepared by the use of potassium hydrogen sulphate may be stereoisomeric forms stable to acids, whilst the hexatriene obtained from the corresponding bromide by means of zinc represents the corresponding unstable stereoisomeride. It is also suggested that *allo*-ocimene has not the formula $CH_2:CH:CH:CH:CHMe$ but is formed from ocimene in the following way:



F. A. M.

The Order of Elimination of Hydrogen Halides from Mixed Halogen Derivatives of Saturated Open-chain and Cyclic Hydrocarbons from the Stereochemical Point of View. AL. FAVORSKI and TATIANA FAVORSKAIĀ (*J. Russ. Phys. Chem. Soc.*, 1922, 54, 304—311).—It has been shown by Favorski and Boshovsky (A., 1912, i, 616) that when 1-chloro-1:2-dibromocyclohexane was treated with an alkali hydroxide, hydrogen chloride and not hydrogen bromide was eliminated, the resulting compound being 1:2-dibromo- Δ^1 -cyclohexene. The reactions leading to the formation of this substance have now been repeated, using diethyl ketone in the place of cyclohexanone as starting material.

Diethyl ketone was converted by the action of phosphorus pentachloride followed by alcoholic potassium hydroxide into γ -chloro- Δ^8 -pentene, $CHMe:CEtCl$, b. p. 90—92°/781 mm., d_4^{20} 0.9305, d_{20}^{20} 0.9125, $[R_L]_D$ 29.66. The action of bromine in chloroform led to γ -chloro- $\beta\gamma$ -dibromopentane, $CHMeBr:CEtClBr$, b. p. 83—85°/14

mm., d_4^{20} 1.8222, d_{20}^{20} 1.7940, which, on treatment with alcoholic sodium ethoxide, loses hydrogen bromide and passes into γ -chloro- β -bromo- Δ^{β} -pentene, b. p. 40—42°/8 mm., d_{20}^{20} 1.4730, $[R_L]_D$ 36.88.

The reason for the difference in the behaviour of the open-chain and the cyclic compound is explained by the fact that in the latter the configuration of the chlorodibromo-compound is such that hydrogen and chlorine are in a *cis*-position to one another, making the elimination of hydrogen bromide impossible, whilst in the open-chain there is free rotation about the two carbon atoms carrying the halogen atoms and the elimination of hydrogen halide can proceed normally.

G. A. R. K.

Chloromethanesulphonic Acid. RENÉ DEMARS (*Bull. Sci. Pharmacol.*, 1922, 29, 425—431; from *Chem. Zentr.*, 1923, i, 500).—Chloromethanesulphonic acid may be prepared by the action of sodium sulphite on chlorobromomethane, $\text{CH}_2\text{ClBr} + \text{Na}_2\text{SO}_3 = \text{NaBr} + \text{CH}_2\text{Cl}\cdot\text{SO}_3\text{Na}$, or by oxidation of chloromethyl thiocyanate with nitric acid and separation by way of the barium salt.

G. W. R.

Preparation of Alcohols and Aldehydes. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 362537; Swiss Pats. 94603 and 95456; Brit. Pat. 175238; from *Chem. Zentr.*, 1923, ii, 478—479).—A modification of earlier patents (D.R.-P. 350048; Swiss Pat. 93277; Brit. Pat. 158906), whereby for the catalytic reduction of acetaldehyde or other aldehydes, a copper catalyst is prepared either by mixing powdered copper and water glass or colloidal silicic acid with pumice, oxidising at 200°, and then reducing at 250°, or by mixing copper formate with pumice and reducing at 200—250°, or by reducing malachite at 200—250°. Other activators may be used in place of water glass or colloidal silicic acid. Ethyl alcohol is prepared by passing acetaldehyde or paracetaldehyde vapour mixed with hydrogen over the catalysts thus prepared, at about 200°. In a similar way, methyl alcohol and benzyl alcohol are prepared from the corresponding aldehydes.

G. W. R.

Tertiary Methylheptenols. I. Their Ketonic Decomposition. VICTOR GRIGNARD and R. ESCOURROU (*Compt. rend.*, 1923, 176, 1860—1863).—A study of the effect of heat, etc., on various substituted methylheptenols, including the *isopropyl*, *butyl*, and *isoamyl* derivatives. These were prepared by Grignard's method from three different samples of methylheptenone, as obtained (1) from citral, (2) from lemon-grass oil, and (3) from the residues of the manufacture of ψ -ionone. All three products consist of the α -form, $\text{CH}_3\cdot\text{CMe}\cdot[\text{CH}_2]_3\cdot\text{CMe}$, and (in larger proportion) the β -form, $\text{CMe}_2\cdot\text{CH}\cdot[\text{CH}_2]_2\cdot\text{CMe}$. In the preparation of a heptenol, the latter substance (two mols.) undergoes condensation to give the compound $\text{CMe}_2\cdot\text{CH}\cdot[\text{CH}_2]_2\cdot\text{CMe}\cdot\text{CAc}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CMe}_2$.

The lower members of the above heptenol series do not readily pass into -dienes except in presence of energetic dehydrating agents, of which the best is metaphosphoric acid, used in large excess to prevent the formation of the pyro-acid, which induces cyclisation.

d d 2

Anhydrous oxalic acid, at 150° , produces simultaneous dehydration and cyclisation to give *cyclogeraniolenes*, except in the case of phenylmethylheptenol, which is dehydrated even if distilled under diminished pressure, in presence of a trace of acid. Benzylmethylheptenol is much less readily dehydrated. In the case of the alkyl derivatives, tendency to lose the elements of water increases with molecular weight. Thus, the preparation, by heating with acetic anhydride, of the acetyl derivatives of the higher members is rendered difficult owing to dehydration and ketonic decomposition. The latter (cf. Mme Ramart-Lucas, A., 1913, i, 1325) consists in the elimination of hydrocarbon: $\text{CMe}_2\cdot\text{CH}\cdot[\text{CH}_2]_2\cdot\text{CMeR}\cdot\text{OH} \rightarrow \text{CMe}_2\cdot\text{CH}\cdot[\text{CH}_2]_2\cdot\text{COMe} + \text{R}\cdot\text{H}$, and first becomes noticeable in the case of the propyl derivative ($\text{R}=\text{Pr}^a$), which undergoes this decomposition on distilling under the ordinary pressure. The *isopropyl* derivative decomposes in this manner to the extent of 75%, even on distilling under 12 mm. pressure.

Phenylmethylheptenol undergoes no ketonic decomposition, but benzylmethylheptenol, on distilling under the ordinary pressure, is converted largely into methylheptenone and toluene. These ketonic decompositions are catalysed by traces of sulphuric acid and by colloidal platinum (*e.g.*, in attempts at catalytic hydrogenation).
E. E. T.

Tertiary Methylheptenols. II. Their Catalytic Hydrogenation. V. GRIGNARD and R. ESCOURROU (*Compt. rend.*, 1923, 177, 93—96; cf. preceding abstract).—A further study of the substituted methylheptenols. Whilst the methyl and ethyl derivatives are readily reduced to the corresponding heptanols, the propyl and higher derivatives undergo ketonic decomposition. This produces the same experimental effect as a catalyst poison, so that either methylheptenone or its reduction product, β -methylheptan- ζ -ol may result (cf. Locquin and Wouseng, A., 1922, i, 710).

Dimethylheptenol, on reduction with hydrogen, in presence of nickel, gives $\beta\zeta$ -dimethylheptane (reduction preceded by dehydration). When the reduction is carried out under diminished pressure, hydrogenation begins at $90^{\circ}/15$ mm., and is very vigorous at 90 — 100° in the case of the methyl, ethyl, and propyl derivatives. Normal reduction takes place without dehydration even at 160 — 170° when a pressure of 14 mm. is used. Thus at 160 — $170^{\circ}/14$ mm., dimethylheptenol is reduced quantitatively to $\beta\zeta$ -dimethylheptan- ζ -ol. Methylpropylheptenol is quantitatively and normally reduced at $100^{\circ}/15$ mm. No ketonic decomposition occurs, nor is the speed of hydrogenation decreased by the use of low pressures. This fact is explained by assuming that, whereas, at the ordinary pressure, the adsorbed alcohol hinders renewed adsorption of hydrogen by the nickel catalyst, at low pressures only hydrogen is adsorbed.

The ease with which the alcohols in question are dehydrated appears to be due to the presence of the ethylenic linking, since the corresponding saturated alcohols, under similar conditions, do not undergo dehydration. The saturated alcohols obtained in the present work are colourless liquids, with b. p. density, and

refractive indices slightly lower than those of the corresponding unsaturated alcohols. They are readily dehydrated if heated with metaphosphoric acid.

The following constants were obtained: Substituted methylheptenols, $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CR}(\text{OH})\cdot\text{CH}_3$. $\text{R}=\text{Me}$, b. p. 77—78°/13 mm., 173—175°/740 mm., d^{10}_{15} 0.8564, n^{10}_{D} 1.45197. $\text{R}=\text{Et}$, b. p. 92.5—93°/13 mm., 197°/736 mm., d^{10}_{15} 0.8572, n^{10}_{D} 1.45658. $\text{R}=\text{Pr}^a$, b. p. 102—103°/13 mm., d^{10}_{15} 0.8592, n^{10}_{D} 1.45727. $\text{R}=\text{Pr}^s$, b. p. 97—98°/12 mm., d^{10}_{15} 0.8717, n^{10}_{D} 1.46295. $\text{R}=n\text{-butyl}$, 95—96°/5 mm., 119°/12 mm., d^{10}_{15} 0.8603, n^{10}_{D} 1.45997. $\text{R}=\text{isoamyl}$, b. p. 123—124°/14 mm., d^{10}_{15} 0.8566, n^{10}_{D} 1.45657. $\text{R}=\text{Ph}$, b. p. 144—145°/11 mm., d^{10}_{15} 0.9679, n^{10}_{D} 1.52316. $\text{R}=\text{benzyl}$, b. p. 153—154°/10 mm., d^{10}_{15} 0.9654, n^{10}_{D} 1.52632.

Substituted methylheptanols, $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CR}(\text{OH})\cdot\text{CH}_3$. $\text{R}=\text{Me}$, b. p. 170—172°/760 mm., d^{10}_{15} 0.8162, n^{10}_{D} 1.42831. $\text{R}=\text{Et}$, b. p. 84—85°/10 mm., d^{10}_{15} 0.8374, n^{10}_{D} 1.43773. $\text{R}=\text{Pr}^a$, b. p. 105—106°/16 mm., 206—208°/741 mm., d^{10}_{15} 0.8458, n^{10}_{D} 1.44917. $\text{R}=n\text{-butyl}$, b. p. 115°/14 mm., d^{10}_{15} 0.8526, n^{10}_{D} 1.45537. $\text{R}=\text{isoamyl}$, b. p. 131—132°/20 mm., d^{10}_{15} 0.8444, n^{10}_{D} 1.45007. $\text{R}=\text{benzyl}$, 155—156°/12 mm., d^{10}_{15} 0.9420, n^{10}_{D} 1.50389. E. E. T.

Alkylglycerols. I. Preparation of Alkylvinylcarbinols.

RAYMOND DELABY (*Bull. Soc. chim.*, 1923, [iv], 33, 602—626).—The synthesis of alkylglycerols from acraldehyde, by conversion of the latter into alkylvinylcarbinols of the general formula $\text{CH}_2\cdot\text{CH}_2\cdot\text{CHR}\cdot\text{OH}$ by means of the Grignard reagents, and subsequent bromination of the vinyl compounds, and replacement of bromine by hydroxyl, is contemplated, and the first stage of the synthesis involving the preparation of the alkylvinylcarbinols is now described. In practice, the best results were obtained by the interaction of equimolecular proportions of acraldehyde and a magnesium alkyl bromide in ethereal solution at a low temperature, decomposition of the product with the theoretical amount of ice and acid, and rectification of the carbinol in a vacuum. The yields with the lower members ranged from about 30—50%. With the higher members, *e.g.*, nonylvinylcarbinol, only traces were obtained. The following constants are given. Methylvinylcarbinol, b. p. 94—96°, d^{10}_{15} 0.854, n^{10}_{D} 1.4087. Ethylvinylcarbinol, b. p. 37°/20 mm., d^{10}_{15} 0.856, n^{10}_{D} 1.4182. Propylvinylcarbinol, b. p. 133.5—134°, d^{10}_{15} 0.851, n^{10}_{D} 1.4215. *n*-Butylvinylcarbinol, b. p. 153.5—154°, d^{10}_{15} 0.852, n^{10}_{D} 1.4275. Nonylvinylcarbinol, b. p. about 112°/9 mm. In the preparation of all these substances considerable quantities of high boiling fractions were invariably obtained. These fractions were fully investigated both by chemical methods including oxidation, acetylation, benzoylation, etc., and also by cryoscopic methods, but no decisive results were obtained. A complicated mixture was apparently in question in every case, one constituent of which was possibly a polymeride of the alkylvinylcarbinol. As the phenylurethanes of these alkylvinylcarbinols were liquid substances, the allophanates were prepared for purposes of characterisation by leading cyanic acid vapours into the carbinol

and crystallising the products from alcohol. The allophanic ester of methylvinylcarbinol, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{O}\cdot\text{CHMe}\cdot\text{CH}\cdot\text{CH}_2$, forms needles, m. p. 151—152°, and the corresponding derivative of ethylvinylcarbinol had m. p. 152—153°, of propylvinylcarbinol, m. p. 139·5—140°, and of butylvinylcarbinol, m. p. 156·5—157°. The phenylurethane of butylvinylcarbinol was a liquid, b. p. 200—202°/24 mm. Experiments on the resolution of butylvinylcarbinol into its optical enantiomorphs are described, involving the crystallisation of the strychnine salt of the acid phthalic ester from acetone. The least soluble salt gave on subsequent hydrolysis *l*-butylvinylcarbinol, having $\alpha_D -23\cdot3^\circ$. The *d*-isomeride was not isolated in a pure condition. G. F. M.

Preparation of Methyl and Ethyl Ethers. J. B. SENDERENS (*Compt. rend.*, 1923, 177, 15—19; cf. this vol., i, 432).—The usual assumption that the equations: (a) $\text{EtOH} + \text{H}_2\text{SO}_4 = \text{EtHSO}_4 + \text{H}_2\text{O}$, (b) $\text{EtHSO}_4 + \text{EtOH} = \text{H}_2\text{SO}_4 + \text{Et}_2\text{O}$, represent fully the etherification process is incorrect. Evidently, not H_2SO_4 , but $\text{H}_2\text{SO}_4\cdot\text{H}_2\text{O}$ is produced in (b), and, as the reaction proceeds, higher hydrates still, depending on the temperature used. When the hydrate, $\text{H}_2\text{SO}_4\cdot 6\text{H}_2\text{O}$, is heated, boiling commences at 121°. The rise of temperature from 121—127° corresponds with the formation of $\text{H}_2\text{SO}_4\cdot 5\text{H}_2\text{O}$, that from 127—135° to $\text{H}_2\text{SO}_4\cdot 4\text{H}_2\text{O}$, that from 135—148° to $\text{H}_2\text{SO}_4\cdot 3\text{H}_2\text{O}$, and that from 148—170° to $\text{H}_2\text{SO}_4\cdot 2\text{H}_2\text{O}$. In presence of alcohol, the penta-, tetra-, tri-, and di-hydrates correspond with the (different) ranges: 110—121°, 121—130°, 130—145°, and 145—162°, respectively. At a temperature as low as 145°, ethylene tends to be formed to the exclusion of ethyl ether. Its formation begins actually at 140°, and is accelerated by the impurities which accumulate in the reaction mixture. No ethylene is formed at 130°, the temperature favoured by many ether manufacturers, but the effective hydrate is here the tetra-hydrate, which has poor etherifying properties.

At 136—138°, whilst very little ethylene is formed, etherification is more rapid than at 130°, the trihydrate being stable at this temperature.

It is better to supply a continuous ether-still with 95% alcohol containing 10% of concentrated sulphuric acid ($d\ 1\cdot842$) than to supply alcohol alone. On the other hand, addition of alcohol containing acid corresponding with $\text{H}_2\text{SO}_4\cdot 2\cdot 5\text{H}_2\text{O}$ has no beneficial effect.

The conversion of methyl alcohol into methyl ether is not complicated by the possibility of ethylene formation, and accordingly the ether can be prepared at such a temperature that the effective hydrate is $\text{H}_2\text{SO}_4\cdot 2\text{H}_2\text{O}$, which is a great advantage. Thus at 160—165°, using quantities of 100 c.c. of methyl alcohol, in a continuous process, methyl ether was formed at the rate of 250—300 c.c. per minute (the tri- and tetra-hydrates giving, at 130°, respectively, 120 and 24 c.c. per minute). E. E. T.

Hydrolysis of the Sulphoxide and the Sulphone of $\beta\beta'$ -Dichlorodiethyl Sulphide. ALBERT ERIC CASHMORE (T., 1923, 123, 1738—1745).

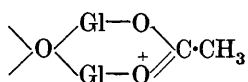
$\alpha\beta$ -Ethylene Sulphides. MARCEL DELÉPINE and SIMON ESCHENBRENNER (*Bull. Soc. chim.*, 1923, [iv], **33**, 703—711).—

Ethylene sulphide, $\begin{smallmatrix} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{smallmatrix} \text{S}$, and its homologues behave in a similar

manner to ethylene oxide in many reactions. Nitric acid oxidises ethylene sulphide to sulphoacetic acid, $\text{SO}_3\text{H}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, and an acid $\text{SO}_3\text{H}\cdot[\text{CH}_2]_2\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, and one-third of the sulphur in the original sulphide appears as sulphuric acid in the products of the reaction. Acetic acid condenses with ethylene sulphide to form a white, insoluble powder, which, however, contains only 7.4% of acetic acid as against 50% required for combination in equimolecular proportions. Ammonia and pyridine give products of unknown constitution. Excess of hydrochloric acid yields three products from ethylene sulphide: (a) β -chloroethyl mercaptan, $\text{HS}\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl}$, a colourless, mobile liquid of mercaptan-like odour, b. p. $43^\circ/13$ mm., $60^\circ/25$ mm., d_4^{20} 1.218, d_4^{25} 1.193, n_D^{20} 1.514; (b) the chlorohydrin, $\text{HS}\cdot[\text{CH}_2]_2\cdot\text{S}\cdot[\text{CH}_2]_2\text{Cl}$, a colourless, feebly odorous liquid, b. p. $120\text{—}127^\circ/20$ mm.; and (c) the compound $\text{S} < \begin{smallmatrix} \text{CH}_2\cdot\text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2\cdot\text{CH}_2 \end{smallmatrix} \text{S}$, m. p. 111° , subliming at 127° . By the action of iodine, (a) is converted into $\beta\beta'$ -dichlorodiethyl disulphide, which, in turn, can be oxidised by means of fuming nitric acid to β -chloroethanesulphonic acid. (a) will also condense with acetone in the presence of hydrogen chloride to give the corresponding $\beta\beta$ -di(β -chloroethylthiol-)propane, $\text{CMe}_2(\text{S}\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl})_2$, an unstable liquid, b. p. $52\text{—}60^\circ/23$ mm. (decomp.). Oxidation of this compound with cold acid permanganate yields the sulphonate derivative $\beta\beta$ -di(β -chloroethylsulphone)propane, $\text{CMe}_2(\text{SO}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl})_2$, as white, nacreous crystals, softening at 60° , m. p. $68\text{—}69^\circ$. Aqueous hydrobromic acid combines with ethylene sulphide to give β -bromoethyl mercaptan, an unstable, colourless liquid, denser than water. Similarly, hydrochloric acid combines with butylene sulphide to give chlorobutane-thiol, b. p. $61^\circ/23$ mm., d 1.07. H. H.

Electrolytic Oxidation of Formic Acid. ERICH MÜLLER (*Z. Elektrochem.*, 1923, **29**, 264—274).—The author has investigated the electrolytic anodic oxidation of formic acid in solutions acidified with sulphuric acid, and the electrolysis of neutral and alkaline solutions of sodium formate, employing a platinum cathode and an anode of platinum, rhodium, palladium, or iridium. Applying a gradually increasing polarising *E.M.F.* between the electrodes, it was found that oxidation of formic acid to carbon dioxide and water occurred at a very low value of the anode potential, of the order 0.1 volt, and after attaining a maximum value decreased to a minimum and then increased rapidly when the anode potential attained a value of the order 1 volt. It is concluded that oxidation is effected in two different ways. The first is effected by a small applied *E.M.F.* when a catalyst metal is present, and the second, necessitating the use of a large *E.M.F.* is operative when the metal is covered with a layer of oxide. The oxidation of formic acid to carbon dioxide and hydrogen was not definitely established. J.S.G.T.

The Structure of Basic Glucinum Acetate. N. V. SIDGWICK (*Nature*, 1923, **111**, 808—809).—A formula is proposed for the compound $\text{Gl}_4\text{O}(\text{C}_2\text{H}_3\text{O}_2)_6$, the crystal structure of which has been described by Bragg (this vol., i, 532). The attachment of



the acetate group to two glucinum atoms, as in the annexed scheme, results in the production of a stable 6-ring, in the formation of which each acetate group loses an electron from its carbonyl oxygen; these six electrons, in addition to two given up by the central oxygen atom, increase the valency electrons of each glucinum atom from two to four. Thus each glucinum atom can form four non-polar links: (1) to the central oxygen atom, and (2), (3), (4) through three acetate groups to each of the other three glucinum atoms, one of these six chelate groups thus corresponding with each edge of the tetrahedron (cf. Tanatar and Kurovski, A., 1907, i, 888; 1908, i, 166, 758).

A. A. E.

Action of Carbon Disulphide on Mercuric Acetate. II. A. BERNARDI and G. ROSSI (*Gazzetta*, 1923, **53**, i, 225—228).—With reference to Miolati's remarks (A., 1922, i, 982) on the authors' work (A., 1922, i, 421), it is shown that the compound obtained by Palm and studied by Borelli (A., 1909, i, 452) exhibits physical properties differing markedly from those of the authors' compound.

T. H. P.

Lead Tetra-acetate as an Oxidising Agent. OTTO DIMROTH and ROBERT SCHWEIZER (*Ber.*, 1923, **56**, [B], 1375—1385).—Lead tetra-acetate is a very efficient agent for the conversion of the hydrogen atom into the hydroxyl group, particularly in the case of substances such as ethyl malonate and ethyl acetoacetate, which contain a mobile hydrogen atom. It can also be applied to the homologues of benzene, such as toluene, diphenylmethane, etc. In general, its use appears to be most successful when it reacts rapidly with the oxidisable substance. Since the concentration of lead tetra-acetate solutions is readily measured volumetrically, it can be used in the titrimetric comparison of the mobility of hydrogen atoms in organic compounds, and may also find application in measuring the additive capacity of double linkings.

An improved method for the preparation of lead tetra-acetate is described in detail. Its estimation is effected by dissolving about 0.5 g. of the sample in warm glacial acetic acid which has been distilled over permanganate, adding a solution of sodium acetate (12 g.) and potassium iodide (1 g.), and titrating after five minutes with thiosulphate solution. Boiling glacial acetic acid is not completely stable towards lead tetra-acetate, but sufficiently so to enable it to be used as a solvent.

Lead tetra-acetate reacts with boiling acetic anhydride, giving *acetoxycetic anhydride*, $\text{O}(\text{CO}\cdot\text{CH}_2\cdot\text{OAc})_2$, a colourless liquid, b. p. 178—180°/20 mm., lead diacetate, and small quantities of carbon dioxide and ethane.

Acetone is oxidised by lead tetra-acetate in the presence of

glacial acetic acid in accordance with the relative proportions employed either to *acetylcarbinyl acetate*, $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OAc}$ (identified as the semicarbazone, m. p. 146°), or the *diacetate*, $\text{OAc}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OAc}$,

colourless needles, m. p. $46\text{--}47^\circ$ (*semicarbazone*, needles, m. p. 93°). Acetophenone is somewhat slowly converted into benzoylcarbinyl acetate.

[With O. SCHAAFF.]—Ethyl malonate is transformed into ethyl acetoxymalonate, the identity of which is established by converting it into tartronic acid.

Ethyl acetoacetate, dissolved in glacial acetic acid or, preferably, in benzene or acetic anhydride, is readily oxidised to *ethyl acetoxycetoacetate*, a yellow liquid which becomes colourless when preserved, b. p. $120\text{--}122^\circ/15\text{ mm.}$ It is decomposed by boiling dilute sulphuric acid into acetol, acetic acid, alcohol, and carbon dioxide. It yields a *semicarbazone*, m. p. 124° , which is decomposed by boiling water. It is converted by an excess of phenylhydrazine into β -acetophenylhydrazide and 4-*hydroxy-1-phenyl-3-methylpyrazol-5-one*, colourless leaflets, m. p. 225° (decomp.), the constitution of which is established by its further conversion by phenylhydrazine into benzeneazo-1-phenyl-3-methylpyrazol-5-one. In a similar manner, ethyl benzoylacetate is transformed into *ethyl α -acetoxycetoacetate*, a pale yellow liquid, b. p. $140\text{--}143^\circ/1\text{ mm.}$, which is hydrolysed by dilute sulphuric acid to benzoylcarbinol. With an excess of phenylhydrazine, it yields benzeneazo-1:3-diphenylpyrazol-5-one, small red needles, m. p. $170\text{--}171^\circ$.

Benzene is very stable towards lead tetra-acetate. Toluene is much more readily attacked with the formation of benzyl acetate. Diphenylmethane in the presence of glacial acetic acid is converted into benzhydryl acetate, m. p. 40° , whereas triphenylmethane is still more easily transformed into triphenylcarbinyl acetate.

Anethole reacts smoothly and readily with lead tetra-acetate, giving the acetate of the two stereoisomeric α -*p*-anisylpropane- $\alpha\beta$ -diols.
H. W.

Action of Uranyl Acetate on some Organic Substances.

II. Action of Uranyl Acetate on Malic Acid. FRITZ KOPATSCHEK (*Anal. Asoc. Quím. Argentina*, 1922, **10**, 318—334; cf. A., 1922, i, 984—985).—Uranyl acetate forms an optically active compound with malic acid analogous to that formed with tartaric acid. No compound is formed with lactic acid, and it is suggested that for the reaction hydroxy-acids with four or more carbon atoms are required. The effect of different substances on the reaction is studied.
G. W. R.

Complex Mixed Bismuthobromoacetates. A. C. VOURNAZOS (*Bull. Soc. chim.*, 1923, [iv], **33**, 699—702).—Although the parent acid, $(\text{BiBr}_3\cdot\text{CH}_3\cdot\text{CO}\cdot\text{O})'\text{H}$, was not isolated, several of its salts are quite stable and are readily prepared by adding a solution of bismuth tribromide in anhydrous acetic acid to a solution of the appro-
*d d**

priate base in the same solvent. It is not considered that the compounds are co-ordination complexes, but rather that the bismuth atom is quinquevalent, thus $\text{Br}_3\text{:Bi}(\text{NH}_4)\text{OAc}$ represents the ammonium salt.

The salts of *ammonium* (hexagonal tablets), *potassium* (hexagonal tablets), *sodium* (isomorphous with the potassium salt), *lithium* (microcrystalline precipitate), *methylamine* (brilliant prisms), *ethylamine* (needles), *aniline* (long, hexagonal tablets), and *o-toluidine* (needles and tetragonal prisms) are described. They all exhibit a yellow colour and are decomposed by cold water with the formation of bismuth oxybromide.

H. H.

Preparation of β -Chloroethyl Acetate. CHEMISCHE FABRIK KALK G. M. B. H. and HERMANN OEHME (D.R.-P. 362747; from *Chem. Zentr.*, 1923, ii, 405).—Ethylene and chlorine, together or successively, are passed into acetic acid in the presence of suitable solvents. β -Chloroethyl acetate has b. p. 145° and d 1.178.

G. W. R.

The Katabolism of Hexoic Acid and its Derivatives. H. D. DAKIN (*J. Biol. Chem.*, 1923, 56, 43—51).—In order to gain information regarding the first stage in the so-called β -oxidation of fatty acids, hexoic acid and its three possible initial oxidation products, Δ^{α} -hexenoic, β -hydroxyhexoic, and butyrylacetic acids have been perfused through a surviving liver. In each case large amounts of acetoacetic acid, acetone, and β -hydroxybutyric acid were produced. The quantitative differences between the products from the various acids were, however, insufficient to indicate which, if any, of the three partly oxidised acids was preferentially produced from hexoic acid. The results suggest that the $\alpha\beta$ -unsaturated, β -ketonic, and β -hydroxy-acids are readily interconvertible and are present in equilibrium. Perfusion experiments have also been made with sorbic acid; both acetoacetic and β -hydroxybutyric acids were produced, but in much smaller yield than with the above acids. Evidently sorbic acid is not a normal metabolite of hexoic acid.

E. S.

Olefine-monocarboxylic Acids. K. VON AUWERS [with TH. MEISSNER, O. SEYDEL, and H. WISSEBACH] (*Annalen*, 1923, 432, 46—84).—Only a few of the homologues of crotonic acid, $\text{R}\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{H}$, are known to exist in stereoisomeric forms, perhaps, amongst other reasons, because, although both forms are produced when the acids are made by the usual methods, the violence of the processes used causes conversion of the less stable into the more stable isomeride. A number of unsaturated acids have therefore been prepared by condensing aldehydes with malonic acid in the presence of pyridine at the ordinary temperature, and the products carefully examined for the presence of isomerides. It is concluded that the elimination of water and carbon dioxide from the hydroxy-dicarboxylic acid which is initially produced leads to the formation of the *trans*-form, but not the *cis*-form, of the $\alpha\beta$ -unsaturated monocarboxylic acid, together with the $\beta\gamma$ -un-

saturated acid. The yield of the latter is greater the greater the number of atoms in the carbon chain. It is also produced with particular ease when the γ -carbon atom carries a *gem*-dimethyl group. Incidentally, a number of derivatives of unsaturated monocarboxylic acids are described.

Acetaldehyde and malonic acid, in the presence of pyridine, at 0°, in the absence of sunlight, react within twenty-four hours, giving a small quantity of β -hydroxybutyric acid, together with crotonic acid (60%). The latter gives a *p*-bromophenacyl ester, $\text{CHMe}:\text{CH}\cdot\text{CO}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_4\text{Br}$, glistening leaflets, m. p. 95–96°. The following data are recorded. Freshly prepared isocrotonic acid had m. p. 14·4–14·6°, b. p. 74·4°/15 mm., or 78·2°/18·5 mm., $d_4^{19.9}$ 1·0267, d_4^{20} 1·027, n_D 1·44223, n_{He} 1·44600, n_B 1·45510, n_Y 1·46311, n_{He}^{20} 1·4460. Ethyl isocrotonate has b. p. 129–130·5°/742 mm., $d_4^{19.8}$ 0·9246, d_4^{20} 0·924, n_D 1·42256, n_{He} 1·42590, n_B 1·43285, n_Y 1·43974 at 19·6°, n_{He}^{20} 1·4257. *p*-Bromophenacyl isocrotonate forms glistening, elongated leaflets, m. p. 80·5–81·5°. Ethyl α -chlorocrotonate (cf. A., 1912, ii, 1015; also Eisenlohr, A., 1912, ii, 2) has b. p. 61°/10 mm., $d_4^{14.3}$ 1·1073, d_4^{20} 1·102, n_D 1·45246, n_{He} 1·45580, n_B 1·46367, n_Y 1·47063 at 14·3°, n_{He}^{20} 1·4532. Ethyl β -chlorocrotonate (*loc. cit.*) has b. p. 66°/10 mm., $d_4^{19.2}$ 1·1018, d_4^{20} 1·101, n_D 1·45639, n_{He} 1·45985, n_B 1·46836, n_Y 1·47583 at 19·2°, n_{He}^{20} 1·4595. Ethyl α -chloroisocrotonate, from the silver salt of the acid and ethyl iodide, has b. p. 58°/12 mm., or 75°/30 mm., d_4^{18} 1·1021, d_4^{20} 1·100, n_D 1·45068, n_{He} 1·45391, n_B 1·46171, n_Y 1·46868 at 18·0°, n_{He}^{20} 1·4530. Ethyl β -chloroisocrotonate (*loc. cit.*) has b. p. 50°/10 mm., $d_4^{14.4}$ 1·0920, d_4^{18} 1·086, n_D 1·45317, n_{He} 1·45679, n_B 1·46561, n_Y 1·47345 at 14·4°, n_{He}^{20} 1·4543. The reaction between malonic acid and propaldehyde, in the presence of pyridine, at the ordinary temperature, gives a small quantity of β -hydroxyvaleric acid, together with Δ^2 -pentene- α -carboxylic acid, which has b. p. 71°/2 mm., 99°/10 mm., or 108°/17 mm.; a sample purified by distillation in a high vacuum had m. p. 10°, $d_4^{14.7}$ 0·9947, d_4^{20} 0·990, n_D 1·44977, n_{He} 1·45370, n_B 1·46269, n_Y 1·47068 at 14·7°, n_{He}^{20} 1·4513. Since, when the acid is purified by distillation with the aid of a water-pump, the optical exaltations are somewhat low, it is concluded that the isomeric Δ^2 -unsaturated acid is present in small amount. The acid chloride of the $\alpha\beta$ -unsaturated acid has b. p. 37°/11 mm., $d_4^{18.0}$ 1·0653, d_4^{20} 1·063, n_D 1·46225, n_{He} 1·46616, n_B 1·47597, n_Y 1·48481 at 18·0°, n_{He}^{20} 1·4653. The ethyl ester has b. p. 157·6–158°/745 mm., or 48°/11 mm. (cf. Wohlgemuth, A., 1915, i, 116), $d_4^{21.9}$ 0·9072, d_4^{20} 0·909, n_D 1·42737, n_{He} 1·43047, n_B 1·43788, n_Y 1·44422 at 21·9°, n_{He}^{20} 1·4313. This ester readily absorbs two atoms of bromine in carbon disulphide solution, giving ethyl $\alpha\beta$ -dibromovalerate, which has b. p. 117–117·5°/14 mm., $d_4^{15.4}$ 1·6199, d_4^{20} 1·613, n_D 1·49527, n_{He} 1·49863, n_B 1·50656, n_Y 1·51332 at 15·4°, n_{He}^{20} 1·4966. Δ^2 -Pentene- α -carboxylic acid gives a *p*-bromophenacyl ester, which forms colourless leaflets, m. p. 67–68°, and an amide, glistening leaflets, m. p. 148°. The latter readily absorbs bromine in glacial acetic acid solution, giving $\alpha\beta$ -dibromovaleramide, hard, white needles, m. p. 168° (decomp.). The unsaturated amide is

converted, by distilling with phosphoric oxide under reduced pressure, into Δ^{α} -pentenenitrile, which has b. p. $36^{\circ}/10$ mm. (cf. Henry, A., 1899, i, 567), $d_4^{15.5}$ 0.8311, d_4^{20} 0.828, n_a 1.43134, n_{He} 1.43472, n_{β} 1.44308, n_{γ} 1.44988 at 15.5° , n_{He}^{20} 1.4327. $\alpha\beta$ -Dibromovaleronitrile, prepared in an analogous manner, has b. p. $110-111^{\circ}/10$ mm., $d_4^{17.6}$ 1.7598, d_4^{20} 1.756, n_a 1.51766, n_{He} 1.52133, n_{β} 1.53019, n_{γ} 1.53881 at 17.6° , n_{He}^{20} 1.5203. Δ^{β} -Pentene- α -carboxylic acid, prepared from methylparaconic acid, had b. p. $92.5^{\circ}/15$ mm., $d_4^{21.5}$ 0.9941, d_4^{20} 0.995, n_a 1.43237, n_{He} 1.43615, n_{β} 1.44200, n_{γ} 1.44796 at 21.5° , n_{He}^{20} 1.4368. Another sample, obtained by the reduction of vinylacrylic acid, had b. p. $94^{\circ}/16$ mm., $d_4^{18.8}$ 0.9885, d_4^{20} 0.987, n_a 1.43285, n_{He} 1.43569, n_{β} 1.44248, n_{γ} 1.44821 at 18.8° , n_{He}^{20} 1.4352. The p-bromophenacyl ester forms glistening leaflets, m. p. $87-88^{\circ}$. The acid chloride has b. p. $53-54^{\circ}/55$ mm., $d_4^{16.9}$ 1.0666, d_4^{20} 1.064, n_a 1.44716, n_{He} 1.44990, n_{β} 1.45733, n_{γ} 1.46383 at 16.9° , n_{He}^{20} 1.4485. The amide, glistening leaflets, m. p. $69-70^{\circ}$, reacts with bromine to give an oily product, and is converted, by means of phosphorus pentoxide, into the nitrile (cf. this vol., i, 661), which has b. p. $75^{\circ}/74$ mm., $d_4^{18.8}$ 0.8423, d_4^{20} 0.841, n_a 1.42084, n_{He} 1.42358, n_{β} 1.42998, n_{γ} 1.43547 at 18.8° , n_{He}^{20} 1.4230. Tiglic acid has $d_4^{29.5}$ 0.9427, and hence $d_4^{99.7}$ 0.9425, n_a 1.42435, n_{He} 1.42746, n_{β} 1.43629, n_{γ} 1.44407 at 99.7° . The ethyl ester of tiglic acid has b. p. $55.5^{\circ}/11$ mm., $64^{\circ}/17$ mm., or $80.5-81.5^{\circ}/45$ mm., $d_4^{19.5}$ 0.9247, d_4^{20} 0.924, n_a 1.43236, n_{He} 1.43554, n_{β} 1.44290, n_{γ} 1.44927 at 19.5° , n_{He}^{20} 1.4353. Angelic acid has $d_4^{59.6}$ 0.9298, and hence d_4^{100} 0.9295, n_a 1.41674, n_{He} 1.41998, n_{β} 1.42846, n_{γ} 1.43593 at 100° , and its ethyl ester has b. p. $48.5-49.5^{\circ}/11$ mm., $58-59^{\circ}/18$ mm., or $72-73^{\circ}/39$ mm., $d_4^{19.5}$ 0.9178, d_4^{20} 0.917, n_a 1.42781, n_{He} 1.43102, n_{β} 1.43802, n_{γ} 1.44435 at 19.5° , n_{He}^{20} 1.4308. Ethyl $\beta\beta$ -dimethylacrylate has $d_4^{15.0}$ 0.9171, d_4^{20} 0.913, n_a 1.43335, n_{He} 1.43679, n_{β} 1.44462, n_{γ} 1.45177 at 15.0° , n_{He}^{20} 1.4345. $\beta\beta$ -Dimethylacrylyl chloride has b. p. $145-147^{\circ}$, $d_4^{12.35}$ 1.0652, d_4^{20} 1.058, n_a 1.47479, n_{He} 1.47980, n_{β} 1.49137, n_{γ} 1.50231, at 12.35° , n_{He}^{20} 1.4763. $\beta\beta$ -Dimethylacrylamide forms white needles, m. p. $65-66^{\circ}$. Δ^{α} -Hexene- α -carboxylic acid has $d_4^{20.0}$ 0.9490, d_4^{20} 0.965, n_a 1.44360, n_{He} 1.44666, n_{β} 1.45538, n_{γ} 1.46287 at 40.0° , n_{He}^{20} 1.4557, and its ethyl ester has b. p. $80.0-80.2^{\circ}/14$ mm., or $93.4-93.8^{\circ}/31$ mm., $d_4^{20.0}$ 0.9005, n_a 1.43165, n_{He} 1.43474, n_{β} 1.44200, n_{γ} 1.44849 at 20.0° . Δ^{β} -Hexene- α -carboxyl chloride has b. p. $41-42^{\circ}/12$ mm. (cf. Ott and Zimmermann, A., 1922, i, 137), $d_4^{19.6}$ 1.0142, d_4^{20} 1.014, n_a 1.44405, n_{He} 1.44730, n_{β} 1.45455, n_{γ} 1.46038 at 19.6° , n_{He}^{20} 1.4471, and the amide, white leaflets, has m. p. 60° . The nitrile is prepared from the latter, and has b. p. $103-104^{\circ}/91$ mm., $d_4^{18.0}$ 0.8424, d_4^{20} 0.841, n_a 1.43023, n_{He} 1.43313, n_{β} 1.43980, n_{γ} 1.44557 at 18.0° , n_{He}^{20} 1.4322. The condensation of isobutaldehyde with malonic acid gives β -hydroxy- γ -methylbutane- α -carboxylic acid and γ -methyl- Δ^{α} -butene- α -carboxylic acid, together with an appreciable quantity of the Δ^{β} -acid. The Δ^{α} -unsaturated acid may be purified by repeated distillation, and has b. p. $106-108^{\circ}/12$ mm., $d_4^{16.0}$ 0.9589, d_4^{20} 0.955, n_a 1.44706, n_{He} 1.45060, n_{β} 1.45931, n_{γ} 1.46689 at 16.0° , n_{He}^{20} 1.4488. Its ethyl ester has b. p.

55—56°/9 mm., $d_4^{18.5}$ 0.8971, d_4^{20} 0.896, n_a 1.43043, n_{He} 1.43363, n_β 1.44079, n_γ 1.44704 at 18.5°, n_{He}^{20} 1.4329. The *p*-bromophenacyl ester forms white leaflets, m. p. 71—72°. The *acid chloride* has b. p. 53—54°/12 mm., $d_4^{14.2}$ 1.0235, d_4^{20} 1.018, n_a 1.45994, n_{He} 1.46396, n_β 1.47348, n_γ 1.48185 at 14.2°, n_{He}^{20} 1.4614. The *amide* forms white leaflets, m. p. 82—86° (indefinite). The *nitrile* has b. p. 43—44°/11 mm. (cf. Henry, A., 1899, i, 256), $d_4^{16.5}$ 0.8258, d_4^{20} 0.823, n_a 1.43245, n_{He} 1.43574, n_β 1.44367, n_γ 1.45039 at 16.5°, n_{He}^{20} 1.4342. α -Bromo- α -ethylbutyryl bromide (Rassow and Bauer, A., 1909, i, 758) has b. p. 83°/13 mm. The solid α -ethylcrotonic acid has $d_4^{16.1}$ 0.9484, n_a 1.44022, n_{He} 1.44260, n_β 1.45102, n_γ 1.45842 at 56.1°, and its ethyl ester has $d_4^{17.0}$ 0.9106, d_4^{20} 0.908, n_a 1.43407, n_{He} 1.43705, n_β 1.44438, n_γ 1.45069 at 17.0°, n_{He}^{20} 1.4357. The *amide* forms white leaflets, m. p. 114—115° (cf. Mannich and Zernik, A., 1908, i, 399). The liquid α -ethylcrotonic acid has $d_4^{15.0}$ 0.9805, d_4^{20} 0.976, n_a 1.45017, n_{He} 1.45337, n_β 1.46170, n_γ 1.46881 at 15.0°, n_{He}^{20} 1.4511, and its ethyl ester has b. p. 158—159°, $d_4^{13.9}$ 0.9042, d_4^{20} 0.899, n_a 1.42779, n_{He} 1.43060, n_β 1.43749, n_γ 1.44320 at 13.9°, n_{He}^{20} 1.4279. Ethyl $\alpha\beta$ -trimethylacrylate has $d_4^{16.0}$ 0.9244, d_4^{20} 0.921, n_a 1.44259, n_{He} 1.44579, n_β 1.45353, n_γ 1.46047 at 16.0°, n_{He}^{20} 1.4440. When the condensation of isovaleraldehyde with malonic acid, in the presence of pyridine, is conducted at the ordinary temperature, the products are β -hydroxyisohexanoic acid and δ -methyl- Δ^a -pentene- α -carboxylic acid; if the reaction is carried out at 100°, the Δ^b -unsaturated acid is also produced in a comparatively large quantity. Three samples of the Δ^a -acid are described. The first had been purified by freezing and had $d_4^{15.3}$ 0.9458, d_4^{20} 0.942, n_a 1.45118, n_{He} 1.45460, n_β 1.46328, n_γ 1.47034 at 15.3°, n_{He}^{20} 1.4511. This material, after distillation, had $d_4^{16.0}$ 0.9444, d_4^{20} 0.941, n_a 1.45087, n_{He} 1.45441, n_β 1.46289, n_γ 1.47036 at 16.0°, n_{He}^{20} 1.4526. The third sample had been purified through the calcium salt, with subsequent distillation under reduced pressure, and had b. p. 123—124°/15 mm., $d_4^{14.5}$ 0.9464, d_4^{20} 0.942, n_a 1.45146, n_{He} 1.45520, n_β 1.46367, n_γ 1.47096 at 14.5°, n_{He}^{20} 1.4527. The ethyl ester has b. p. 190°, $d_4^{15.2}$ 0.8930, d_4^{20} 0.889, n_a 1.43538, n_{He} 1.43845, n_β 1.44576, n_γ 1.45226 at 15.2°, n_{He}^{20} 1.4363. The *p*-bromophenacyl ester forms white leaflets having a silky lustre, and has m. p. 87—88°. The *acid chloride* has b. p. 64°/12 mm., $d_4^{17.1}$ 0.9940, d_4^{20} 0.991, n_a 1.45887, n_{He} 1.46259, n_β 1.47202, n_γ 1.48011 at 17.1°, n_{He}^{20} 1.4613. The *amide* forms white, lustrous scales, m. p. 127—128°, and reacts with bromine in glacial acetic acid solution in the presence of sunlight, giving $\alpha\beta$ -dibromoisohexoamide, glistening, white needles, m. p. 169—170°. The Δ^a -unsaturated *nitrile* has b. p. 65°/13 mm., $d_4^{12.0}$ 0.8286, d_4^{20} 0.823, n_a 1.44020, n_{He} 1.44346, n_β 1.45132, n_γ 1.45807 at 12.0°, n_{He}^{20} 1.4399. Δ^a -Nonene- α -carboxylic acid, prepared from heptaldehyde and malonic acid, and purified through the barium salt (Harding and Weizmann, T., 1910, 97, 299) has $d_4^{17.1}$ 0.9345, d_4^{20} 0.932, n_a 1.45398, n_{He} 1.45730, n_β 1.46473, n_γ 1.47124 at 17.1°, n_{He}^{20} 1.4560. A second sample has been prepared by condensing heptaldehyde with ethyl bromoacetate and zinc in

benzene solution, dehydrating the hydroxy-ester by means of sodium hydrogen sulphate, and hydrolysing the unsaturated ester by means of 20% sulphuric acid. For this sample the values quoted are $d_4^{15.6}$ 0.9334, d_4^{20} 0.930, n_D 1.45267, n_{He} 1.45581, n_B 1.46318, n_γ 1.46956 at 15.6°, n_{He}^{20} 1.4538. The ethyl ester (*loc. cit.*) has b. p. 114—115°/12 mm., $d_4^{19.0}$ 0.8901, d_4^{20} 0.889, n_D 1.43972, n_{He} 1.44263, n_B 1.44946, n_γ 1.45544 at 19.0°, n_{He}^{20} 1.4422. The acid chloride (*loc. cit.*) has b. p. 90—91°/12 mm., $d_4^{19.2}$ 0.9675, d_4^{20} 0.967, n_D 1.45738, n_{He} 1.46075, n_B 1.46876, n_γ 1.47608 at 19.2°, n_{He}^{20} 1.4604. The amide (*loc. cit.*) has m. p. 118—119°, and is converted in the usual way into the *nitrile*, which has b. p. 99—100°/10 mm., $d_4^{15.1}$ 0.8365, d_4^{20} 0.833, n_D 1.44454, n_{He} 1.44758, n_B 1.45483, n_γ 1.46096 at 15.1°, n_{He}^{20} 1.4454. W. S. N.

Metallic Hydroxy-acid Complexes. I. Cuprilactates.
IAN WILLIAM WARK (T., 1923, 123, 1815—1826).

Catalytic Hydrogenation of Castor Oil and its Derivatives. Dehydrogenation of the Hydro-oil. ANDRÉ BROCHET (*Bull. Soc. chim.*, 1923, [iv], 33, 626—632).—Castor oil was readily hydrogenised at 100—120°, employing an active nickel catalyst and hydrogen at 10—12 atm. pressure. The maximum absorption was about 70 c.c. of hydrogen per g. of oil, and the product was a solid fat m. p. 86°, iodine value 2. Methyl ricinoleate prepared by the methanolysis of castor oil, was readily hydrogenised in a similar way at 105—106°, with formation of *methyl λ -hydroxystearate*, m. p. 55°, and free ricinoleic acid gave a crude hydroxystearic acid, m. p. 75°. The pure λ -hydroxystearic acid was obtained by hydrolysis of the methyl ester. It melted at 81°. When the hydrogenised castor oil was heated with the catalyst at temperatures above 150°, progressively increasing dehydrogenation occurred, reaching a maximum at 270—280°. The product finally obtained did not correspond with the original castor oil, but was a soft semi-solid, m. p. 74°, iodine value 20. G. F. M.

Decomposition of the Oxalates on Heating in a Vacuum. I. Lead Oxalate. JOSEF SVÉDA (*Chem. Listy*, 1923, 17, 47—50, 81—84, 112—114).—Tanatar (A., 1901, ii, 451) and Herschkowitsch (A., 1921, i, 495) stated that the product of the decomposition of lead oxalate on heating at 300° is a suboxide of lead, Pb_2O , whilst Maumené took this product to be a mixture in molecular proportions of lead and litharge. In order to decide this question, lead oxalate is heated at 280—300° in a vacuum obtained by means of a mercury pump, and the evolved gases are collected and analysed. They consist at this temperature of 70% of carbon dioxide and 30% of carbon monoxide, whilst the residue contains 65% of litharge and 35% of lead. The above figures for the gases would correspond with the equation $2PbC_2O_4 \rightarrow Pb_2O + 3CO_2 + CO$. These relations are, however, altered by conducting the decomposition at 330—370°, and again by heating at 350—400°, owing to reduction of litharge by carbon monoxide. An abnormally high value which was in some cases obtained for the residue is

explained by the absorption by the latter of mercury vapour present in the atmosphere. The relative density of the residue is intermediate between those of lead and litharge, and measurements of the heat of solution in acetic acid indicate that the residue consists solely of lead and litharge. The decomposition of lead oxalate is hence concluded to consist of the following processes: $\text{PbC}_2\text{O}_4 \rightarrow \text{PbO} + \text{CO}_2 + \text{CO}$, $\text{PbO} + \text{CO} \rightarrow \text{Pb} + \text{CO}_2$, and the formation of Pb_2O under these conditions is definitely disproved. R. T.

β -Hydroxyglutarodinitrile, β -Bromoglutarodinitrile, and Glutaconodinitrile. R. LESPIEAU (*Bull. Soc. chim.*, 1923, [iv], 33, 725—733).—Partly an account of work already published (this vol., i, 447). *Glutaconodinitrile*, $\text{CN}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CN}$, crystallises in prisms, m. p. 31.5° , b. p. $129\text{--}130^\circ/12\text{ mm.}$, and is obtained by dehydrating β -hydroxyglutarodinitrile by distillation in a vacuum with phosphoric oxide. A specimen, m. p. 27° , had d_{20}^{20} 1.0302 and n_D^{20} 1.469 in the superfused state. This nitrile is difficult to hydrolyse to the corresponding acid, but hydrolysis may be effected with aqueous potassium hydroxide on the water-bath. *Ethyl β -hydroxyglutarate* is obtained by hydrolysis of the corresponding nitrile by means of sulphuric acid in the presence of ethyl alcohol. This ester boils at $150\text{--}153^\circ/16\text{ mm.}$, and has d_{23}^{23} 1.10 and n_D^{20} 1.444. *Ethyl γ -cyano- β -hydroxybutyrate*, $\text{CN}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, is prepared by hydrolysis and esterification of the corresponding chloronitrile, and then acting on the resulting ester with potassium cyanide. It is a liquid, b. p. $155\text{--}157^\circ/10\text{ mm.}$, d_{16}^{16} 1.1257, n_D^{16} 1.451. H. H.

A Much-delayed Correction. CH. M. VAN DEVENTER (*Chem. Weekblad*, 1923, 20, 331).—In the original papers by J. H. van't Hoff and the author (A., 1886, 968), the discovery of sodium ammonium racemate is incorrectly ascribed to Staedel (A., 1879, 223); it was, in fact, first prepared by Fresenius (*Annalen*, 1842, 41, 9), and the crystal form correctly described by Scacchi (*Rendiconti*, Naples, 1865). S. I. L.

Polarimetric Observations on Potassium Antimonyl Tartrate, and on Uranyl Tartrate and Malate. E. DARMOIS (*Compt. rend.*, 1923, 177, 49—51).—It is known that when a solution of potassium antimonyl tartrate is slowly treated with potassium hydroxide, antimony trioxide is precipitated, 96% of the total antimony appearing in this form when a certain amount of alkali has been added. The precipitate redissolves in excess of the reagent, and was formerly supposed to pass into potassium antimonite. A study of the rotatory power, however, indicates that actually it passes into a new levorotatory substance containing, in addition, potassium and a tartaric acid residue.

Uranyl tartrate, regarded hitherto either as a neutral salt or as a complex acid, is shown, from its behaviour with bases, to be a substance of the latter type. The existence of a disodium salt (unstable in dilute solutions) is deduced from measurements of rotatory power. Similar results, indicating the existence of a

disodium salt, were obtained with uranyl malate (cf. Itzig, A., 1902, i, 259). E. E. T.

Metallic Hydroxy-acid Complexes. II. Cuprimalates. Their Formation, Properties, and Composition. IAN WILLIAM WARK (T., 1923, 123, 1826—1840).

Constitutional Studies in the Monocarboxylic Acids derived from Sugars. I. Tetramethyl Galactonolactone and the Structure of Galactose. JOHN PRYDE (T., 1923, 123, 1808—1815).

The Oxidation of Hydrocarbons, with Special Reference to the Production of Formaldehyde. III. The Action of Oxygen on Mixtures of Methane and Ethylene and their Oxidation Products. T. SHERLOCK WHEELER and E. W. BLAIR (*J. Soc. Chem. Ind.*, 1923, 42, 260—266T).—Continuing previous work in which methane and ethylene have now been investigated, this gas being a natural mixture of methane and ethylene with two of its oxidation products, hydrogen and carbon monoxide. The washed gas was diluted with nitrogen and mixed with a quantity of oxygen insufficient to form an explosive mixture. It was then passed through a tube heated at temperatures between 400° and 720° in different experiments, the time of heating varying between 0.8 and 2.4 secs. The gas was analysed before and after heating. As the temperature rises, first one and then another constituent is oxidised and the rates of reaction rapidly increase until they appear to attain a constant ratio to one another. Hydrogen is first attacked, then methane, and then carbon monoxide; under conditions which cause the decomposition of formaldehyde, water and carbon monoxide are the chief products. The rapid increase in the rate of oxidation of carbon monoxide explains the presence of carbon dioxide in the products at high temperatures. The yield of formaldehyde in these experiments was lower than that obtained from methane only, probably because the ethylene present gives a lower yield. Decomposition of formaldehyde may be induced by the simultaneous oxidation of hydrogen and carbon monoxide. The effect of temperature and other conditions on the yield was similar to that observed in experiments with methane. The effect of surfaces and catalysts was also investigated. Ignited pumice at 510° causes complete oxidation of hydrogen and carbon monoxide, but the hydrocarbons are only slightly attacked; at higher temperatures these are oxidised. Ferric oxide has a similar action, but in addition it causes decomposition of formaldehyde. When the gas is passed over ferric oxide at 400° without addition of oxygen, hydrogen and carbon monoxide are oxidised exclusively, the hydrocarbons not at all. It is suggested that a method of partial combustion for gas analysis might be based on this observation. The catalytic effect of mercury is small. E. H. R.

Preparation of Formaldehyde. CONSORTIUM FÜR ELEKTRO-CHEMISCHE INDUSTRIE, G. M. B. H. (Brit. Pat. 178842).—Formalde-

hyde is produced by passing acetaldehyde vapour mixed with air or oxygen over heated catalysts such as copper, silver, gold, cadmium, lead, bismuth, iron, cobalt, nickel, platinum, or metallic oxides which have several grades of oxidation. Thus when a stream of air containing 1 kg. of acetaldehyde per cu. metre is passed over a coil of copper wire netting at the rate of 500 c.c. per sq. cm. cross section per minute, flameless combustion occurs, and a solution of formaldehyde collects in the receiver amounting in yield to about 50% of the acetaldehyde employed. The process can be carried out in the presence of steam or other indifferent gases or vapours.

G. F. M.

The Catalytic Synthesis of the Acetals and their Halogenation. JOSEPH S. REICHERT, JAMES H. BAILEY, and J. A. NIEUWLAND (*J. Amer. Chem. Soc.*, 1923, **45**, 1552—1557).—Dimethylacetal and diethylacetal are prepared by passing acetylene into the corresponding alcohol in the presence of concentrated sulphuric acid and mercuric sulphate, the yields being 25—30% and 30—35%, respectively. Propyl, isopropyl, butyl, isobutyl, allyl, and amyl alcohols give a very small yield of the corresponding acetals. The rate of absorption of acetylene by the mixture of alcohol, acid, and catalyst decreases with increasing molecular weight of the alcohol. The normal alcohols react more rapidly than the secondary isomerides. The rate of absorption of acetylene is proportional to the amount of catalyst used. The chlorination of dimethylacetal leads primarily to the formation of methyl $\alpha\beta$ -dichloroethyl ether, with production of methyl alcohol, which is converted into formaldehyde, monochlorodimethyl ether, trioxymethylene, and *s*-dichlorodimethyl ether. The bromination of dimethylacetal leads to the production of formaldehyde, water, hydrobromic acid, methyl alcohol, monobromodimethyl ether, methyl $\alpha\beta\beta\beta$ -tetrabromoethyl ether, methyl $\alpha\beta\beta$ -tribromoethyl ether, and *s*-dibromodimethyl ether. Chloral is obtained by the chlorination, preferably at 60—80°, of diethylacetal, or the partly neutralised liquid from the preparation of diethylacetal by the catalytic process described.

W. S. N.

Action of Formic Acid on Ethylglycerol [Pentane- $\alpha\beta\gamma$ -triol]. Conversion into β -Ethylacraldehyde. RAYMOND DELABY (*Compt. rend.*, 1923, **176**, 1898—1901).—If ethylglycerol is boiled with two and a half times its weight of 96—100% formic acid, a mixture (b. p. 150—152°/15 mm.) of the unchanged triol and its formic esters is obtained (on cooling, the *triformate* separates in needles, m. p. 60—61°). At 270°, the mixture is converted into ethylvinylcarbinol (b. p. 114—116°, Δ^{β} -penten- α -ol (b. p. 139—140°, d_4^{20} 0.864, d_4^{15} 0.855, n_D^{15} 1.4378), and the formic esters of these alcohols. The new pentenol forms an *allophanate*, $C_7H_{12}O_3N_2$, m. p. 157—157.5°, is oxidised by chromic acid mixture to propionic and oxalic acids, whilst cautious oxidation by chromic acid gives the *aldehyde*, $CH_2Et:CH:CHO$ (b. p. 126—130°, d_4^{20} 0.867, d_4^{15} 0.854, n_D^{15} 1.4387) which forms a *semicarbazone*, m. p. 177—178°. Silver oxide converts ethylacraldehyde into ethylacrylic acid. E. E. T.

The Correlation of Additive Reactions with Tautomeric Change. I. The Aldol Reaction. EDITH HILDA USHERWOOD (T., 1923, 123, 1717—1726).

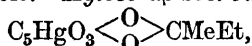
Influence of Hydrogen Chloride on the Enolising Action of Grignard's Reagent. VINAYAK KESHAV BHAGWAT (T., 1923, 123, 1803—1807).

Oximes. ALICJA DORABIAŁSKI (*Istny Zjazd Chemików Polskich*, 1923, 25; cf. 1922, A., ii, 548).—Methylglyoxime is shown to exist in two stereoisomeric forms, m. p. 132° and 151° , which may be converted one into the other with great facility. Thermal analysis of methylglyoxime appears to point to the existence of a condition of unstable equilibrium of the oximino-groups, thus militating against the Hantzsch-Werner theory. R. T.

The Oxidation of Dextrose by Yellow Mercuric Oxide. Preparation of Gluconic Acid. LÉONCE BERT (*Bull. Soc. chim.*, 1923, [iv], 33, 733—734; cf. this vol., i, 539, and A., 1889, 857).—The formation of mercurous gluconate when dextrose is boiled with mercurous oxide occurs only when the latter is freshly prepared. The results obtained by Blanchetière (this vol., i, 539) are probably due to the fact that he used old preparations of mercuric oxide. [Cf. *J.S.C.I.*, 1923, Aug.] H. H.

Methyl-ethyl-ketone-xyloses [Xylose sec.-Butylidene Ethers] and Mixed Ketonic Compounds of Xylose. OLAF SVANBERG and KNUT SJÖBERG (*Ber.*, 1923, 56, [B], 1448—1453).—An extension of previous work (Svanberg and Sjöberg, this vol., i, 540).

Xylose condenses with methyl ethyl ketone in the presence of sulphuric acid with nearly the same readiness as with acetone. The mixture of di- and mono-sec.-butylidene ethers is roughly effected by treatment with light petroleum, in which the former substance is soluble. The final purification is accomplished by distillation in a high vacuum, supplemented in the case of the mono-derivative by solution in water, in which the di-compound is very sparingly soluble. *Xylose $\alpha\beta$ -sec.-butylidene ether*,

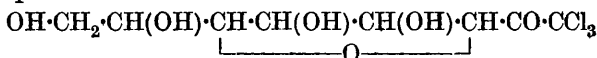


is a liquid, b. p. $127\text{—}129^{\circ}/0\text{—}0.5$ mm., which occasionally solidifies in the receiver; it has $[\alpha]_{\text{Hg yellow}} -8.0^{\circ}$ in aqueous solution. *Xylose (?) $\alpha\beta\delta\epsilon$ -di-sec.-butylidene ether*, $\text{C}_5\text{H}_6\text{O}(\text{O}_2\text{CMeEt})_2$, has b. p. $104\text{—}106^{\circ}/0\text{—}0.5$ mm., $[\alpha]_{\text{Hg yellow}} +17.4^{\circ}$ when dissolved in water. It is hydrolysed by dilute hydrochloric acid in much the same manner as xylose diisopropylidene ether. It is readily converted into the mono-derivative by agitation with a quantity of dilute hydrochloric acid which is insufficient for its complete solution. *Xylose $\alpha\beta$ -isopropylidene $\delta\epsilon(?)$ -sec.-butylidene ether* is a liquid, b. p. $104\text{—}105^{\circ}/\text{high vacuum}$, $[\alpha]_{\text{Hg yellow}} +16.1^{\circ} (\pm 0.5^{\circ})$ in aqueous solution. *Xylose $\delta\epsilon$ -isopropylidene $\alpha\beta$ -sec.-butylidene ether* is a colourless, viscous liquid, b. p. $102\text{—}104^{\circ}/\text{high vacuum}$, $[\alpha]_{\text{Hg yellow}} +15.7^{\circ} (\pm 0.5^{\circ})$ when dissolved in water.

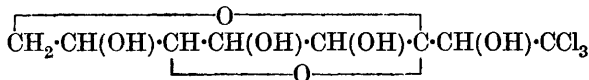
Messenger's method is applicable to the estimation of ketonic groups in *sec.*-butylidene ethers of sugars, a small correction being, however, necessary for the iodine consumed by the carbohydrate.

The observations that the mono*isopropylidene* ethers of xylose are *lævorotatory*, whereas the corresponding di-derivatives are *dextrorotatory*, appears to invalidate Irvine's application of Hudson's rules (T., 1922, 121, 2146). H. W.

The Action of Chloral on Glucosans. AMÉ PICTET and FRANK H. REICHEL (*Helv. Chim. Acta*, 1923, 6, 621—627).—When glucosan is triturated with anhydrous chloral and concentrated sulphuric acid, there are obtained an insoluble substance together with the parachloralose obtained by the action of chloral on dextrose. *Lævoglucosan*, on the other hand, gives the same insoluble substance and chloralose, which is also obtained from chloral and dextrose. It is probable therefore that in the formation of chloralose and parachloralose from dextrose, dehydration of the dextrose first occurs with formation of the two glucosans which react with the chloral before they have time to polymerise. A consideration of their properties leads to the formula



for parachloralose and



for chloralose.

The insoluble substance formed from both glucosan and *lævo*-glucosan is a mixture of two substances, $\text{C}_{10}\text{H}_{10}\text{O}_6\text{Cl}_6$, called provisionally *isodichloralglucose A* and *B*. They are separated by alcohol, *A* being less soluble. *isoDichloralglucose-A* forms hexagonal lamellæ, m. p. 268°; it forms an *acetyl* derivative, $\text{C}_{12}\text{H}_{12}\text{O}_7\text{Cl}_6$, m. p. 198°. *isoDichloralglucose-B* is amorphous, m. p. 85°. Neither substance reduces Fehling's solution or potassium permanganate.

E. H. R.

α -1-Glucosyl-2-glucose. AMÉ PICTET and JACQUES PICTET (*Helv. Chim. Acta*, 1923, 6, 617—621).—The diglucosan obtained by polymerisation of glucosan (A., 1921, i, 766) should be the anhydride of a disaccharide. By treatment with cold concentrated hydrochloric acid it gave an amorphous, hygroscopic mixture of chlorides which, by treatment with silver carbonate in alcoholic solution, was converted into a mixture of dextrose and a disaccharide. The latter, which is less soluble than dextrose in aqueous alcohol, was separated. It forms an amorphous, hygroscopic powder, containing $1\text{H}_2\text{O}$, and after dehydrating has m. p. 116—117°. It shows mutarotation, $[\alpha]_D$ immediately +77.2°; after twenty-four hours +70.2°. It does not give an osazone, and reduces Fehling's solution to the extent of 38.47% as much as dextrose. It is not fermented by emulsin or by brewer's yeast and forms an *octa-acetyl* derivative, apparently cubic crystals, m. p. 85—86°. It gives

The Nature of "Celloisobiose." GABRIEL BERTRAND and (Mlle) S. BENOIST (*Compt. rend.*, 1923, 177, 85—87).—The "celloisobiose" of Ost and Prosiegel (A., 1920, i, 423) is shown to be a mixture of cellobiose and procellose (preceding abstract). If the product is extracted systematically with alcohol (70%) for several days, with daily renewal of the solvent, procellose is left, and may be obtained pure by one crystallisation from 85% alcohol.

E. E. T.

Dextrinazol, the Odorous Constituent of certain Commercial Dextrins, and Ozols in general. HERMANN KUNZ-KRAUSE (*Ber. Deut. pharm. Ges.*, 1923, 33, 149—155).—The characteristic odour of commercial dextrins is conditioned by the presence of a solid, non-volatile constituent, to which the name dextrinazol is given. This appears to be an ester-like compound, either of an unsaturated acid readily convertible into an aliphatic acid with a radicle allied to the terpenes or of an aliphatic or higher dicarboxylic acid with an alcohol radicle of the olefine, acetylene, or terpene series. Treatment of dextrinazol successively with potassium hydroxide solution and hydrochloric acid yields (1) a compound apparently identical with myristic acid, and (2) a compound which is possibly either a phenol analogous to those of the camphor series or a cyclic alcohol.

T. H. P.

Nature of the Swelling Process. VIII. Reversal of the Swelling of Cellulose Acetate. E. KNOEVENAGEL (*Koll. Chem. Beihefte*, 1923, 18, 39—43; cf. this vol., i, 306).—Cellulose acetate which has been brought into equilibrium in a solvent or mixture of solvents of high swelling power will, when placed in another solvent of lower swelling power, slowly shrink until it comes into equilibrium with the second solvent, that is, until the degree of swelling is that proper for the second solvent. Cellulose acetate which has been swollen to equilibrium with a given solvent when placed in a vacuum over an adsorbent for the swelling liquid gives up the liquid it has adsorbed rapidly at first and then increasingly more slowly. This is shown by the figures 1.0191 g. of cellulose acetate increasing in weight to 1.0656 when swollen with alcohol; after two days in a vacuum the weight fell to 1.0510; seven days, 1.0417; twenty days 1.0386; forty-three days, 1.0361; one hundred and two days, 1.0225. Swelling is a reversible process which comes to an equilibrium value from either side.

J. F. S.

Soluble Cellulose Esters of the Higher Fatty Acids. H. GAULT and P. EHRLMANN (*Compt. rend.*, 1923, 177, 124—127; cf. Karrer, Peyer, and Zega, this vol., i, 276).—Hydrocellulose (1 part) is readily converted into soluble esters by means of acid chlorides (5 parts) in presence of an excess of pyridine, using benzene as a solvent and heating at 110—120° for two or three hours. The distearic, dipalmitic, and dilauric esters have been obtained as amorphous substances which are insoluble in water, alcohol, acetone, or acetic acid, but soluble in most organic solvents. They do not depress the freezing point of benzene.

E. E. T.

Lignin and its Relation to Coal. AMÉ PICTET and MADELEINE GAULIS (*Helv. Chim. Acta*, 1923, 6, 627—640).—Similar reasoning to that which led Fischer and Schrader to put forward the hypothesis that coal is formed from the lignin of wood after the destruction of the cellulose by bacteria (A., 1921, ii, 210) led the authors to study the products of the vacuum distillation of lignin. The lignin (obtained from fir) was distilled at 350—390°/5 to 25 mm. The tar obtained was 15% of the weight of the lignin. From its solution in ether, after extracting with sodium hydroxide solution to remove phenols and acids, a brown oil was obtained amounting to 2% of the weight of the lignin. The oil was separated into saturated and unsaturated hydrocarbons by means of liquid sulphur dioxide and the two fractions were purified by boiling with sodium and fractionally distilled. They consisted entirely of hydroaromatic hydrocarbons. The saturated hydrocarbons gave five fractions having approximately the following compositions: 235—240°, $C_{13}H_{26}$; 260—270°, $C_{14}H_{26}$; 270—280°, $C_{16}H_{30}$; 315—320°, $C_{24}H_{44}$; above 320°, $C_{30}H_{60}$. The third fraction appears to be identical with a fraction, 275—285°, from coal tar; the last is identical with melene, a hydrocarbon found in some coal tars and in Galician petroleum. The unsaturated hydrocarbons gave three fractions, 200—210°, $C_{11}H_{16}$; 230—240°, $C_{12}H_{16}$; 250—260°, $C_{13}H_{16}$. Of these, the first appears to be identical with a coal tar fraction. The last fraction gives a tetrabromo-derivative, $C_{13}H_{12}Br_4$, m. p. 193°; it appears to be related to the hexahydrofluorene of coal tar. These results appear to establish a relationship between lignin tar and coal tar, and to some extent support the hypothesis of Fischer and Schrader. From the phenolic substances of the lignin tar, eugenol was isolated; this observation supports the view that lignin contains the grouping of coniferyl alcohol. The existence of a hydroaromatic ring also follows from the above observations. Lignin contains a high methoxy-group content, 14·19%, and it is now found that lignite contains 3·30% and coal from the Saar 0·79% and from St. Étienne 0·24%, whilst anthracite contains none. The objection to Fischer and Schrader's hypothesis that coal contains no methoxy-group therefore falls to the ground.
E. H. R.

Two "Internal Salts" [Betaine and Taurine]. A. REYCHLER (*Bull. Soc. chim. Belg.*, 1923, 32, 247—250).—An examination of some properties of betaine and taurine. (1) Betaine was prepared by heating alcoholic solutions of ethyl chloroacetate and trimethylamine, hydrolysing the product with hydrochloric acid, and treating the betaine hydrochloride obtained (82% yield) with moist silver oxide; the free betaine forms brilliant, deliquescent crystals, $C_5H_{11}O_2N \cdot H_2O$ (80% yield). (2) Bromoethylphthalimide was heated with concentrated hydrochloric acid for two hours in a sealed tube at 180° and the resultant bromoethylamine hydrochloride solution heated with ammonium sulphite solution; taurine crystallised out partly on cooling, yield about 70%. The molecular weights of betaine hydrochloride determined by cryoscopic

measurements in water lay between one-third and one-half of the theoretical value. The specific electric conductivities in aqueous solution were found to be as follows (the figures in brackets indicate the dilutions in litres): *Betaine*, (2 l.)=0.000013; (4 l.)=0.000011; (8 l.)=0.000009; (16 l.)=0.000009. *Taurine*, (2 l.)=0.000012; (4 l.)=0.000008; (8 l.)=0.000008; (16 l.)=0.000010. *Betaine and taurine in equimolecular amounts*, (2 l.)=0.000019; (4 l.)=0.000012; (8 l.)=0.000011; (16 l.)=0.000011. F. A. M.

The Bismuthamines, a New Class of Compounds. A. CH. VOURNAZOS (*Compt. rend.*, 1923, 176, 1555—1558).—These compounds may be prepared by direct combination of a trivalent bismuth salt with an inorganic or organic ammonium salt, with salts of primary or secondary amines, either aromatic or aliphatic, and with salts of primary hydrazines. Halides of bismuth yield the most characteristic compounds, but they are also given by the trioxide, nitrate, and phosphate. The bismuthamines are of two kinds, simple, in which the bismuth salt and the amine salt are derived from the same acid and mixed, in which derivatives of different acids unite. As most bismuth salts are easily hydrolysed, bismuthamines can only be prepared in organic solvents, and from these they separate in crystalline form. The following are described: *Ammonium bismuthochloroiodide*, $[\text{BiCl}_3\text{I}]\text{NH}_4$, transparent needles; *ammonium bismuthobromoacetate*, $[\text{BiBr}_3\cdot\text{OAc}]\text{NH}_4$, yellow, hexagonal tablets; *methylamine bismuthobromoformate*, $\text{BiBr}_3\cdot\text{NH}_2\text{Me}\cdot\text{HCO}_2\text{H}$, yellow, prismatic crystals; *ethylamine bismuthiodoacetate*, $\text{BiI}_3\cdot\text{NH}_2\text{Et}\cdot\text{CH}_3\cdot\text{CO}_2\text{H}$, crimson-scarlet crystals; *methylamine bismuthonitrate*, $\text{Bi}(\text{NO}_3)_3\cdot\text{NH}_2\text{Me}\cdot\text{NO}_3$, masses of white crystals; *hydrazine bismuthochloroacetate*, $\text{BiI}_3\cdot\text{N}_2\text{H}_4\cdot\text{AcOH}$, colourless prisms; *aniline bismuthofluoroacetate*, $\text{BiF}_3\cdot\text{NH}_2\text{Ph}\cdot\text{OAc}$, colourless, prismatic crystals; *aniline bismuthobromoacetate*, pale yellow, hexagonal tables; *o-toluidine bismuthochloropropionate*,

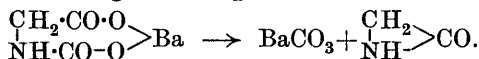
$\text{BiCl}_3\cdot\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2\cdot\text{EtCO}_2\text{H}$, colourless, tetragonal prisms; *n-propylamine bismuthobromobenzoate*, $\text{BiBr}_3\cdot\text{NH}_2\text{Pr}\cdot\text{Ph}\cdot\text{CO}_2\text{H}$, tangled, yellow needles. Details of a general method of preparation are given. H. J. E.

Hexamethylenetetramine. RUDOLF PUMMERER and JOSEF HOFMANN (*Ber.*, 1923, 56, [B], 1255—1259).—Hexamethylenetetramine does not appear to contain a double bond in its molecule, since in aqueous solution it does not unite with hydrogen in the presence of spongy platinum. The observed values for the molecular weight of hexamethylenetetramine are usually somewhat lower than those calculated; in aqueous solution, they are independent of variations in concentration between 1 and 15%. The compound has usually been regarded as a strong base, probably on account of its ability to form well-defined mono-acid salts. It does not, however, redden phenolphthalein; in aqueous solution, it has $K=2\times 10^{-8}$.

Hexamethylenetetramine forms additive compounds with three molecular proportions of phenol or of the cresols (the latter compounds are prepared readily by grinding the components together

at the atmospheric temperature in the presence of a few drops of alcohol). Determinations of molecular weight show these compounds to be almost completely resolved into their components when dissolved in water or benzene. On the other hand, measurements of electrolytic conductivity indicate distinctly the formation of salts. H. W.

The Action of Dry Heat on the Alkaline-earth Salts of Carbamic Acids. A. BLANCHETIÈRE (*Compt. rend.*, 1923, 176, 1629—1631).—Specimens of the dry barium salt of carboxylaminoacetic acid were heated at 130°, 150°, and 170°, respectively, and the resulting products examined mainly with a view to determine their respective nitrogen contents. In each case a substance was obtained which is richer in nitrogen than the original amino-acid, and these substances showed extreme readiness to revert in presence of water to the amino-acid from which they were derived. The hypothesis put forward to account for the change is that formation of glycine mixed with its internal anhydride occurs, the latter substance being formed according to the equation



In the case of barium aminopropionate, the results obtained were indefinite. H. J. E.

Preparation of α -Dialkylaminoethyl- β -aracylhydroxybutyric Esters. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 364038; Swiss Pat. 94324; from *Chem. Zentr.*, 1923, ii, 189—190; cf. A., 1922, i, 639).—Ethyl α -diethylaminoethylacetate (A., 1922, i, 639) is reduced either with sodium amalgam in weak mineral acid solution or electrolytically, using lead electrodes. Ethyl β -hydroxy- α -diethylaminoethylbutyrate thereby obtained is a colourless liquid, b. p. 135—136°/10 mm. The benzoyl derivative is a colourless oil which gives a hydrochloride, forming colourless needles, m. p. 130—131°. Ethyl β -p-nitrobenzoyl- α -diethylaminoethylbutyrate is an oil which does not solidify. The hydrochloride has m. p. 143°. By reduction it gives the corresponding amino-ester, an oil, which forms a crystalline hydrochloride, m. p. 160°. Phenylcarbimide gives with ethyl β -hydroxy- α -diethylaminoethylbutyrate an oily phenylurethane, the hydrochloride of which has m. p. 136°. G. W. R.

Graphical Determination of the Structure of Carbamide and Tin Tetraiodide from Röntgen Ray Analysis. H. MARK and K. WEISSENBERG (*Z. Physik*, 1923, 16, 1—21).—Independently of chemical and crystallographic characteristics, it is shown that one, and only one, form of crystal lattice in which the atoms can be arranged in one way only, affords a crystal structure in the case of carbamide which is compatible with the Röntgen ray diagram afforded by a crystal of the substance. Urea crystallises in the tetragonal scalenohedral (V_d^3) system, with $a=5.63$ and $c=4.70$ Å.U. The elementary cell is a simple-primitive structure and

contains two molecules of carbamide. The distance between two nitrogen atoms in the molecule is approximately 2 Å.U.; the distances between the centres of two adjacent molecules is greater than 3.98 Å.U. and less than 4.62 Å.U. In a similar manner, it is shown that tin tetraiodide forms cubical crystals having $a=6.04$ Å.U., and that the four iodine atoms in the molecule are arranged tetrahedrally around the tin atom. J. S. G. T.

Methylene Derivatives of Succinimide and Phthalimide.

MARIO PASSERINI (*Gazzetta*, 1923, 53, i, 333—338).—The author confirms Bechert's conclusion that the compound, m. p. 290—295°, obtained by the action of trioxymethylene on ethylene cyanide in acetic acid solution containing a little sulphuric acid is methylene-succinimide (A., 1894, i, 488), and shows that, when hydrolysed gradually, this compound yields first methylenedisuccinamic acid and afterwards ammonia, formaldehyde, and succinic acid; the same compound may be obtained by the action of succinic acid on hexamethylenetetramine. The compound, m. p. 208—209°, obtained by the action of formaldehyde on succinimide in a sealed tube at 150—160°, is not, as Breslauer and Pictet state (A., 1907, i, 915), identical with Bechert's compound, but has the composition $C_{15}H_{18}O_6N_4$ and the normal molecular weight in freezing naphthalene; it decomposes, yielding succinic acid, formaldehyde (3 mols.), and ammonia when treated with dilute sulphuric acid, and is, hence, trisuccinimidotrimethyleneamine, $N(CH_2 \cdot N \begin{smallmatrix} \text{CO} \cdot CH_2 \\ \text{CO} \cdot CH_2 \end{smallmatrix})_3$.

Treatment of hexamethylenetetramine with phthalic acid yields mainly methylenediphtalimide, whilst hexamethylenetetramine and phthalimide give methylphthalimide as principal product.

T. H. P.

Peralkylated Guanidine. HANS LECHER and FRITZ GRAF (*Ber.*, 1923, 56, [B], 1326—1330).—*Pentamethylguanidine*, $NMe:C(NMe)_2$, is obtained in 35% yield by heating a mixture of dimethylamine and tetramethyl- ψ -thiocarbamide in the presence of mercuric chloride at 100°. It is a colourless, hygroscopic liquid, b. p. 155—160°, which readily absorbs atmospheric carbon dioxide. It is a strong mono-acid base. The picrate crystallises in yellow needles, m. p. 165—166° (corr. decomp.). It unites readily with methyl iodide, giving *hexamethylguanidinium iodide*, colourless, crystalline leaflets which remain unchanged below 300°.

Peralkylated guanidines could not be obtained by the action of magnesium ethyl bromide and diethylamine on tetramethyl- ψ -thiocarbamide in the presence of ether or toluene or by the action of dry carbon dioxide or carbon tetrachloride on magnesium ethyl bromide and diethylamine. H. W.

Magnetic Properties of Cyanic and Cyanuric Compounds.

PAUL PASCAL (*Compt. rend.*, 1923, 176, 1887—1889).—From a study of the magnetic susceptibilities of compounds of the above types, conclusions are drawn as to the constitution of the compounds. Metallic cyanates appear to possess the isocyanate

structure, whilst cyanuric acid and its salts and ethers are substituted triazines [the acid being written as a centric 6-membered ring composed of three $\cdot\text{N}\cdot\text{C}(\text{OH})\cdot$ groups in sequence]. Cyamelide, from its (magnetic) resemblance to isocyanurates, is regarded as possessing three $\cdot\text{O}\cdot\text{C}(\text{NH})\cdot$ groups in sequence in a 6-membered ring; it is therefore the imide corresponding with trioxymethylene.

E. E. T.

Oxidation of Alkali Cyanides in Aqueous Solution. LUDWIG HESS (*Ber. Deut. pharm. Ges.*, 1923, 33, 178—181).—The cyanate prepared by oxidising alkali cyanide in aqueous solution by means of sodium hypochlorite (cf. Riedel, A., 1920, i, 156) may be separated in solid form from the solution under suitable conditions. The preparation of the hypochlorite and the oxidation of the cyanide may be effected simultaneously by passing chlorine into a solution of alkali hydroxide and cyanide. Potassium ferricyanide also serves as a suitable agent to bring about this oxidation.

T. H. P.

A New Method for the Formation of Cyanates. W. MARCKWALD and M. WILLE (*Ber.*, 1923, 56, [B], 1325).—According to Raschig (A., 1909, ii, 232), the action of potassium cyanide on chloroamine leads to the production of cyanogen chloride, $\text{NH}_2\text{Cl} + \text{KCN} + \text{H}_2\text{O} = \text{NH}_3 + \text{CNCl} + \text{KOH}$. The authors have been unable to confirm this observation; they find that considerable quantities of cyanate are produced.

Potassium cyanate is rapidly produced when equivalent quantities of potassium hypochlorite and potassium cyanide are mixed in aqueous solution.

H. W.

Butenonitriles. III. P. BRUYLANTS (*Bull. Soc. chim. Belg.*, 1923, 32, 256—269; cf. A., 1922, i, 817, 924).—The action of ammonia or of simple aliphatic amines on vinylacetonitrile leads to the formation of β -amino- or β -alkylamino-butyronitriles, which can be reduced to the corresponding diamines by sodium and alcohol. Fatty amines containing more than three carbon atoms do not form stable additive products, but merely cause isomerisation of the vinylacetonitrile to the crotononitriles.

When vinylacetonitrile is left in contact with an aqueous solution of ammonia for some time at a moderate temperature, the product saturated with potassium carbonate, dried, and distilled under reduced pressure, β -aminobutyronitrile, $\text{CH}_3\cdot\text{CH}(\text{NH}_2)\cdot\text{CH}_2\cdot\text{CN}$, is obtained as a mobile liquid with a faintly basic odour, b. p. $186^\circ/760$ mm. (slight decomp.), $76\text{--}77^\circ/18$ mm., d_4^{20} 0.91565, n_{D}^{20} 1.43283, n_{D}^{20} 1.43533, n_{H}^{20} 1.45213. The hydrochloride has m. p. 157° , the chloroplatinate forms golden spangles, m. p. 236° (decomp.), and the benzoyl derivative has m. p. $118\text{--}119^\circ$. Reduction of β -aminobutyronitrile with sodium and alcohol yields $\alpha\gamma$ -diaminobutane, b. p. $139\text{--}141^\circ$, previously obtained by Tafel (A., 1901, i, 72), the dihydrochloride has m. p. 169° , the dibenzoyl derivative, m. p. $165\text{--}166^\circ$.

Hydrolysis of the nitrile with concentrated hydrochloric acid

yields β -aminobutyric acid hydrochloride (*ethyl* ester, b. p. 64—65°/15 mm.), thus proving that the ammonia joins on to the β - and not the γ -carbon atom of the nitrile. A by-product formed in the preparation of the aminonitrile is a colourless basic liquid having the character of a secondary base, b. p. 177°/18 mm., which forms an unstable yellow *nitroso*-derivative. It appears to be *iminodi- β -butyronitrile*, $\text{NH}(\text{CHMe}\cdot\text{CH}_2\cdot\text{CN})_2$, d_4^{20} 0.9766, $n_{\text{H}_a}^{20}$ 1.45654, n_{D}^{20} 1.45907, $n_{\text{H}_\beta}^{20}$ 1.46524. *Chloroplatinate*, deep brown octahedra. The two crotononitriles are also formed as by-products.

With ethylamine, vinylacetonitrile yields β -*ethylaminobutyronitrile*, $\text{CH}_3\cdot\text{CH}(\text{NHEt})\cdot\text{CH}_2\cdot\text{CN}$, in 80% yield as a colourless liquid with a faint odour, b. p. 192—193°/760 mm. (decomp.), 77—78°/14 mm., d_4^{20} 0.8763, $n_{\text{H}_a}^{20}$ 1.43142, n_{D}^{20} 1.43372, $n_{\text{H}_\beta}^{20}$ 1.43953. The crotononitriles are formed as by-products. The *nitroso*-derivative forms a yellow liquid, d_4^{20} 1.2647. Reduction of β -ethylaminobutyronitrile with sodium and alcohol gives a good yield of α -*amino- γ -ethylaminobutane* (γ -*ethylamino-n- α -butylamine*), $\text{NHEt}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2$, as a colourless basic liquid fuming in the air, b. p. 163—164°/753 mm.; the *chloroplatinate* forms fine yellow needles, m. p. 242° (decomp.).

Monomethylamine and vinylacetonitrile yield β -*methylaminobutyronitrile*, $\text{NHMe}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CN}$, b. p. 82—83°/16 mm., 183—184°/765 mm. (decomp.); reduced by sodium and alcohol to α -*amino- β -methylaminobutane* (γ -*methylamino-n- α -butylamine*), $\text{NHMe}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2$, a colourless, fuming liquid, b. p. 152—153°; the *chloroplatinate* forms clear yellow needles.

Dimethylamine yields with vinylacetonitrile β -*dimethylaminobutyronitrile*, $\text{NMe}_2\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CN}$, in 95% yield, as a colourless, odourless liquid, b. p. 79—80°/13 mm., 186—188°/760 mm., with slight decomp., d_4^{20} 0.88180, $n_{\text{H}_a}^{20}$ 1.4338, n_{D}^{20} 1.4363, $n_{\text{H}_\beta}^{20}$ 1.4422. The same product was also obtained by the action of dimethylamine on crotononitrile, thus confirming the position of the amino-group. It was also formed by treating vinylacetonitrile with trimethylamine and distilling the product. It unites with ethyl iodide to form the ethiodide, m. p. about 164°, after drying in a vacuum; it is unstable and partly liquefies on keeping. On dry distillation, it yields the mixed crotononitriles.

Reduction of β -dimethylaminobutyronitrile with sodium and alcohol yields α -*amino- γ -dimethylaminobutane* (γ -*dimethylamino-n- α -butylamine*), $\text{NMe}_2\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2$, which forms a strongly fuming liquid, b. p. 154—156°/753 mm.; it appears to form a *hydrate* boiling indefinitely between 145° and 155°; the *chloroplatinate*, $\text{C}_6\text{H}_{16}\text{N}_2\cdot\text{H}_2\text{PtCl}_6$, forms fine, yellow needles, m. p. 233° (decomp.). A second *chloroplatinate*, $(\text{C}_6\text{H}_{16}\text{N}_2)_2\cdot 2\text{HCl}\cdot\text{H}_2\text{PtCl}_6$, was also obtained as pearly yellow spangles, m. p. 245°.

On treatment with magnesium methyl bromide, β -dimethylaminobutyronitrile reacts vigorously with evolution of dimethylamine and formation of a triple polymeride of crotononitrile. On treating vinylacetonitrile with diethylamine and distilling the product, only a mixture of the crotononitriles was obtained, b. p.

112—115°, and a similar result was observed when using *isobutylamine* or ethylenediamine. With piperidine, however, a fairly vigorous reaction occurs, and after distilling in a vacuum, β -*piperidylbutyronitrile*, $C_5NH_{10} \cdot CHMe \cdot CH_2 \cdot CN$, is obtained as a colourless, odourless liquid, b. p. 126—127°/12 mm., d_4^{20} 0.9444, $n_{D_H}^{20}$ 1.4703, n_D^{20} 1.4727, $n_{H_B}^{20}$ 1.4789. On heating at 160°, it dissociates completely into the crotononitriles.

Aromatic amines were found to be without action on vinyl-acetonitrile, which could be recovered practically unchanged even, for instance, after heating under reflux with aniline for five hours.

F. A. M.

iso-Nitriles [Carbylamines]. V. Reaction with Lævulic Acid. MARIO PASSERINI (*Gazzetta*, 1923, 53, i, 331—333; cf. this vol., i, 63).—The interaction of lævulic acid with phenyl-carbylamine in ethereal solution results in the formation of the lactone of β -anilino- β -hydroxybutane- $\beta\delta$ -dicarboxylic acid, so that in this reaction lævulic acid behaves as though its structure were $CH_2 < \begin{matrix} CH_2 \cdot CMe \cdot OH \\ CO-O \end{matrix}$. This lactone, $NHPh \cdot CO \cdot CMe < \begin{matrix} O-CO \\ CH_2 \cdot CH_2 \end{matrix}$, is a pale yellow, amorphous substance, m. p. 44—46°, and yields aniline and β -hydroxybutane- $\beta\delta$ -dicarboxylic acid on hydrolysis.

T. H. P.

New Syntheses of Hydrocyanic Acid by means of the Silent Electric Discharge. L. FRANCESCONI and ADOLFO CIURLO (*Gazzetta*, 1923, 53, i, 327—330).—Under the influence of the silent discharge, a mixture of ethylene and nitrogen undergoes change in accordance with the equations, $C_2H_4 + N_2 = 2HCN + H_2$ and $C_2H_4 + HCN = Et \cdot N \cdot C$. If a mixture of ethylene and hydrogen cyanide is used, both nitrile and *isonitrile* are formed: $C_2H_4 + C \cdot N \cdot H = Et \cdot N \cdot C$ and $C_2H_4 + H \cdot C \cdot N = Et \cdot C \cdot N$. Preliminary experiments with a mixture of acetylene and hydrogen cyanide indicate the formation, in this case also, of both nitrile and *isonitrile*.

T. H. P.

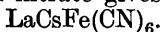
A New Phototropic Compound of Mercury. Y. VENKATARAMAIAH and BH. S. V. RAGHAVA RAO (*Nature*, 1923, 111, 775).—Interaction of a mercuric salt with ammonium thiocyanate and thiocarbamide in acetic acid solution in the presence of an oxidising agent, or the action of hydrogen sulphide on mercuric thiocyanate, yields the phototropic compound $HS \cdot Hg \cdot CNS$.

A. A. E.

The Influence of Alkali on the Titration of some Metals with Ferrocyanide. II. W. D. TREADWELL and D. CHERVET. With a Note by W. D. TREADWELL (*Helv. Chim. Acta*, 1923, 6, 550—559, 559—561).—Using the electrometric method of titration, it has been shown that in ferrocyanides of cadmium, zinc, and lead the heavy metal can be partly displaced by an alkali metal (A., 1922, ii, 786). Continuing this work, it is found that when zinc sulphate is titrated in neutral solution with sodium ferrocyanide, the titration figure corresponds with the ratio $Zn : Fe(CN)_6 = 2 : 1$, but in presence of potassium chloride and hydrochloric

acid the ratio is only 1·5 : 1, on account of the formation of a double salt. Similarly, a double salt is formed when a zinc salt is titrated with potassium ferrocyanide in presence of a rubidium salt. Nickel salts behave similarly to those of zinc; with lithium ferrocyanide, $\text{Ni}_2\text{Fe}(\text{CN})_6$, is formed, with sodium ferrocyanide, $\text{Ni}_3\text{Na}_2[\text{Fe}(\text{CN})_6]_2$, and with potassium ferrocyanide, especially in presence of a caesium salt, the precipitate approximates to $\text{NiK}_2\text{Fe}(\text{CN})_6$. In the case of cobalt salts, the displacement of the heavy metal by alkali can be followed visually by the change in colour of the precipitate from green to yellow; in composition, the precipitates correspond with those obtained with nickel salts. Owing to the comparatively high solubility of manganese ferrocyanide, manganese salts can only be titrated electrometrically in neutral or weak acetic acid solution. Lithium and sodium ferrocyanides both precipitate $\text{Mn}_2\text{Fe}(\text{CN})_6$, whilst potassium ferrocyanide gives $\text{MnK}_2\text{Fe}(\text{CN})_6$; the stage $\text{Mn}_3\text{K}_2[\text{Fe}(\text{CN})_6]_2$ is not formed. In the case of silver, which forms a ferrocyanide of extremely low solubility, titration with lithium, sodium, or potassium ferrocyanide in the cold gives $\text{Ag}_4\text{Fe}(\text{CN})_6$, even in presence of a caesium salt. Addition of excess of ferrocyanide, however, in presence of a caesium salt results in the formation of $\text{Ag}_3\text{CsFe}(\text{CN})_6$. The same compound is formed by running the silver solution into potassium ferrocyanide in presence of caesium chloride, but on further addition of silver salt it is wholly converted into $\text{Ag}_4\text{Fe}(\text{CN})_6$. The end-point of a titration of sodium ferrocyanide with a silver salt is very clearly marked by the sudden clearing of the cloudy solution caused by the flocculation of the precipitate.

Cerium chloride can be titrated electrometrically with potassium ferrocyanide in presence of caesium chloride, the precipitate being $\text{Ce}_4[\text{Fe}(\text{CN})_6]_3$; lanthanum nitrate gives a precipitate of



NOTE.—The facility with which the alkali metals replace the heavy metals in the ferrocyanides increases from lithium to caesium, that is, with the atomic volume. A similar order is found in the facility of basic exchange of silver by alkali metals in the permittes. This effect is probably due to the decreasing degree of hydration and energy of hydration of the ion of the alkali metal with increasing atomic volume. When the energy necessary for the basic exchange is exceeded by the difference between the energies of hydration of the heavy metal and of the alkali metal, the latter being the smaller, basic exchange will occur. The tendency to exchange must be smaller when, as in the case of silver and lead ferrocyanides, the energy of hydration of the heavy metal approximates to that of the alkali metal.

E. H. R.

Additive Reactions of Thiocyanogen. H. P. KAUFMANN and J. LIEPE (*Ber. Deut. pharm. Ges.*, 1923, **33**, 139—148).—The addition of free, especially nascent, thiocyanogen to unsaturated compounds which takes place somewhat less energetically than that of bromine serves as a suitable means of preparing new derivatives of thiocyanogen. Thus 1 : 2-dithiocyanoethane

(ethylene dithiocyanate) may be prepared by gradual addition of an ethereal solution of iodine to an ethereal suspension of mercuric thiocyanate through which a rapid stream of ethylene is passing, and 1-phenyl-1:2-dithiocyanoethane (styrene dithiocyanate) by adding a solution of lead thiocyanate and bromine in carbon tetrachloride to a solution in the latter of styrene, leaving for six weeks, filtering, and extracting the filtrate with boiling water. Allyl alcohol dithiocyanate (glycerol dithiocyanohydrin) may be obtained by the interaction of allyl alcohol and thiocyanogen in carbon disulphide solution (cf. Engle, A., 1899, i, 3). α -p-Methoxyphenyl- $\alpha\beta$ -dithiocyanopropane (anethole dithiocyanate), $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{SCN})\cdot\text{CHMe}(\text{SCN})$, crystallises in needles, m. p. 87° . isoSafrole dithiocyanate, $\text{C}_{12}\text{H}_{10}\text{O}_2\text{N}_2\text{S}_2$, forms crystals, m. p. 109° .

Treatment of ethyl acetoacetate in carbon disulphide solution containing a little alkali with thiocyanogen yields a compound, which is probably the dithiocyano-derivative of the ester but is readily decomposed by moisture, giving ethyl-2-oxo-4-methylthiazole-5-carboxylate, $\text{CO}_2\text{Et}\cdot\text{C}\begin{smallmatrix} \text{CMe}\cdot\text{N} \\ \parallel \\ \text{S}-\text{CO} \end{smallmatrix}$, crystallising in white needles, m. p. 128° .

1-Thiocyano- β -naphthol, $\text{C}_{11}\text{H}_8\text{ONS}$, forms crystals, m. p. $68-70^\circ$, and slowly decomposes.

1-Thiol- β -naphthol, $\text{OH}\cdot\text{C}_{10}\text{H}_7\cdot\text{SH}$, obtained when the preceding compound is heated with zinc and alcoholic hydrochloric acid, crystallises in long, white needles, m. p. 106° , and, when oxidised by means of hydrogen peroxide, yields dihydroxydi- β -naphthyl $\alpha:\alpha'$ -disulphide (cf. Henriques, A., 1895, i, 104).

1-Thiocyano- β -naphthyl methyl ether, $\text{C}_{12}\text{H}_9\text{ONS}$, forms white crystals, m. p. 134° , and, when heated with zinc and alcoholic hydrochloric acid, yields

1-Thiol- β -naphthyl methyl ether, $\text{C}_{11}\text{H}_{10}\text{OS}$, which crystallises in long, white needles, m. p. 98° .

4-Thiocyano- α -naphthol, $\text{C}_{11}\text{H}_8\text{ONS}$, is stable in the air, forms crystals, m. p. $85-87^\circ$, and, when boiled with zinc and alcoholic hydrochloric acid, yields 4-thiol- α -naphthol (cf. Zincke and Ruppersberg, A., 1915, i, 135), which yields the corresponding disulphide, m. p. 152° , when oxidised by means of hydrogen peroxide (cf. Zincke and Ruppersberg, *loc. cit.*). T. H. P.

Some Derivatives of Butylarsine: Butylarsinic Acid.

JULES TIFFENEAU (*Bull. Sci. Pharmacol.*, 1922, 29, 440-442; from *Chem. Zentr.*, 1923, i, 508).—n-Butylarsine dichloride, prepared from arsenious chloride and mercury n-dibutyl (A., 1921, i, 655), is a colourless liquid; it has b. p. $175-180^\circ/760\text{ mm.}$; $d_{25}^{25} 1.54$. It is decomposed by alkali hydroxides with formation of n-butylarsine oxide, $\text{C}_4\text{H}_9\text{AsO}$, a wax-like mass which cannot be distilled without decomposition. Oxidation of n-butylarsine chloride gives n-butylarsinic acid, $\text{C}_4\text{H}_9\cdot\text{AsO}(\text{OH})_2$; it forms needles, m. p. 158° . Phenyl-n-butylarsine chloride, $\text{C}_4\text{H}_9\cdot\text{AsPhCl}$, is prepared from mercury n-dibutyl and phenylarsine chloride. It has b. p. $165-166^\circ/14\text{ mm.}$, $d_{20}^{20} 1.350$. G. W. R.

Is a New Structural Formula for Benzene Necessary?

P. H. HERMANS (*Chem. Weekblad*, 1923, 20, 326—330).—From a survey of the various conceptions of valency and structure in organic compounds from the time of Kekulé onwards, it is concluded that attempts to formulate geometrical conceptions of valency and arrangement of atoms have now failed and must always fail to explain completely the mechanism of molecular structure. In spite of innumerable attempts to bring forward “structural formulæ” for benzene, the original conception of Kekulé alone satisfies our present knowledge, which is insufficient to elucidate the balance of forces within the benzene molecule. S. I. L.

Direct Introduction of Substituents in the Benzene Nucleus.

C. W. A. LELY (*Chem. Weekblad*, 1923, 20, 244).—Those groups which require a hydrogen atom to give their most stable compounds induce substitution in the ortho- and para-positions, whilst groups which form their most stable compounds by addition of an hydroxyl group induce substitution to the meta-position. S. I. L.

Direct Substitution in the Benzene Nucleus.

P. G. VAN DE VLIET (*Chem. Weekblad*, 1923, 20, 279).—The fact that the carboxyl group induces substitution in the meta-position is an obvious exception to Lely’s rule (preceding abstract) that groups which form their most stable compounds by addition of one hydrogen atom induce substitution in the ortho- and para-positions. S. I. L.

Lely’s Substitution Rule. P. H. HERMANS (*Chem. Weekblad*, 1923, 20, 279—280).—Lely’s rule (see preceding abstracts) is merely a less satisfactory form of Posner’s, that a radicle induces substitution in the meta-position if its hydrogen compound can be directly oxidised to its hydroxyl compound. Lely’s benzene formula is obtained by juggling with speculative hypotheses. S. I. L.

The Substitution Rule of C. W. A. Lely. J. JÜRGENS (*Chem. Weekblad*, 1923, 20, 297).—Lely’s rule leads to conclusions contrary to experience of the directing influence of such groups as COOH, COOR (R=an alkyl group), CONH₂, CCl₃, and NH₂ in strongly acid solutions. Such rules serve rather to complicate than clarify the problem (see preceding abstracts). S. I. L.

The Substitution Rule. C. W. A. LELY (*Chem. Weekblad*, 1923, 20, 361—362).—A reply to Hermans and to Jürgens (preceding abstracts). The rule is said to apply only to simple cases, and exceptions where the directing group is complex are admitted. Probably no rule can hold in all cases without a new structural formula for benzene. S. I. L.

Kinetics of Catalytic Dehydrogenation. N. ZELINSKY and N. PAVLOV (*Ber.*, 1923, 56, [B], 1249—1255).—The catalytic dehydrogenation of cyclohexane to benzene and hydrogen in the

presence of platinised or palladised asbestos has been examined between the temperature limits 151° and 408.5° . The hydrocarbon is dropped at a uniform rate into an electrically heated tube containing the catalyst at the desired temperature, the liquid products of the reaction are condensed, and the evolved hydrogen is measured. The course of the change is deduced from the index of refraction of the liquid condensate or, preferably, from the volume of hydrogen. Platinised asbestos, prepared by soaking asbestos in concentrated chloroplatinic acid and formalin and precipitating the metal by means of sodium hydroxide, causes sensible dehydrogenation of *cyclohexane* at 150° , and the action becomes rapidly more marked as the temperature increases. Even at 407° , dehydrogenation does not appear to be accompanied by appreciable carbonisation of benzene or *cyclohexane*. Similar observations are recorded with palladised asbestos, the activity of which appears to be less than that of platinum. Deposition of carbon is not observed at any temperature below 408° . For some unexplained reason the efficiency of the catalyst diminishes somewhat after it has been once used, and then becomes constant. Metallic nickel is much less suitable as a dehydrogenating catalyst, since it acts much more slowly than platinum or palladium, and also causes side reactions such as the decomposition of *cyclohexane* into benzene and methane. The slight activity is attributed to the catalyst becoming coated with a thin layer of carbon, which diminishes its dehydrogenating power. H. W.

The Mechanism of the Pinacol-Pinacolin and Wagner-Meerwein Transformations. CHRISTOPHER KELK INGOLD (T., 1923, 123, 1706—1713).

The Volatilisation of Toluene in Steam. JEAN BARBAUDY (*Compt. rend.*, 1923, 176, 1616—1618).—A study of the toluene-water system, pressure being constant at 760 mm., showed that the vapour was richer in water when the temperature rose above 84.34° than would be expected from a consideration of the relative vapour pressures of the two substances. The distillate on condensation yielded pure water, so that the conditions are represented by a point on the water condensation curve. On reducing the temperature to 84.34° , toluene appeared in the condensate and total condensation occurred. When the vapour contained less than 53.73% of water, pure toluene was the first liquid to be condensed and the conditions are, in the new case, represented by a point on the toluene condensation curve. Thus the equilibrium is represented by the two condensation curves and an ebullition line passing through their point of intersection, this last point being a true eutectic. This is in agreement with Dupré's vapour tension formula, which also holds when the vapour is saturated with respect to only one liquid. The last case is shown by the author to hold for the system investigated by determinations of the solubility of water in a mixture of toluene and water vapours, experimental details of which are given. H. J. E.

Unsaturation and Molecular Compound Formation. III. O. MAASS, E. H. BOOMER, and D. M. MORRISON (*J. Amer. Chem. Soc.*, 1923, 45, 1433—1438; cf. A., 1918, i, 534; 1921, i, 761).—The freezing points of the systems *o*-xylene, *p*-xylene, *m*-xylene, propylbenzene, and methylcyclohexane respectively with hydrogen bromide have been determined with molecular percentages of the hydrocarbon from one to one hundred. From the results it is shown that molecular compounds are formed with *m*-xylene and propylbenzene. The formation of molecular compounds is shown to be due to unsaturation. Failure to form a molecular compound in spite of unsaturation is due to the relatively great attraction of the hydrocarbon molecules for one another. J. F. S.

Catalytic Action. II. Catalytic Preparation of *p*-Cymene and its Formation in Sulphite Turpentine. SHIGERU KOMATSU, HISASHI NAKAMURA, and MASAO KURATA (*Mem. Coll. Sci. Kyoto*, 1923, 6, 183—186).—The turpentine obtained from spruce and other woods in the manufacture of pulp by the sulphite process consists mainly of *p*-cymene, not of terpenes. It is shown experimentally that pinene and menthene, but not menthol or borneol, can be dehydrogenated by heating with sulphur at 200° for twenty-four hours, forming *p*-cymene. It is suggested that *p*-cymene is formed in this manner from terpenes in the manufacturing process, since free sulphur is known to be present in the digester liquors. E. H. R.

Influence of certain Substituents in the Benzene Nucleus on the Mobility of the Chlorine in a Side Chain, with Special Reference to the Problem of Substitution in the Benzene Nucleus. S. C. J. OLIVIER (*Rec. trav. chim.*, 1923, 42, 516—523; cf. A., 1922, i, 646).—In continuation of previous work, the author has examined the rates of hydrolysis in aqueous alcohol of substances of the type $\text{CH}_2\text{Cl}\cdot\text{C}_6\text{H}_4\text{X}$, where X is either I or CO_2H . The rates were found to be in the order: $\text{I}(p) > \text{I}(o) > \text{CO}_2\text{H}(m) > \text{I}(m) > \text{CO}_2\text{H}(p)$. The materials used were prepared in the following manner: *p*-chloromethylbenzoic acid, m. p. 202·5—203° (literature 199° uncorr.), by hydrolysis of *p*-chloromethylbenzonitrile. *m*-Chloromethylbenzoic acid, m. p. 137·5—138·5° (literature 135°), from the nitrile, m. p. 67·4—67·8° (literature 67°). Attempts to prepare *o*-chloromethylbenzoic acid were unsuccessful. The *o*-, *m*-, and *p*-iodobenzyl chlorides were prepared from the corresponding iodotoluenes by bromination at 150—200°, the resultant iodobenzyl bromides were hydrolysed by refluxing with water, and the iodobenzyl alcohols so formed were treated with phosphorus pentachloride. *p*-Iodobenzyl bromide, m. p. 79·5—80° (literature 78·7°). *p*-Iodobenzyl alcohol, m. p. 72—73°; *p*-iodobenzyl chloride, m. p. 53—53·5° (described in the literature as a liquid). *m*-Iodobenzyl bromide, prisms, m. p. 50—50·5°, easily soluble in ether, chloroform, or carbon disulphide, moderately soluble in alcohol, insoluble in water. *m*-Iodobenzyl alcohol, b. p. 154°/10 mm. (literature gives 165°/16 mm.). *m*-Iodobenzyl chloride, crystals, m. p. 26·5—

27.5°. *o*-Iodobenzyl bromide, m. p. 55—55.5° (literature gives 52—53°). *o*-Iodobenzyl alcohol, needles, m. p. 89.5—90°. Easily soluble in ether or alcohol, sparingly soluble in hot water. *o*-Iodobenzyl chloride, m. p. 28.5—29.5°, easily soluble in organic solvents. Insoluble in water. F. A. M.

Hydrogenation of ω -Nitrostyrene. A. GARCÍA BANÚS and J. PASCUAL VILA (*Anal. Fis. Quím.*, 1922, **20**, 689—692).—The catalytic hydrogenation of ω -nitrostyrene was attempted with the object of obtaining β -nitrophenylethane and, by reduction, the corresponding amino-compound. In ethereal solution, a grey precipitate is formed, which on recrystallisation gives white crystals, m. p. 237° (cf. Sonn and Schellenberg, A., 1918, i, 9). In ether-acetic acid solution, the oxime of phenylacetaldehyde, m. p. 95°, is obtained. An apparatus for the preparation of electrolytic hydrogen is described. G. W. R.

Alkylation. I. The Preparation of Esters of Aromatic Sulphonic Acids. V. A. IZMAILSKI and B. A. RAZORENOV (*J. Russ. Phys. Chem. Soc.*, 1920, **52**, 359—366).—The esters of aromatic sulphonic acids, which can be used as alkylating agents (see following abstract), are most conveniently prepared from the corresponding acid chlorides by the action of the relevant alcohol in the presence of aqueous 25% sodium hydroxide at a low temperature, the alkali being slowly added to the mixture of chloride and alcohol. The preparation of methyl and ethyl toluene-*p*-sulphonates is described, the yields being 92% and 85%, respectively. G. A. R. K.

Alkylation. II. The Alkylation of the Nitrophenols. V. A. IZMAILSKI and B. A. RAZORENOV (*J. Russ. Phys. Chem. Soc.*, 1920, **52**, 366—368).—The alkylation of the *o*- and *p*-nitrophenols is usually carried out by the action of alkyl halides on the dry sodium phenoxides, an operation necessitating the use of autoclaves and giving somewhat unsatisfactory yields of alkyl ethers. The action of methyl and ethyl toluene-*p*-sulphonates on the phenols in the presence of aqueous sodium hydroxide at 95—100° leads to a much more satisfactory result. Thus *o*-nitroanisole and *p*-nitrophenetole can be easily obtained in 90% yields by this method. G. A. R. K.

Derivatives of Diphenyl. V. Nitrodiphenyls. A. GARCÍA BANÚS and J. GUÍTERAS (*Anal. Fis. Quím.*, 1923, **21**, 126—131).—By gentle nitration of 4-hydroxydiphenyl in acetic acid solution no mononitro-derivative is obtained, but only 3:5-dinitro-4-hydroxydiphenyl, m. p. 154—155°. More intense nitration gives 3:5:4'-trinitro-4-hydroxydiphenyl, m. p. 201—202°. Oxidation of the latter compound with chromic acid gives *p*-nitrobenzoic acid. G. W. R.

Studies in Polymerisation. IX. The Polymerisation of *as*-Diphenylethylene. S. V. LEBEDEV, I. A. ANDREEVSKI, and A. A. MATIUSCHKINA (*J. Russ. Phys. Chem. Soc.*, 1922, **54**, 223—233).—It has been observed by Hildebrand (*Diss. Strassburg*,

1909) that on heating *as*-diphenylethylene with a trace of iodine a dimeric substance, m. p. 112° , was obtained which he considered to be 1:1:3:3-tetraphenylcyclobutane. It is now shown that by polymerisation of the hydrocarbon in the presence of sulphuric acid, or the silicate floridine, a mixture of two substances is found, namely, Hildebrand's compound (m. p. 113.5° when pure) and a new dimeric compound (m. p. 143°). The first of these is shown to be $\alpha\alpha\gamma\gamma$ -tetraphenyl- Δ^{α} -butylene, $\text{CPh}_2\cdot\text{CH}\cdot\text{CMePh}_2$, for although it is very inert and is not attacked by permanganate, it gives a colour with tetranitromethane, forms a liquid *dibromide*, and an *ozonide*, $\text{C}_{28}\text{H}_{24}\text{O}_3$, which is a viscous, yellow liquid, yielding benzophenone, $\alpha\alpha$ -diphenylpropaldehyde, and $\alpha\alpha$ -diphenylpropionic acid by the action of water in addition to *benzophenone peroxide*, a microcrystalline compound insoluble in alcohol, decomposing into oxygen and benzophenone at about 170° . If the ozonisation of the compound, m. p. 113.5° , is very prolonged, some of the ozonide of *as*-diphenylethylene is also formed, which can be separated owing to its insolubility in light petroleum and gives benzophenone and formic acid on fission.

The dimeric compound, m. p. 143° , appears to be fully saturated in its behaviour towards ozone and bromine, and can be obtained by the isomerisation of the compound, m. p. 113.5° , by heating with floridine; it is suggested that it is 1:1:3:3-tetraphenylcyclobutane.

G. A. R. K.

The Hydrogenation of Aromatic Compounds with the Aid of Platinum. VI. The Hydrogenation of Naphthalene.

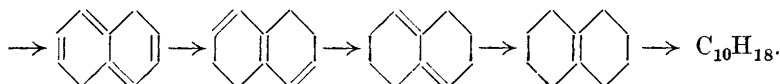
RICHARD WILLSTÄTTER and FRITZ SEITZ (*Ber.*, 1923, 56, [B], 1388—1407).—The hydrogenation of naphthalene in the presence of spongy platinum leads directly to the production of decahydronaphthalene (Willstätter and Hatt, A., 1912, i, 545; Willstätter and King, A., 1913, i, 353). Since this result appears at variance with the technical production of tetrahydronaphthalene, the problem has been again examined. Mixtures of naphthalene and its tetrahydro-derivative are treated with hydrogen, either pure or containing a small proportion of oxygen, in the presence of spongy platinum which is free from, moderately charged, or highly charged with oxygen.

Naphthalene is converted by hydrogen in the presence of spongy platinum rich in oxygen into tetrahydronaphthalene, whereas decahydronaphthalene is formed (without the production of a detectable intermediate product) if the catalyst is poor in oxygen. The primary formation of a dihydro-compound occurs in such a manner that the hydrogen atoms become attached to one or to both of the benzene nuclei of naphthalene. Hydrogenation at one nucleus leads to a distinct break in the process (tetrahydronaphthalene) after which the addition continues much more slowly than with naphthalene itself. On the other hand, the addition of a hydrogen atom to each nucleus is followed by the production of a sequence of intermediate compounds each of which is less

saturated than naphthalene, and is hydrogenated at a much greater rate than the latter.

It appears very probable that the hydrogenation of naphthalene occurs in three distinct manners: (1) tetrahydronaphthalene is predominately produced when the oxygen content of catalyst and hydrogen is at a minimum; (2) the chief product is decahydronaphthalene when the oxygen content of platinum and hydrogen is low, and (3) tetrahydronaphthalene predominates when the oxygen content is considerable. The simplest explanation of these observations consists in the hypothesis that different dihydronaphthalenes are formed intermediately; three such substances are probably involved, one of which is the most stable and is capable of existence in the presence of a catalyst rich in oxygen, whereas another is so little stable towards spongy platinum that its formation is inhibited by the presence of even a small proportion of oxygen in the catalyst or hydrogen.

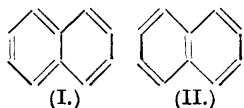
Hydrogenation occurring in both nuclei can lead through 1 : 5-dihydronaphthalene to the following intermediate products:



Incidental observations by Bamberger and his co-workers appear to show that the products of the hydrogenation of naphthalene by sodium and ethyl or amyl alcohols contain components in which the hydrogen is present in both nuclei.

Δ^2 - and Δ^1 -Dihydronaphthalenes are the only primary products of the hydrogenation of naphthalene at a single benzene nucleus which require to be considered. The former of these probably loses its hydrogen more readily, and is therefore the less stable towards spongy platinum rich in oxygen. The Δ^1 compound is the more stable and is the probable intermediate product in the formation of tetrahydronaphthalene in the presence of platinum rich in oxygen.

The author reaffirms his contention (cf. Willstätter and King, *loc. cit.*) that it is impossible to explain the peculiarities of the behaviour of naphthalene by a single structural formula. The unsymmetrical structure, (I), explains the production of derivatives hydrogenated in only one benzene nucleus, whereas the symmetrical configuration (II) is in accordance with the production of binuclear hydro-derivatives.



The hydrogenation of naphthalene is not catalysed by very finely divided platinum which is free from oxygen. Spongy platinum, poor and richer in oxygen, catalytically accelerates the hydrogenation; the action of the metal is different under the different conditions. A more rigid discrimination is necessary between specimens of spongy platinum containing, respectively, the minimum necessary amount, small quantities, and larger proportions of oxygen.

Spongy platinum saturated with oxygen appears to induce hydrogenation through the most stable intermediate products, whereas that poorer in oxygen causes the change to occur through intermediate phases of smaller stability. H. W.

The Series of the Methylnaphthalenes. FRITZ MAYER and OTTO SCHNECKO (*Ber.*, 1923, 56, [B], 1408—1415).—An extension of previous work (A., 1922, i, 740).

2-Iodo-1-methylnaphthalene, colourless leaflets, m. p. 53°, b. p. 196—199°/30 mm., is prepared from 1-methyl- β -naphthylamine by diazotisation and treatment of the product with potassium iodide. It is converted by successive treatment with magnesium and carbon dioxide into 1-methyl-2-naphthoic acid, colourless needles, m. p. 178° (ethyl ester, colourless crystals, m. p. 27—28°, b. p. 190°/20 mm.), which, like the isomeric 2-methyl-1-naphthoic acid (*loc. cit.*) could not be oxidised to the corresponding dicarboxylic acid; 1:1'-dimethyl-2:2'-dinaphthyl, colourless needles, m. p. 227°, is obtained as a by-product of the preparation of the acid.

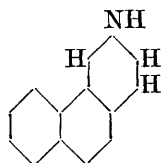
6-Amino-5-methyl-1:2:3:4-tetrahydronaphthalene, a colourless liquid which does not absorb carbon dioxide from the air and can be diazotised and coupled with β -naphthol, b. p. 170—175°/30 mm., is prepared by reducing 1-methyl- β -naphthylamine with sodium and amyl alcohol; the corresponding acetyl derivative, lustrous leaflets, m. p. 134°; the benzoyl derivative, m. p. 222°, and the hydrochloride, colourless needles, m. p. 263—264°, are described.

Dinaphtholmethane is converted by ammonium sulphite and ammonia at 150—160° into 1:2:1':2'-dinaphthacridine, straw-yellow needles, m. p. 216°, whereas at 110—120° 2-amino-2'-hydroxy-di-1:1'-naphthylmethane, lustrous leaflets, m. p. 121°, is produced (the corresponding acetyl derivative, lustrous leaflets, m. p. 132°, and the benzoyl compound, colourless needles, m. p. 159°, are described).

Ethyl 2- β -naphthylpropionate, colourless leaflets, m. p. 28°, b. p. 195—198°/25 mm., is converted by hydrazine hydrate in boiling alcoholic solution into the corresponding hydrazide, slender needles, m. p. 156°, which is transformed successively into the unstable azide, the urethane, colourless leaflets, m. p. 83°, and 2- β -naphthylethylamine, b. p. 174—175°/25 mm. (benzoyl derivative, rhombic prisms, m. p. 140—141°; picrate, long, yellow needles, m. p. 196°). Alternatively, the amine is produced by converting β -naphthylmethyl bromide into the corresponding cyanide, m. p. 86°, b. p. 202—205°/28 mm., and reducing the latter under pressure with hydrogen in the presence of nickel as catalyst and tetrahydronaphthalene as solvent; the primary base is thereby obtained in 60% yield together with di-2- β -naphthylethylamine, colourless needles, m. p. 87° (nitroso-derivative, lustrous leaflets, m. p. 179°; picrate, yellow needles, m. p. 138—139°; hydrochloride, lustrous leaflets, m. p. 289°). α -Naphthylmethyl cyanide is similarly hydrogenated to a mixture of β -1-naphthylethylamine, a colourless liquid, b. p.

182—183°/18 mm. (*picrate*, yellow needles, m. p. 201—202°; *benzoyl* derivative, colourless needles, m. p. 97° after softening at 87°), and *di-β-1-naphthylethylamine*, a colourless, viscous liquid, b. p. above 320°/200 mm. (*picrate*, lustrous leaflets, m. p. 179°; *nitroso*-derivative, lustrous leaflets, m. p. 114—115°; *hydrochloride*, m. p. 222°). The course of the hydrogenation depends greatly on the purity of the α -naphthylmethyl cyanide; traces of admixed bromo-compounds inhibit the change.

β -2-Naphthylethylamine condenses with methylal to give 1:2:3:4-tetrahydronaphthaisoquinoline, b. p. 200—205°/20 mm., m. p. 40°, in poor yield. With formaldehyde in the presence of ether it slowly gives the compound $C_{10}H_7 \cdot CH_2 \cdot CH_2 \cdot N \cdot CH_2$, needles, m. p. 117°, in 80 % yield. The latter substance is converted by warm, concentrated hydrochloric acid into naphthatetrahydroisoquinoline (annexed formula); the *picrate*, needles, m. p. 225—226°; the *dithiocarbamate*, $C_{27}H_{26}N_2S_2$, m. p. 192° after previous darkening; the *nitrosoamine*, lustrous leaflets, m. p. 105°; the *hydrochloride*, colourless needles, m. p. 275—276°; the *carbonate*, a white powder, incipient decomp., 124°, and the *o-nitrobenzoyl* derivative, m. p. 240°, after previous darkening, are described. The base is oxidised by successive treatment with potassium permanganate and nitric acid to benzene-1:2:3:4-tetracarboxylic acid, m. p. 238°. Attempts to obtain a quinoline derivative from β -1-naphthylethylamine were unsuccessful by reason of the tendency for ring closure to occur in the peri-position.



H. W.

Equations for Vapour Pressures and Latent Heats of Vaporisation of Naphthalene, Anthracene, Phenanthrene, and Anthraquinone. O. A. NELSON and C. E. SENSEMAN (*Ind. Eng. Chem.*, 1923, 15, 621—622).—The observed vapour pressures of the above are in close agreement with the values calculated from the Clapeyron equation of state, $dP/dT = L/(V - v)T$ (1). Approximating, this equation may be written $dP/dT = L/(RT^2/P)$ (2), which gives $L = (\log P_2 - \log P_1) T_1 T_2 \left(\frac{2.303 R}{T_2 - T_1} \right)$ (3). By plotting the calculated decrease in L against increase in temperature or pressure the equation for L is obtained. Whilst L decreases appreciably in the first three cases, with anthraquinone only a slight decrease is observed. In each case, L could be represented, over the temperatures and pressures studied, by a linear equation, $L = a + bT$, although this linear function only holds for short temperature intervals. Substituting in (2), the Clapeyron equation becomes $\log P = C - \frac{a}{4.5795 T} - \frac{b}{1.9885} \log T$. Calculations of the entropy of vaporisation, L/RT (cf. Hildebrand, *J. Amer. Chem. Soc.*, 1915, 37, 970) give values in the neighbourhood of 13.7, whence it is concluded that the above compounds all form normal liquids.

W. T. K. B.

Preparation of 9-Anthracyl Sulphide and 9-Anthracyl-mercaptan. PETRI & STARK, G. M. B. H. (D.R.-P. 360608; from *Chem. Zentr.*, 1923, ii, 481).—Anthracene is treated with sulphur monochloride in the presence of a catalyst with or without a solvent or diluent, according as the temperature of reaction is about 100° or the ordinary temperature, respectively. The product of reaction is treated with a reducing agent. For example, anthracene is heated with sulphur monochloride with the addition of benzene in the presence or absence of zinc dust, aluminium, or aluminium chloride, until evolution of hydrogen chloride ceases. After removal of benzene by distillation, the product is heated at 130° with hydrous sodium sulphide, whereby the sodium salt of 9-anthracyl mercaptan is obtained as light yellow leaflets. Treatment of the sodium salt with acid yields 9-anthracyl mercaptan, $C_{14}H_9 \cdot SH$. It forms yellow prisms and gives by mild oxidation 9-anthracyl sulphide, lustrous, orange-yellow prisms, m. p. 220—221°. The methyl ether of anthracyl mercaptan, $C_{14}H_9 \cdot SMe$, forms yellow needles, m. p. 157°. By oxidation with strong oxidising agents such as chromic oxide, these compounds yield anthraquinone.
G. W. R.

Certain Bromo-derivatives of Acenaphthene. REMO DE FAZI (*Atti R. Accad. Lincei*, 1923, [v], 32, i, 343—345).—Replacement by chloroform of the ether used as solvent in Graebe and Guinibourg's method for preparing 4-bromoacenaphthene (A., 1903, i, 408) results in the formation of a certain proportion of tetrabromoacenaphthene (cf. Ewan and Cohen, T., 1889, 55, 578). Oxidation of 4-bromoacenaphthene yields 4-bromonaphthalene-1 : 8-dicarboxylic acid, m. p. 220—221°, and 4-bromoacenaphthenequinone, m. p. 236.5—237°; the melting points given in the literature for these compounds are, respectively, 210° and 194°. T. H. P.

Substitution in Acenaphthene. I. The Sulphonation of Acenaphthene. K. DZIEWOŃSKI and T. STOŁYHWO (*Istny Zjazd Chemików Polskich*, 1923, 57).—The sulphonation of acenaphthene leads to the production of two isomeric monosulphonic acids and of four isomeric disulphonic acids. The oxidation of these products shows that substitution has occurred in the naphthalene nucleus, contrary to the generally accepted view. The monosulphonic acids, however, on distillation with potassium cyanide yield a product in which the sulphonic group is substituted in the side ring. R. T.

Substitution in Acenaphthene. II. The Bromo-nitro-, Bromo-sulphono-, and Nitro-sulphono-derivatives of Acenaphthene. K. DZIEWOŃSKI, (Mlle) A. GLASNERÓWNA, and T. ORZELSKI (*Istny Zjazd Chemików Polskich*, 1923, 57).—Substitution in α -nitroacenaphthene is extremely difficult, the α -nitro-sulphonic or halogen derivatives being prepared by the nitration of halogen substituted acenaphthenes, or of the acenaphthenesulphonic acids. The products thus obtained exhibit great chemical activity, and mobility of the substituents. α -Bromoacenaphthene is easily converted into α -bromoacenaphthenedisulphonic acid. R. T.

The Polymerisation of Acenaphthylene. I. Polyacenaphthylene and Allopolyacenaphthylene. K. DZIEWOŃSKI and (MILE) J. OLESIŃNA (*Istny Zjazd Chemików Polskich*, 1923, 58).—Acenaphthylene is converted by strong acids into *polyacenaphthylene*, $(C_{12}H_8)_n$, and *allopolyacenaphthylene* $(C_{12}H_8)_n$. Polyacenaphthylene is converted by bromination into *bromopolyacenaphthylene*, $C_{264}H_{144}Br_{221}$. R. T.

The Nitration of 1:1'-Dinaphthyl. C. S. SCHOEPPLE (*J. Amer. Chem. Soc.*, 1923, 45, 1566—1571).—It is shown that β -dinaphthol, when distilled with zinc dust, gives β -dinaphthylene oxide and not 1:1'-dinaphthyl as stated by Walder (A., 1883, 208). Consequently the compounds described as mono- and di-nitro-1:1'-dinaphthyl (Julius, A., 1887, 56) are mono- and di-nitro- β -naphthylene oxide, respectively.

1-Iodonaphthalene, from which Ullmann and Bielecki (A., 1901, i, 586) prepared 1:1'-dinaphthyl by the action of copper powder at 285° , is not readily obtainable, but 1-bromonaphthalene may be used, the yield of dinaphthyl being satisfactory if the reaction is conducted at 280 — 285° in the presence of a small amount of iodine. Small quantities of 1:2-dinaphthyl, 2:2'-dinaphthyl, perylene, and a compound, m. p. 282 — 283° , probably dinaphthyl-naphthalene (Weitzenböck and Seer, A., 1913, i, 847), are also produced.

The nitration of 1:1'-dinaphthyl in acetic acid solution at 90 — 95° gives an 85% yield of 4-nitro-1:1'-dinaphthyl, pale yellow needles, m. p. 104° ; the further nitration of this compound, which need not be isolated, gives 4:4'-dinitro-1:1'-dinaphthyl, pale yellow crystals, m. p. 246° , in 60% yield, together with small amounts of two isomeric dinitro-derivatives, which melt at 144° and 228° , respectively. The structures of 4-nitro-1:1'-dinaphthyl and 4:4'-dinitro-1:1'-dinaphthyl have been verified by synthesising the latter, by the action of copper powder at 220 — 230° on 4-nitro-1-iodonaphthalene. W. S. N.

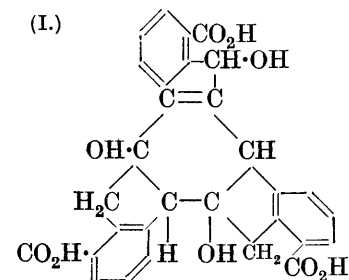
Decacycene. I. The Reduction of Decacycene. K. DZIEWOŃSKI and J. SUSZKO (*Istny Zjazd Chemików Polskich*, 1923, 55; cf. A., 1903, i, 431).—Decacycene (trinaphthalenebenzene) is reduced by means of hydriodic acid and red phosphorus, at 270 — 280° under pressure. A series of reduction products is obtained having the composition $C_{36}H_{24}$, $C_{36}H_{26}$, $C_{36}H_{30}$, $C_{36}H_{34}$, $C_{36}H_{36}$ and $C_{36}H_{44}$. In all these the benzene nucleus remains unattacked, showing that the benzene ring in compounds of this type is much more stable than in free benzene. R. T.

Decacycene. II. The Oxidation and Degradation of Decacycene. K. DZIEWOŃSKI, (MILE) J. ŁAZOWSKA, and D. WANDYCZ (*Istny Zjazd Chemików Polskich*, 1923, 55—56; cf. A., 1913, i, 848).—Decacycene is oxidised by means of chromic acid, and the product shown to be a mixture of two keto-acids $(C_{12}H_6O_5)_3$ or $(C_{12}H_5O_4)_3$, and $(C_{10}H_4O_3)_2$. The first of these acids is the primary oxidation product, as on oxidation it yields the second acid, which on further oxidation yields a truxene derivative, and finally a benzenetricarboxylic acid. R. T.

Decacyclene. III. The Sulphonation of Decacyclene. K. DZIEWOŃSKI and J. POCHWAŁSKI (*Istny Zjazd Chemików Polskich*, 1923, 56).—The action of concentrated sulphuric acid on decacyclene is to produce *decacyclenetrisulphonic acid*, $C_{36}H_{15}(SO_3H)_3$, a yellow acid dye, which on oxidation is converted into various coloured substances of a phenolic or quinonoid nature, and finally into the two keto-acids obtained by the direct oxidation of decacyclene.

R. T.

Degradation of Decacyclene [Trinaphthylenebenzene]. K. DZIEWOŃSKI and J. PODGÓRSKA (*Bull. Acad. Sci. Cracow*, 1915; from *Chem. Zentr.*, 1923, i, 525—526; cf. A., 1913, i, 848).—*Trimethyl tribenzoylbenzenetricarboxylate* (*truxenquinonetricarboxylate*) forms yellow needles,



calcium hydroxide, *truxenol*,

m. p. 324—328°. Reduction of the acid with zinc dust or sodium hydrogen sulphite yields *trihydroxy-tetrahydrotruxenetricarboxylic acid* (I), a microcrystalline mass (tablets), m. p. above 400° after darkening at 340°. On keeping in air or heating in alkaline solution it forms a dark, amorphous product. The calcium salt forms light yellow tablets. By distillation of the calcium salt with

$OH \cdot CH - C_6H_4 - C_6 \left(\begin{smallmatrix} CH_2 \\ C_6H_4 \end{smallmatrix} \right)_2$, is obtained by elimination of carbon dioxide. It forms satin-like needles, m. p.

338—340°. By reduction, *truxene*, $C_6 \left(\begin{smallmatrix} CH_2 \\ C_6H_4 \end{smallmatrix} \right)_3$, is formed; light yellow needles or tablets, m. p. 364—365°. The hydrocarbon dissolves in sulphuric acid containing a trace of nitric acid.

G. W. R.

Picrates of some Tertiary Amines. SHIGERU KOMATSU and UMESABURO TAKIMOTO (*Mem. Coll. Sci. Kyoto*, 1923, 6, 173—176).—The melting points of the picrates of some aromatic tertiary amines determined by Komatsu (A., 1913, i, 39) have been criticised by Singh (T., 1916, 109, 789). Some of these have now been redetermined, and slightly higher values have been found, although not so high as those found by Singh. The new values given are dimethylaniline picrate, 158—159.5°; diethylaniline picrate, 137—138°; methylethylaniline picrate, 127—128.3°. E. H. R.

Catalytic Decomposition of Anilides. A. MAILHE (*Compt. rend.*, 1923, 176, 1716—1719).—The catalytic decomposition of the anilides of acetic, propionic acid, etc., occurs along the same lines as that of formanilide (this vol., i, 458), the secondary amine produced by the loss of carbon monoxide being further decomposed into primary amine and aliphatic hydrocarbon. Subsidiary reactions result in the formation of carbon dioxide, hydrogen, methane, and small amounts of ammonia and carbon.

ee*

could be found by means of which the formation of the secondary amine could be catalysed and its subsequent decomposition suppressed, although both precipitated copper and alumina were tried instead of nickel. G. F. M.

β -Nitroarylhydroxylamines. I. β -2:4- and β -2:6-Dinitrophenylhydroxylamine. W. BORSCHÉ (*Ber.*, 1923, 56, [B], 1494—1501).—The unexpected reactivity of 2:4-dinitroanisole and 2:4-dinitrodiphenyl ether (Borsche, this vol., i, 780) has led the authors to examine the behaviour of these and associated substances towards hydroxylamine. A series of β -nitrophenylhydroxylamines which are otherwise very difficultly accessible has thereby been obtained.

β -2:4-Dinitrophenylhydroxylamine, leaflets or flattened needles, m. p. about 80° (decomp.), according to the rate of heating, is prepared by heating 2:4-dinitroanisole or 2:4-dinitrodiphenyl ether with hydroxylamine in alcoholic solution. The substance is stable when dry, but decomposes very readily in solution with evolution of nitric oxide and formation of dark red or brownish-black resins; the solutions can be stabilised in certain cases by the addition of salts of hydroxylamine. β -2:4-Dinitrophenylhydroxylamine has pronouncedly acidic properties; the sodium and barium salts, the ammonium compound, $C_6H_4O_5N_3 \cdot NH_4$, $C_6H_5O_5N_3$, black needles with a green reflex, m. p. 142° (decomp.), and the aniline compound, $C_6H_5O_5N_3 \cdot NH_2Ph$, dark-red plates, m. p. 111—112° (decomp.), are described. It is reduced by ammonium sulphide to 4-nitro-*o*-phenylenediamine. It is oxidised by chromic acid in the presence of glacial acetic acid to 1:3-dinitro-4-nitrosobenzene, dark yellow needles, m. p. 133°, to a dark green liquid, and by fuming nitric acid (*d* 1.54) to 1:2:4-trinitrobenzene, m. p. 60°. *O*-Acetyl- β -2:4-dinitrophenylhydroxylamine, lustrous, yellow needles, m. p. 164° (decomp.), after previous darkening and softening, is prepared by the action of acetic anhydride on β -2:4-dinitrophenylhydroxylamine at the atmospheric temperature. In contrast to the parent substance, it is relatively stable towards boiling acetic anhydride, by which it is converted into diacetyl- β -2:4-dinitrophenylhydroxylamine, $C_{10}H_9O_7N_3$, pale yellow leaflets, m. p. 141°, and much resinous matter. *O*-Benzoyl- β -2:4-dinitrophenylhydroxylamine, obtained by the aid of benzoyl chloride in the presence of pyridine, crystallises in long, dark yellow needles, m. p. 163—164° (slow decomp.). β -2:4-Dinitrophenylhydroxylamine methyl ether, dark-yellow, acute prisms, m. p. 110—111°, is prepared by the action of methyl sulphate and sodium hydroxide on the hydroxylamine. It is reduced by ammonium sulphide to 4-nitro-*o*-phenylenediamine. It is converted by diazomethane in the presence of ether into the dimethyl compound, $C_8H_9O_5N_3$, pale yellow needles, m. p. 87°. β -Benzoyl- β -2:4-dinitrophenylhydroxylamine methyl ether crystallises in pale yellow needles, m. p. 155°.

β -2:6-Dinitrophenylhydroxylamine, coarse needles, m. p. 115° (decomp.), is prepared in 81% yield from 2:6-dinitrodiphenyl ether; it is less stable in substance, more stable in solution, than the

isomeric 2 : 4-dinitro-compound. *Dibenzoyl-β-2 : 6-dinitrodiphenylhydroxylamine* crystallises in pale yellow, lustrous prisms, m. p. 168—169°. The hydroxylamine is oxidised by fuming nitric acid (*d* 1·54) to 1 : 2 : 3-trinitrobenzene, long, pale yellow needles, m. p. 121°. H. W.

Preparation of Pure Dehydrothiotoluidine. R. F. HUNTER (*J. Soc. Chem. Ind.*, 1923, 42, 302r).—A description of a laboratory preparation of dehydrothio-*p*-toluidine by heating *p*-toluidine and sulphur. A maximum yield amounting to 30% of theory was obtained, m. p. 191°. [According to Paul, *Z. angew. Chem.*, 1896, 9, 681; *J. Soc. Chem. Ind.*, 1897, 730; and Casseller, D.R.-P. 53938, yields of 50% to 75% of theory are readily obtainable by using naphthalene as a solvent.] F. A. M.

Destructive Action of Nitric Acid on Phenols. MOTOE IWATA (*J. Chem. Soc. Japan*, 1923, 44, 391—406).—If 60% nitric acid is dropped gradually on gallic acid, and, when reaction has ceased, the mixture heated on a water-bath, the gallic acid (1 mol.) is almost completely decomposed into carbon dioxide, hydrocyanic acid, oxalic acid (nearly 1 mol.), and water; acetic acid could not be detected. The hydrocyanic acid is regarded as a by-product, the amount being only 1—2%. For the production of oxalic acid the concentration of the nitric acid (30—60%) has scarcely any effect. Using the production of hydrocyanic and oxalic acids as a test, the decomposing action of nitric acid on phenols and carboxylic acids has been examined; the percentages given below are those of nitric acid at the lower limit for the decomposition at the ordinary temperature (*a*) and on heating (100°) (*b*) respectively: gallic acid, *a* 30%, *b* 8%; protocatechuic acid, *a* 30%, *b* 1·5—2%; salicylic acid, *a* no action, *b* 8·1%; pyrogallol, *a* 30%, *b* 20%; phloroglucinol, *a* no action, *b* 15% (no decomposition by 8% acid); resorcinol, *a* no action, *b* 15%; quinol, *a* 30%, *b* 15% (no decomposition by 8% acid); guaiacol, *a* 30%, *b* 8% (no decomposition by 6% acid); phenol, *a* 50% accompanied by nitration, *b* 8·1—11%; thymol, *a* and *b* concentrated acid; benzoic acid, *a* and *b* no decomposition by concentrated acid; toluene, benzene, and naphthalene, *a* and *b* no decomposition; gallotannin, *a* concentrated acid, *b* 30%. With α - and β -naphthols, hydrocyanic acid is produced on warming, but no oxalic acid. The entrance of hydroxyl and carboxyl groups into the benzene nucleus promotes the decomposition. K. K.

2-Phenylcyclohexanol and 2-Bromocyclohexanol. PIERRE BEDOS (*Compt. rend.*, 1923, 177, 111—113; cf. A., 1922, i, 334, and this vol., i, 101).—Magnesium phenyl bromide converts cyclohexene oxide into 2-phenylcyclohexanol and, as secondary product, a cyclohexenol, $C_6H_{10}O$. The former alcohol is a colourless liquid, with b. p. 138—140°/11 mm., d_{20}^{16} 1·035, n_D^{16} 1·5415, phenylurethane, m. p. 135—136°, and hydrogen phthalate, m. p. 185—186°. When distilled with potassium hydrogen sulphate it gives a phenylcyclohexene, b. p. 125—126°/17 mm., d_{20}^{14} 0·982, and n_D^{14} 1·5505. The cyclohexenol has b. p. 65°/7 mm., d_{20}^{26} 1·0, and n_D^{26} 1·499; the phenyl-

urethane, m. p. 107—108°, is identical with that obtained by Brunel (*Thesis*, Paris, 1905) from a *cyclohexenol* obtained from a different source.

The above *phenylcyclohexanol* is probably a stereoisomeride of that (m. p. 54—55°, *phenylurethane*, m. p. 138—139°) obtained by Braun, Grüber, and Kirschbaum (this vol., i, 107). The *hexanol* melting at 54—55° has been obtained by reducing 2-*phenylcyclohexanone* (Le Brazidic, A., 1915, i, 12) with sodium and alcohol.

2-*Bromocyclohexanol* is obtained by the action of water on the intermediate Grignard additive compound (above) (cf. Blaise, A., 1902, i, 357). It is a colourless liquid, b. p. 87—88°/9 mm., d_{15}^{20} 1.402, n_D^{20} 1.528; *phenylurethane*, m. p. 87—88°. E. E. T.

The Decomposition of Ethers by Metallic Sodium. J. F. DURAND (*Bull. Soc. chim.*, 1923, [iv], 33, 734—735; cf. this vol., i, 207, and A., 1921, i, 89).—A claim for priority against Schorigin. H. H.

The Exchange of the Group ·OR in Nitrophenyl Ethers by other Radicles. W. BORSCHÉ (*Ber.*, 1923, 56, [B], 1488—1493).—The action of ammonia, aniline, hydrazine, phenylhydrazine, and ethyl sodioacetoacetate on a number of nitrophenyl ethers has been investigated under comparable conditions. It is found that the hydrazino-group is most readily introduced into the benzene nucleus in place of the group ·OR and that the phenyl ethers of the nitrated phenols are more reactive than the alkyl ethers.

A full description is given of the preparation of 2:4-dinitroanisole, 2:4-dinitrodiphenyl ether, 3:5-dinitro-*o*-tolylmethyl ether, 3:5-dinitro-*p*-tolylmethyl ether, 3-nitroanisonitrile, ethyl 3-nitroanisate, 3-nitro-4-phenoxybenzonitrile, acute, pale yellow prisms, m. p. 79°, and ethyl 3-nitro-4-phenoxybenzoate, pale yellow, coarse crystals, m. p. 93—94°.

2:4-Dinitroanisole is converted by ammonia in aqueous alcoholic solution at 40—50° to a small extent into dinitroaniline which, under analogous conditions, is formed in good yield from 2:4-dinitrodiphenyl ether.

2:4-Dinitrodiphenylamine, m. p. 155—156°, is formed from the corresponding phenyl ether and aniline at 180°, whereas 2:4-dinitroanisole is converted into smeary products; 3:5-dinitro-*o*- and -*p*-tolyl methyl ethers are only partly changed, whereas 3-nitro-4-phenoxybenzonitrile is almost unaffected.

The following compounds are obtained by the use of hydrazine: 2:4-dinitrophenylhydrazine, m. p. 197—198° (decomp.); 6-nitro-1-hydroxy-4-methyl-1:2:3-benzotriazole, $\text{NO}_2 \cdot \text{C}_6\text{H}_2\text{Me} \langle \text{N}(\text{OH}) \rangle \text{N}$, pale yellow leaflets, m. p. 225° (decomp.), and the corresponding hydrazine salt, small, yellow needles, from 3:5-dinitro-*o*-tolyl methyl ether; 4-nitro-6-methyl-1:2:3-benzotriazole, slender, pale yellow needles, m. p. 241° (decomp.), from 3:5-dinitro-*p*-tolyl methyl ether; 3-nitro-4-hydrazinobenzonitrile, m. p. 221—222°, from 3-nitroanisonitrile or 3-nitro-4-phenoxybenzonitrile; ethyl 3-nitro-

4-hydrazinobenzoate, yellow needles, m. p. 103° , from ethyl 3-nitro-anisate or ethyl 3-nitro-4-phenoxybenzoate; 1:2:3-benztriazole, m. p. (hydrated) 104° (decomp.), followed by resolidification and fusion at 157 — 158° , m. p. (anhydrous) 157 — 158° , from *o*-nitro-anisole or *o*-nitrodiphenyl ether; under similar conditions, *p*-nitro-anisole remains unchanged.

2:4-Dinitrodiphenyl ether is converted by phenylhydrazine in boiling alcoholic solution into 5-nitro-2-phenyl-2:1:3-benztriazole, $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \llcorner \text{N} \text{> NPh}$, m. p. 176 — 178° , whereas under like conditions 2:4-dinitroanisole is almost unaffected. 3:5-Dinitro-*o*-tolyl methyl ether is transformed similarly into 5-nitro-2-phenyl-7-methyl-2:1:3-benztriazole, brownish-yellow needles, m. p. 164° . 3:5-Dinitro-*p*-tolyl methyl ether, 3-nitroanisonitrile, and 3-nitro-4-phenoxybenzonitrile do not react with an equivalent amount of boiling phenylhydrazine.

2:4-Dinitroanisole and 2:4-dinitrodiphenyl ether are transformed by ethyl sodioacetoacetate in the presence of alcohol and benzene into ethyl α -2:4-dinitrophenylacetoacetate, coarse yellow needles, m. p. 97 — 98° . 3:5-Dinitro-*o*-tolyl methyl ether does not react with ethyl sodioacetoacetate under similar conditions.

H. W.

Improved Preparation of Thymol. HOWARD & SONS, LTD., and J. W. BLAGDEN (Brit. Pat. 1923, 197848).—By condensing isopropyl alcohol at 90° with polysulphonated *m*-cresol in presence of sulphuric acid, polysulphonated thymol is obtained in satisfactory yield. The sulphonic acid groups are eliminated from the product by treatment with superheated steam.

T. S. W.

Synthesis of Thymol from *p*-Cymene. I. MAX PHILLIPS and H. D. GIBBS (*J. Ind. Eng. Chem.*, 1920, **12**, 733—734).—*p*-Cymene is isolated from a crude oil obtained from a sulphite spruce pulp mill. After purification, it is nitrated, and the nitro-cymene reduced to cymidine by means of iron powder and hydrochloric acid. Sulphonation of cymidine gives a mixture of *o*- and *p*-cymidinesulphonic acids, which, by diazotisation and subsequent treatment with ethyl alcohol and copper powder, are successively converted into the corresponding diazocymenesulphonic acids and the same cymene-3-sulphonic acid, the sodium salt of which yields thymol on fusion with sodium hydroxide (cf. following abstract).

W. S. N.

Synthesis of Thymol from *p*-Cymene. II. MAX PHILLIPS (*J. Amer. Chem. Soc.*, 1923, **45**, 1489—1493).—The synthesis of thymol from *p*-cymene (cf. preceding abstract) has been modified and improved. Conditions of working are given by which nitro-cymene may be reduced to cymidine, by means of iron powder and hydrochloric acid, in 80—85% yield, and a process is described by which cymidine may be sulphonated, giving an 80% yield of cymidinesulphonic acid. A new method for the elimination of the amino-group is adopted. Cymidinesulphonic acid is diazotised,

and the diazocymenesulphonic acid collected and treated with cold aqueous sodium hydrogen sulphite. After one hour the orange-coloured solution is heated to boiling and treated with hydrochloric acid. On concentration, *cymylhydrazine-p-sulphonic acid*, m. p. 260° (decomp.), is obtained in 70–75% yield. It forms a *barium* salt, pale yellow plates. The hydrazinesulphonic acid is treated in boiling aqueous solution with an excess of copper sulphate, and the resulting cymene-*p*-sulphonic acid isolated as its sodium salt. For the production of thymol by the fusion of this salt with alkali, potassium hydroxide is far superior to sodium hydroxide. The best yield (59%) is obtained using three parts of potassium hydroxide to one part of sulphonate at 350° , with a fusion period of thirty minutes. W. S. N.

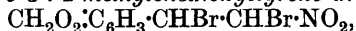
Catalytic Action. I. Catalytic Reduction of α -Naphthol and α -Naphthylamine. SHIGERU KOMATSU and RYUZABURO NODZU (*Mem. Coll. Sci. Kyoto*, 1923, **6**, 177–181).—When α -naphthol was passed with pure hydrogen over reduced nickel at 100 – 110° , a yield of about 41% of crude *ar*-tetrahydro- α -naphthol was obtained, together with 51% of α -ketotetrahydronaphthalene containing some tetrahydronaphthalene. At 135 – 145° , only 10% of the *ar*-compound was obtained and 90% of mixed *ac*-compound and hydrocarbon. When α -naphthylamine was reduced in a similar manner at 135 – 145° , 90% was converted into *ar*-tetrahydro- α -naphthylamine, the remainder being tetrahydronaphthalene formed from *ac*-tetrahydro- α -naphthylamine. E. H. R.

Dinitrosoresorcinol. W. R. ORNDORFF and M. L. NICHOLS (*J. Amer. Chem. Soc.*, 1923, **45**, 1536–1539).—Dinitrosoresorcinol, when dried to constant weight under reduced pressure over sulphuric acid, contains one molecule of water of crystallisation, and decomposes at 162 – 163° (cf. Morgan and Moss, T., 1922, **121**, 2861; Bülow, A., 1904, i, 609). It forms thin, rhombic plates [$a : b : c = 0.9 (?) : 1 : 0.613$]. W. S. N.

The Bromination of Organic Compounds. K. W. ROSENMUND and W. KUHNHENN (*Ber.*, 1923, **56**, [B], 1262–1269).—Difficulties are not infrequently encountered in the bromination of aliphatic and aromatic compounds by reason of the impossibility of limiting the action in the desired manner. As mild brominating agents, pyridine and quinoline dibromide hydrobromides (particularly the former) are found to be very useful reagents, the reaction being usually effected in a glacial acetic acid solution. A very convenient modification of the method consists in dissolving the substance to be brominated and pyridine or quinoline hydrochloride or hydrogen sulphate in glacial acetic acid and adding the calculated amount of bromine solution from a burette; with colourless or faintly coloured substances, the termination of the reaction is fairly sharply indicated by the production of the orange-yellow coloration due to the formation of the dibromide hydrobromide.

Improved methods for the preparation of pyridine and quinoline dibromide hydrobromides are given.

The following compounds are described: $\beta\gamma$ -Dibromo- α -3 : 3-methylenedioxyphenylpropane, $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}_2\cdot\text{CHBr}\cdot\text{CH}_2\text{Br}$, a colourless, viscous liquid, b. p. $189^\circ/12$ mm., prepared from safrole and pyridine dibromide hydrobromide in the presence of glacial acetic acid at $3-6^\circ$ and converted by successive treatment with silver acetate and potassium hydroxide into $\beta\gamma$ -dihydroxy- α -3 : 4-methylenedioxyphenylpropane, m. p. $82-83^\circ$. ω -Nitro- p -methoxystyrenedibromide, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHBr}\cdot\text{CHBr}\cdot\text{NO}_2$, a brown liquid which solidifies when preserved in a desiccator and is converted by an alcoholic solution of potassium acetate into ω -bromo- ω -nitro- p -methoxystyrene, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CBr}\cdot\text{NO}_2$, lemon-yellow crystals, m. p. $67.5-68^\circ$. ω -Nitro-3 : 4-methylenedioxy-styrene dibromide,



coarse, colourless prisms, which is readily converted into ω -bromo- ω -nitro-3 : 4-methylenedioxy-styrene, yellow needles, m. p. $101-102^\circ$. Monobromopyrogallol, needles, decomp. 140° after darkening at $120-130^\circ$, and its triacetate, hexagonal plates, m. p. 118° . Dibromopyrogallol, m. p. 160° (decomp.), and its monohydrate, decomp. 137° , and triacetate, m. p. 145° . Dibromoresorcinol, long needles, m. p. $110-112^\circ$, and its diacetate, coarse prisms, m. p. $96.5-97^\circ$. Bromocatechol, coarse prisms, or long needles, m. p. 87° , and its dibenzoate, m. p. 111° .
H. W.

Orcinol. JOHN MISSENDEN (*Chem. Age*, 1922, 7, 709; from *Chem. Zentr.*, 1923, i, 299).—Orcinol is a characteristic constituent of certain lichens of the genera *Variolaria*, *Rocella*, and *Lecanora*. It is extractable by chloroform in the form of the sodium salt, as a red solution changing to green on addition of water. It crystallises from sodium chloride solution in hexagonal tablets or prisms, m. p. 107.3° . The following derivatives are mentioned: acetate, pyramids, m. p. 24.45° ; monomethyl ether, a yellow, viscid liquid, b. p. 285° ; azobenzene derivative, red crystals, m. p. 188.5° ; diethyl dicarbonate, a viscid liquid, b. p. 313° .
G. W. R.

Phenols Derived from Cymene. G. BARGELLINI (*Gazzetta*, 1923, 53, i, 234—245).—Thiele (A., 1898, i, 469) has shown that the action of acetic anhydride in presence of a small quantity of concentrated sulphuric acid converts p -benzoquinone into the triacetyl derivative of hydroxyquinol, the latter being then obtainable on hydrolysis. This reaction serves as a general means of introducing a new phenolic hydroxyl group into the molecule of quinols (cf. Thiele and Winter, A., 1900, i, 500, 504; Thiele and Günther, A., 1906, i, 743).

By applying this reaction to thymoquinone, the author has obtained a mixture of two triacetyl derivatives, the constitutions of which were determined by hydrolysing them and oxidising the trihydroxy-derivatives to the corresponding hydroxythymoquinones, both of which are known. The mixture of triacetyl derivatives consists of about two parts of the 2 : 5 : 6-trihydroxycymene derivative and one part of the 2 : 3 : 5-trihydroxycymene derivative; possibly the p -isopropyl group offers greater resistance than the methyl group to the entrance of the new substituent.

Application of Thiele's reaction to the two isomeric hydroxy-thymoquinones results, in either case, in the formation of the tetra-acetyl derivative of tetrahydroxycymene, but the latter is more easily obtained pure by passing a current of air through a cold alkaline solution of either 3- or 6-hydroxythymoquinone or of a mixture of the two.

2-Nitrosothymol, m. p. 161—162°, is readily obtained pure by gradual addition of aqueous sodium nitrite solution to a solution of thymol in a mixture of alcohol and 50% acetic acid solution. Its reduction to 2-aminothymol may be effected conveniently by means of sodium sulphide.

The *diacetyl* derivative of 2:5-thymoquinol, $C_6H_2MePr^2(OAc)_2$, forms white needles, m. p. 73—75°.

The *triacetyl* derivative of 2:3:5-trihydroxycymene, $C_6HMePr^3(OAc)_3$, forms white crystals, m. p. 135—137°, and is converted by hydrolysis and subsequent oxidation by ferric chloride into the 3-hydroxy-thymoquinone ($O:OH:O=2:3:5$) obtained by Mazzara (A., 1890, 965) from carvacrol.

The *triacetyl* derivative of 2:5:6-trihydroxycymene crystallises in white needles, m. p. 83—85°, and is convertible into 6-hydroxy-thymoquinone ($O:O:OH=2:5:6$).

3:6-Dihydroxythymoquinone (cf. Ladenberg and Engelbrecht, A., 1878, 60) may be conveniently prepared by passing a current of air through a solution of 3- or 6-hydroxythymoquinone in about 10% sodium or potassium hydroxide solution until the violet-red colour changes to deep garnet-red.

Reduction of the preceding compound by passage of a stream of hydrogen through its alcoholic solution containing platinum black in suspension appears to yield tetrahydroxycymene (cf. Henderson and Boyd, T., 1910, 97, 1663), but this could not be isolated, owing to the readiness with which it undergoes reoxidation to dihydroxythymoquinone. When, however, the latter is heated in a reflux apparatus with zinc dust and acetic anhydride, it yields the *tetra-acetyl* derivative of tetrahydroxycymene, $C_{18}H_{22}O_8$, which crystallises in white leaflets or needles, m. p. 186—188°, and dissolves in concentrated sulphuric acid to a yellow solution, this being decolorised by a drop of nitric acid. The tetra-acetyl derivative may be obtained also by dissolving either 3- or 6-hydroxy-thymoquinone in acetic anhydride and adding concentrated sulphuric acid to the hot solution.

T. H. P.

The Benzil Rearrangement. II. ARTHUR LACHMAN (*J. Amer. Chem. Soc.*, 1923, 45, 1509—1514).—Benzil forms, with sodium ethoxide, a white, additive product, $OEt \cdot CPh(ONa) \cdot CPh$, which is instantly decomposed, in the presence of water, into benzil, sodium hydroxide, and alcohol. When allowed to remain in dry alcoholic solution it breaks down into benzaldehyde and ethyl benzoate, only traces of benzoic acid being formed. Hence benzil sodium ethoxide does not undergo intramolecular oxidation and reduction, since migration of the sodiumoxy- or ethoxy-group would

give, respectively, sodium ethylbenzilate, or ethyl benzilate. Fission probably occurs according to the equation $\text{OEt}\cdot\text{CPh}(\text{ONa})\cdot\text{COPh} + \text{EtOH} = \text{Ph}\cdot\text{CO}_2\text{Et} + \text{Ph}\cdot\text{CHO} + \text{EtONa}$, although the possibility of the reaction, $\text{OEt}\cdot\text{CPh}(\text{ONa})\cdot\text{COPh} = \text{Ph}\cdot\text{CO}_2\text{Et} + \text{Na}\cdot\text{COPh}$, is not entirely excluded. When increasing amounts of water are added to the alcoholic solution the production of benzoic acid increases rapidly, the intermediate compound probably being $\text{CPh}(\text{OH})_2\cdot\text{COPh}$, or, if much sodium hydroxide is present, $\text{OH}\cdot\text{CPh}(\text{ONa})\cdot\text{COPh}$. These results show that the hydroxyl group, in accordance with the theory previously advanced (A., 1922, i, 459), is necessary for the intramolecular oxidation and reduction ("rearrangement") of benzil, the sodiumoxy- and ethoxy-radicals, although chemically similar, being incapable of shifting.

W. S. N.

The Benzil Rearrangement. III. ARTHUR LACHMAN (*J. Amer. Chem. Soc.*, 1923, 45, 1522—1529).—Hydrocyanic acid and potassium cyanide act on benzil in alcoholic solution with formation of ethyl benzoate and benzaldehyde (cf. Jourdan, A., 1883, 805; Michael and Palmer, A., 1886, 155). Benzil-cyanohydrin is probably an intermediate stage; this breaks down into benzaldehyde and benzoyl cyanide, the latter producing ethyl benzoate as a secondary reaction product. Benzoic acid is not formed in this reaction, in spite of the presence of a hydroxyl group in benzil-cyanohydrin. If, however, the latter is ionised, the ion contains no hydroxyl. The non-formation of benzoic acid may also be accounted for on the assumption that the presence of hydroxyl, although necessary, is not a sufficient condition for the intramolecular rearrangement (cf. preceding abstract).

The action of anhydrous hydrogen cyanide on benzil at 140° gives α -cyanobenzyl benzoate, $\text{CN}\cdot\text{CHPh}\cdot\text{O}\cdot\text{COPh}$, m. p. 61° , b. p. $200^\circ/10$ mm. or $178^\circ/5$ mm. It is evident that benzil-dicyanohydrin is first formed; this then dissociates into benzoyl cyanide and mandelonitrile: $\text{OH}\cdot\text{CPh}(\text{CN})\cdot\text{CPh}(\text{CN})\cdot\text{OH} = \text{Ph}\cdot\text{CO}\cdot\text{CN} + \text{OH}\cdot\text{CHPh}\cdot\text{CN}$, which have actually been shown to give the above ester, when heated together under similar conditions. The latter reaction excludes the possibility that the compound formed is the isomeric benzil-monocyanohydrin.

W. S. N.

The Benzil Rearrangement. IV. Benzoin. ARTHUR LACHMAN (*J. Amer. Chem. Soc.*, 1923, 45, 1529—1535).—It is suggested that the production of benzyl alcohol and ethyl benzoate by the action of alcoholic hydrocyanic acid on benzoin (Michael and Palmer, A., 1886, 155) proceeds similarly to the formation of benzaldehyde and ethyl benzoate from benzil (cf. preceding abstract), since benzaldehyde, which Michael and Palmer assume to be an intermediate product, does not give ethyl benzoate when heated with alcoholic hydrocyanic acid. Benzoin, like benzil, gives an additive product with sodium ethoxide.

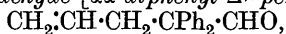
The rearrangement of benzil is not brought about by alkali, but the action of 1.5–6.0*M*-sulphuric acid or phosphoric acid at 175 – 230° leads to the formation of diphenylacetic acid, which partly decomposes into carbon dioxide and diphenylmethane.

The production of the latter when benzoin is heated (Engler and Grimm, A., 1898, i, 175) undoubtedly proceeds in the same way.

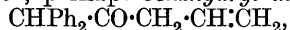
The rearrangements of hydrobenzoin, with loss of water, to diphenylacetaldehyde, of benzoin to diphenylacetic acid, and of benzil, with addition of water, to benzoic acid, are held to agree with the assumption of a mobile hydroxyl group, capable of exchanging places with phenyl, whilst any theory, such as that of Tiffeneau, which has as its basis the formation of unsaturated valencies by loss of water, is inadequate.

The great tendency to production of the carbonyl group is noted, numerous examples being given. W. S. N.

The Mechanism of the Transformation of α -Glycols by the Action of Dehydrating Agents. I. The Dehydration of Allylhydrobenzoin. S. DANILOV (*J. Russ. Phys. Chem. Soc.*, 1920, 52, 369—399; cf. this vol., i, 680).—Allylhydrobenzoin, $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{CPh}(\text{OH})\cdot\text{CHPh}\cdot\text{OH}$, has been prepared by Jakubovitsch (A., 1913, i, 264) who described it as having m. p. 89° and giving on dehydration with dilute sulphuric acid a compound, m. p. 126° . It is now found that the glycol prepared by the same process has m. p. 100° when pure; its *monoacetate* has m. p. 120 — 121° . The substance is practically not attacked by sulphuric acid under the conditions used by Jakubovitsch; more drastic treatment is necessary. The formation of the substance, m. p. 126° , was not observed; the reaction product consists principally of *diphenylallylacetaldehyde* [α -*diphenyl*- Δ^7 -*pentaldehyde*],



but another substance, perhaps *benzhydryl allyl ketone*,



is also present giving a compound with semicarbazide, m. p. 190° (decomp.). Oxidation of the crude reaction mixture by permanganate leads to the production of benzophenone in addition to a mixture of acids; this shows that one of the reactions occurring during the dehydration of the glycol involves the wandering of a phenyl group. The lowest boiling fraction, a golden-yellow, viscous oil, b. p. 177 — $179^\circ/9$ mm., d_4^{20} 1.0933, d_4^{30} 1.0769, d_4^{40} 1.0749, n_D^{20} 1.58116, n_D 1.58693, consists of the practically pure aldehyde, and readily gives the *semicarbazone*, groups of needles or rhombic crystals, m. p. 172.5° , and the *oxime*, rosettes of colourless needles, m. p. 126° . The regeneration of the aldehyde from the semicarbazone was not successful. Both the oxime and the semicarbazone are readily reduced by means of hydrogen and colloidal palladium (Skita's method) to the corresponding derivatives of α -diphenyl-*n*-valeraldehyde, the oxime of which melts at 115.5° and the semicarbazone at 145° . Attempts to oxidise the aldehyde to the corresponding acid failed; the oxime was therefore dehydrated by means of acetic anhydride to the *nitrile*, a colourless liquid, b. p. 192 — $195^\circ/14$ mm., but on treatment with hydrogen chloride in acetic acid this substance, instead of yielding the desired acid, passes into a *lactone*, opaque leaflets, m. p. 113.5° , probably the

lactone of γ -hydroxy- α -diphenyl-valeric acid, $\text{CPh}_2\cdot\text{CH}\cdot\text{CHMe}$; $\text{CO}\text{---}\text{O}$; it is

thought that the substance, m. p. 109—110°, obtained in somewhat comparable circumstances by Ramart-Lucas (A., 1912, i, 556) may have a similar structure.

The crude aldehyde boiling at 179—181°/11 mm., is readily hydrogenated by Skita's method to the saturated α -diphenylvaleraldehyde, $\text{CPr}^a\text{Ph}_2\cdot\text{CHO}$, b. p. 180·5°/11 mm., d_4^{20} 1·0683, d_{20}^{20} 1·0542, d_4^{20} 1·0523, n_D 1·56334, n_D 1·56875, n_f 1·58232, n_g 1·59429, forming an *oxime*, rhombic crystals, m. p. 115·5°, and a *semicarbazone*, existing in two forms, rhombic plates, m. p. 145°, and rosettes of microscopic crystals, m. p. 188°; the latter is the more sparingly soluble in alcohol.

The more soluble form is identical with the substance obtained by hydrating the semicarbazone of the unsaturated aldehyde. The substance, m. p. 188°, may perhaps be the semicarbazone of a hydrogenated substance corresponding with the unsaturated ketone probably present in the original mixture.

On oxidation with chromium trioxide in acetic acid, the saturated aldehyde passes into α -diphenylvaleric acid, $\text{CPr}^a\text{Ph}_2\cdot\text{CO}_2\text{H}$, rhombic plates from alcohol, m. p. 155·5°; the same acid can be obtained from the oxime of the aldehyde by dehydration and hydrolysis; the *benzyl* ester has m. p. 68—69°; the *anilide*, m. p. 112°, and the *amide*, m. p. 102°, were prepared. G. A. R. K.

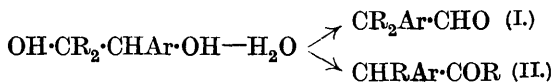
The Mechanism of the Transformation of α -Glycols by the Action of Dehydrating Agents. II. The Dehydration of isoPropylhydrobenzoin. S. DANILOV (*J. Russ. Phys. Chem. Soc.*, 1920, 52, 400—417).—*isoPropylhydrobenzoin* ($\alpha\beta$ -diphenyl- γ -methylbutane- $\alpha\beta$ -diol) is obtained in 50% yield by the action of magnesium isopropyl bromide on benzoin, and forms thin prisms, m. p. 108·5°; the *monoacetate*, prepared by means of acetyl chloride, forms small needles, m. p. 124—125°, and is accompanied by a *substance*, m. p. 94—95°, isomeric with the starting material. The product obtained by dehydrating the glycol with aqueous sulphuric acid consists mainly of a solid ketone, m. p. 77°, together with a liquid mixture of products.

The ketone, m. p. 77°, crystallises from alcohol in silky rods and has b. p. 170—171°/9 mm.; it is *benzhydryl isopropyl ketone* (α -diphenyl- γ -methylbutane- β -one), $\text{CHPh}_2\cdot\text{CO}\cdot\text{CHMe}_2$. It is not readily oxidised by chromic acid; by heating with alcoholic potassium hydroxide in a sealed tube it is quantitatively split into diphenylmethane and isobutyric acid. The *oxime* forms large, prismatic plates, m. p. 128·5°; the *semicarbazone* crystallises in opaque plates, m. p. 165—166°. The ketone could not be reduced to the corresponding *alcohol* by means of sodium amalgam, but the use of magnesium *tert.*-butyl chloride was successful. α -Diphenyl- γ -methylbutane- β -ol boils at 180·5—181·5°/13 mm., m. p. 34°, d_4^{20} 1·0591, d_{20}^{20} 1·0446, d_4^{20} 1·0427, n_D 1·55986, n_D 1·56502, n_f 1·57741, n_g 1·58818. The *benzoate*, soft needles, m. p. 105—106°, and the *phenylurethane*, fine, silky needles, m. p. 127·5°, were prepared.

The liquid mixture obtained by the dehydration of the hydrobenzoin contains considerable quantities of the ketone, m. p. 77° , which can be isolated by means of semicarbazide; another *semicarbazone*, $C_{18}H_{21}ON_3$, melting at $184-185^{\circ}$, can also be isolated and is probably derived from *diphenylisopropylacetaldehyde* [α -*diphenyl- γ -methylbutaldehyde*], $CPr^2Ph_2 \cdot CHO$; it is more abundant in the higher boiling portions of the oil. The oxidation of the oil by means of chromium trioxide gives acetone, a little benzoic acid, and benzophenone, also a neutral substance, m. p. $75-76^{\circ}$. The action of alcoholic potash on the oil leads to the formation of formic and isobutyric acids, benzhydrol, diphenylmethane and another hydrocarbon which was not identified. The absence of benzoic acid and diphenylisobutane amongst these products is taken as proof that no isopropyldeoxybenzoin is produced in the dehydration of isopropylhydrobenzoin; the ketone, m. p. 77° , and diphenylmethylbutaldehyde appear to constitute the bulk of the reaction mixture.

G. A. R. K.

Semi-pinacolic Transformations. I. Dehydration of Aryldialkyl Glycols by Heat and Acids. M. TIFFENEAU and (MILLE) J. LÉVY (*Bull. Soc. chim.*, 1923, [iv], **33**, 735—759; cf. this vol., i, 213).—Aryldialkyl glycols are intermediate in structure between hydrobenzoin and pinacones, and hence should give both semi-hydrobenzoin transformations (I) in which the tertiary hydroxyl group is eliminated as water, and semi-pinacolic transformations (II) in which the secondary hydroxyl group is so eliminated.



Reaction (I) is the more general with regard to the effect both of heat and of dilute acids. More vigorous dehydration generally leads to the formation of an ethylene oxide, but sulphuric acid in the cold causes the reaction to follow course (II). Increase of molecular weight of the group R inhibits the dehydration of the compound by heat. The following compounds are described. *γ -Phenylhexan- δ -one*, b. p. $114-116^{\circ}/13$ mm., *oxime*, m. p. $57-58^{\circ}$, *semicarbazone*, m. p. $139-140^{\circ}$, *γ -phenylhexane- $\gamma\delta$ -diol*, b. p. $160-161^{\circ}$, m. p. $49-50^{\circ}$; *α -phenyl- α -ethylbutaldehyde*, b. p. $119-121^{\circ}/14$ mm., *semicarbazone*, m. p. 181° ; *α -phenyl- β -propylpentane- $\alpha\beta$ -diol*, b. p. $290-300^{\circ}$, or $175-180^{\circ}/20$ mm., m. p. $100-101^{\circ}$; *δ -phenyloctan- ϵ -one*, $154-157^{\circ}/30$ mm., *semicarbazone*, m. p. $107-108^{\circ}$, *δ -phenyloctane- $\delta\epsilon$ -diol*, b. p. $178-179^{\circ}/18$ mm., m. p. $59-60^{\circ}$; *α -phenyl- α -propylvaleraldehydesemicarbazone*, m. p. $160-161^{\circ}$; *α -phenyl- β -n-butylhexane- $\alpha\beta$ -diol*, b. p. $330-340^{\circ}$, or $220-230^{\circ}/20$ mm., m. p. $102-103^{\circ}$; *ϵ -phenyldecan- ζ -one*, b. p. $165-170^{\circ}/20$ mm., *semicarbazone*, m. p. $100-101^{\circ}$, *oxime*, m. p. $55-56^{\circ}$; *dibutylacetophenone*, b. p. $285-290^{\circ}$; *α -anisyl- β -ethylbutane- $\alpha\beta$ -diol*, m. p. $78-79^{\circ}$; (?) *α -anisyl- α -ethylbutaldehyde*, b. p. $165-167^{\circ}/25$ mm., *semicarbazone*, m. p. $131-133^{\circ}$.

H. H.

Semi-pinacolic Transformations. II. Migrational Aptitudes of Various Acyclic Groups in Pinacolic and Semi-pinacolic Transformations. M. Tiffeneau and (Mlle) J. Lévy

(*Bull. Soc. chim.*, 1923, [iv], 33, 759—779; cf. preceding abstract).—It is shown that the migrational aptitude of the ethyl and benzyl radicles is superior to that of the methyl group in both pinacolic and semi-pinacolic transformations, but that this superiority is not always exclusive. The following compounds are described. *α-Phenyl-β-methyl-Δ⁴-butylene*, b. p. 199—200°/769 mm., 98—100°/23 mm.; *nitrosite*, m. p. 129—130°; *αβ-oxido-α-phenyl-β-methyl-butane*, b. p. 205—207°/760 mm.; *α-hydroxy-β-phenyl-α-methyl-propionic acid*, m. p. 95—97°; *ethyl ester*, b. p. 160—161°/30 mm.; *αα-diphenyl-β-benzylpropane-αβ-diol*, m. p. 81—82°; *αββ-triphenyl-butan-γ-one*, m. p. 64°; *αγ-diphenyl-β-methylpropan-β-ol*, b. p. 194—199°/20 mm.; *αγ-diphenyl-β-methylpropylene*,



b. p. 180—183°/25 mm., *nitrosite*, m. p. 122—123°. H. H.

Reduction Products of Benzylidenepinacolin. G. A. Hill, C. S. Spear, and J. S. Lachowicz (*J. Amer. Chem. Soc.*, 1923, 45, 1557—1562).—The reduction of benzylidenepinacolin by means of hydrogen and palladium black in alcoholic solution leads to the formation of *ω-benzylpinacolin*, a fragrant, nearly colourless, highly refractive liquid, b. p. 153°/40—42 mm., or 247° at atmospheric pressure, *oxime*, slender, white crystals, m. p. 95°. The constitution of this ketone is proved by its synthesis, by the action of benzyl chloride in ethereal solution on the sodium derivative of pinacolin, prepared in ethereal solution by the action of sodamide. Reduction of benzylidenepinacolin by means of aluminium amalgam, magnesium amalgam, sodium amalgam, sodium and ethyl alcohol, sodium and moist ether, or zinc and acetic acid gives the same product, together with a white, finely crystalline substance, m. p. 142°, presumably *β-phenylethyl-tert.-butylcarbinol*, and the dimeric product, *ββu-tetramethyl-εζ-diphenyldecan-γθ-dione*, a white, micro-crystalline compound, which is also formed by the action of sodium on *α-chloro-α-phenyl-δδ-dimethylpentan-γ-one* in ethereal solution.

W. S. N.

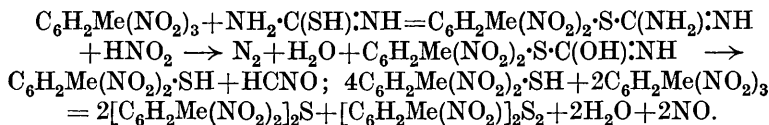
The Action of Potassium Hydroxide on Tetratolyl- and Tetraphenyl-butenediols. G. Arбузов and (Mlle) T. Temnikova (*J. Russ. Phys. Chem. Soc.*, 1922, 54, 219—222).—It is found that tetra-*p*-tolylbutinenediol, prepared by the action of dimagnesium acetylene dibromide (Locitsch, A., 1914, i, 393) on di-*p*-tolyl ketone, small needles, m. p. 156°, is not decomposed by aqueous potassium hydroxide; the solid alkali causes decomposition at 125° into di-*p*-tolyl ketone and acetylene. The glycol in ethereal solution readily forms a monopotassium salt from which it is regenerated by water, whilst on heating, the dry salt decomposes into acetylene and di-*p*-tolyl ketone. The glycol appears to possess only one active hydroxyl group as shown by the Zerevitinov-Tschugaev test.

The *tetraphenyl* compound also forms a monopotassium salt

and is decomposed by solid potassium hydroxide at a somewhat higher temperature than the preceding compound, the product being acetylene and benzophenone. G. A. R. K.

New Method of Preparation of certain Aromatic Sulphides.

I and II. MICHELE GIUA and ANTONIO RUGGERI (*Gazzetta*, 1923, **53**, i, 290—296; 341—345).—I. When heated together in presence of a little alcohol, thiocarbamide and 3:4:6-trinitrotoluene interact, giving, in addition to various secondary products, a mixture of di-4:6-dinitro-*m*-tolyl sulphide and di-4:6-dinitro-*m*-tolyl disulphide, the reaction apparently taking place in accordance with the equations:



The *N*-substituted derivatives of thiocarbamide also react with 3:4:6-trinitrotoluene, the principal product obtained in the case of allylthiocarbamide being di-4:6-dinitro-*m*-tolyl sulphide.

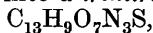
The interaction of 3:4:6-trinitrotoluene and thiophenol in alcoholic solution is expressed by the equation, $2\text{C}_6\text{H}_2\text{Me}(\text{NO}_2)_3 + 4\text{Ph}\cdot\text{SH} = 2\text{C}_6\text{H}_2\text{Me}(\text{NO}_2)_2\cdot\text{SPh} + \text{Ph}\cdot\text{S}\cdot\text{S}\cdot\text{Ph} + 2\text{H}_2\text{O} + 2\text{NO}$, the yield of the sulphide being almost theoretical. Ethyl mercaptan does not react when heated with 3:4:6-trinitrotoluene.

Di-4:6-dinitro-m-tolyl sulphide crystallises in pale yellow prisms, *m. p.* 189—190°, and in alcoholic solution gives a reddish-brown coloration with alkali.

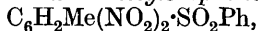
The *disulphide* crystallises in lustrous, yellow lamellæ, *m. p.* 263—265° (rapid heating), and is readily attacked by fuming nitric acid, with formation of 4:6-dinitro-*m*-tolylsulphonic acid, *m. p.* 120—135°.

Di-4:6-dinitro-m-tolyl sulphoxide $[\text{C}_6\text{H}_2\text{Me}(\text{NO}_2)_2]_2\text{SO}$, obtained by the action of nitric acid (*d* 1.5) on the sulphide, forms lustrous, white prisms, *m. p.* above 260° (decomp.).

Phenyl 4:6-dinitro-m-tolyl sulphide, $\text{SPh}\cdot\text{C}_6\text{H}_2\text{Me}(\text{NO}_2)_2$, prepared from 3:4:6-trinitrophenol and thiophenol, crystallises in lustrous, yellow laminae, *m. p.* 142—143°, and in alcoholic solution gives a dark red coloration with alkali. By excess of nitric acid (*d* 1.5) in the cold it is converted into a *trinitrophenyl m-tolylsulphoxide*,



crystallising in lustrous needles, *m. p.* 203—204°; the new nitro-group probably occupies the para-position in the second phenyl residue. *Phenyl 4:6-dinitro-m-tolylsulphone*,



prepared by the action of chromic anhydride on the sulphide in acetic acid solution, crystallises in small lamellæ, *m. p.* 164—165°.

II. When 1-chloro-2:4-dinitrobenzene (1 mol.) is heated on the water-bath with thiocarbamide (1 mol.), 2:4-dinitrophenyl mercaptan, 2:4:2':4'-tetranitrodiphenyl disulphide and a small proportion of 2:4:2':4'-tetranitrodiphenyl sulphide are formed.

The last of these compounds, however, constitutes the principal product when the proportion of the thiocarbamide is halved and the reaction is carried out in presence of ethyl alcohol and sodium acetate; the formation of the sulphide is due to the action of the chlorodinitro-compound on the mercaptan formed in the first stage of the reaction. In the former case, the reactions are expressed by the equations: $\text{C}_6\text{H}_3\text{Cl}(\text{NO}_2)_2 + \text{SH}\cdot\text{C}(\text{NH}_2)_2\text{NH} \rightarrow \text{C}_6\text{H}_3(\text{NO}_2)_2\cdot\text{S}\cdot\text{C}(\text{NH}_2)_2\text{NH} \rightarrow \text{C}_6\text{H}_3(\text{NO}_2)_2\cdot\text{SH} + \text{NC}\cdot\text{NH}_2$ and $\text{NC}\cdot\text{NH}_2 + \text{HCl} + \text{Et}\cdot\text{OH} = \text{OEt}\cdot\text{C}(\text{NH}_2)_2\text{NH}\cdot\text{HCl}$ (cf. Stieglitz and McKee, A., 1900, i, 340, 431; Stieglitz and Noble, A., 1905, i, 639; McKee, A., 1901, i, 755; 1909, i, 635; Bruce, A., 1904, i, 491, 573). At the temperature of boiling alcohol, the reaction proceeds according to the equation $\text{C}_6\text{H}_3(\text{NO}_2)_2\text{Cl} + \text{CS}(\text{NH}_2)_2 + \text{Et}\cdot\text{OH} = \text{C}_6\text{H}_3(\text{NO}_2)_2\cdot\text{SH} + \text{OEt}\cdot\text{C}(\text{NH}_2)_2\text{NH}\cdot\text{HCl}$, which is analogous to that given by Willgerodt (A., 1878, 141) for the temperature range 150–200°.

T. H. P.

Deaminisation of Methyl *d*-cis-3-Amino-1 : 2 : 2-trimethylcyclopentane-1-carboxylate. GLENN S. SKINNER (*J. Amer. Chem. Soc.*, 1923, 45, 1498–1509).— α -*d*-Camphoramidic acid is converted by treatment with sodium hypobromite into *d*-cis-3-amino-1 : 2 : 2-trimethylcyclopentane-1-carboxylic acid, the hydrochloride of which gives, by esterification by means of methyl alcohol and hydrogen chloride, the hydrochloride of methyl-*d*-cis-3-amino-1 : 2 : 2-trimethylcyclopentane-1-carboxylate, m. p. 237–238°, $[\alpha]_D^{25} + 29\cdot4^\circ$ (0·05 g./c.c. absolute alcohol), $[\alpha]_D^{25} + 29\cdot2^\circ$ (0·10 g./c.c. absolute alcohol), $[\alpha]_D^{25} + 20\cdot4^\circ$ (0·04 g./c.c. water). When this hydrochloride is treated with aqueous sodium nitrite on a large scale, no ether of a free hydroxy-acid is produced. The products are formed in the following proportions: esters of unsaturated acids, 62%; esters of hydroxy-acids, 36%; esters of chloro-acids, 2% (cf. Noyes and Skinner, A., 1918, i, 65).

The unsaturated ester obtained has b. p. 85°/21 mm., 75°/15 mm., 72°/12 mm., 65°/9 mm., 56°/5·5 mm., or 51°/4 mm., d_4^{20} 0·9649, d_4^{25} 0·9607, α_D^{25} 68·5°, α_D^{23} 66·5°, for a solution containing 0·1037 g. per c.c. of absolute alcohol, n_{706} 1·4484, n_{587} 1·45267, n_{501} 1·4580, n_{486} 1·4590, n_{477} 1·4631 at 25°. The mixture of unsaturated acids, obtained by hydrolysis by means of ethyl-alcoholic sodium hydroxide, has b. p. 108°/4 mm., $[\alpha]_D^{25} + 97\cdot3^\circ$, $[\alpha]_D^{28\cdot1} + 93\cdot6^\circ$, $[\alpha]_D^{23} + 74\cdot9^\circ$, $[\alpha]_D^{27\cdot9} + 71\cdot6^\circ$ (0·0976 g./c.c. absolute alcohol), n_{706} 1·4569, n_{587} 1·47056, n_{486} 1·4775, n_{447} 1·4811, and consists of *d*-lauronic acid and 1 : 2 : 3-trimethyl- Δ^4 -cyclopentane-1-carboxylic acid, in the ratio 7 : 3. The presence of the latter is proved by the production of α -carboxy- $\alpha\beta\beta$ -trimethylglutaric acid, on oxidation by means of alkaline potassium permanganate. Moreover, the action of bromine in ice-cold chloroform solution gives a dibromo-acid, large, transparent crystals, m. p. 189°, $[\alpha]_D^{21} + 94\cdot1^\circ$, $[\alpha]_D^{29} + 91\cdot6^\circ$ (0·0994 g./c.c. absolute alcohol), which is converted by means of sodium carbonate into the lactone of 5-bromo-4-hydroxy-1 : 2 : 2-trimethylcyclopentane-1-carboxylic acid. A second product of the bromination is the lactone of 2-bromo-3-hydroxy-1 : 2 : 3-trimethylcyclopentane-

1-carboxylic acid (*loc. cit.*), which is derived from lauronolic acid, and passes on boiling with water into the *i*-lactone of 2 : 3-dihydroxy-1 : 2 : 3-trimethylcyclopentane-1-carboxylic acid, long needles, m. p. 214—215°. The action of sodium ethoxide on the other bromolactone gives the sodium salt of the dihydroxy-acid, from which the lactone of 4 : 5-dihydroxy-1 : 2 : 2-trimethylcyclopentane-1-carboxylic acid, long, six-sided, monoclinic prisms, m. p. 225—226°, is obtained on acidification.

The ester fraction which boils at 88—89°/2.5—3 mm. gives, on hydrolysis, *d*-cis-2-hydroxy-1 : 2 : 3-trimethylcyclopentane-1-carboxylic acid (*loc. cit.*), which has $[\alpha]_D^{23} + 35.7$ (0.0569 g./c.c. absolute alcohol). This fraction of ester contains the largest percentage (6%) of esters of chloro-acids, $C_{18}H_{14}Cl \cdot CO_2Me$. The methyl ester boiling at 108—110°/4 mm. has $d_4^{20} 1.0711$, $[\alpha]_D^{23} + 29.9^\circ$, $[\alpha]_D^{28} + 29.6^\circ$ (0.967 g./c.c. absolute alcohol), and gives, on hydrolysis, *i*-2-hydroxy-1 : 5 : 5-trimethylcyclopentane-1-carboxylic acid, m. p. 209—210°, which does not pass into a lactone when heated at 255°, but sublimes unchanged. On oxidation by means of Beckmann's chromic acid mixture, it gives an acid, m. p. 218°, which is not oxidised to camphoronic acid by means of potassium permanganate. The methyl ester boiling at 105—107°/5 mm. has $[\alpha]_D^{23} + 22.4^\circ$, and gives, on hydrolysis, *l*-trans-3-hydroxy-1 : 5 : 5-trimethylcyclopentane-1-carboxylic acid, silky tufts of slender needles, m. p. 121—122°, b. p. 165°/5 mm., $[\alpha]_D^{27} - 10.3^\circ$ (0.0329 g./c.c. absolute alcohol), which is not converted into a lactone when heated at 225°. Oxidation of this acid by means of Beckmann's chromic acid mixture gives a gummy acid, which is further oxidised by means of potassium permanganate to camphoronic acid. The hydroxy-acid is converted by means of hydrogen iodide in carbon disulphide solution into the unstable iodide, which, on treatment with alkalis, gives an unsaturated acid, probably the Δ^2 -acid, $[\alpha]_D 35^\circ$ (0.0091 g./c.c. absolute alcohol), and a small quantity of an inactive lactone, m. p. 47—48°.

An acid, m. p. 132—133°, has also been isolated, but in such small amount that characterisation was impossible. W. S. N.

Preparation of *n*-Butyl *p*-Aminobenzoate. SOCIÉTÉ CHIMIQUE DES USINES DU RHÔNE (Swiss Pat. 96144; from *Chem. Zentr.*, 1923, ii, 480; cf. A., 1922, i, 827—828).—*n*-Butyl *p*-nitrobenzoate is prepared by heating *p*-nitrobenzoic acid or *p*-nitrobenzoyl chloride with *n*-butyl alcohol in the presence of strong sulphuric acid. It forms colourless leaflets, m. p. 35°; b. p. 160°/8 mm. Reduction by the usual methods gives the amino-ester.

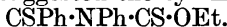
G. W. R.

Preparation of Ethyl *p*- β -Diethylaminoethylamino-benzoate. SOCIÉTÉ CHIMIQUE DES USINES DU RHÔNE (Swiss Pat. 93120; from *Chem. Zentr.*, 1923, ii, 479—480).—Ethyl *p*- β -chloroethylaminobenzoate, $CH_2Cl \cdot CH_2 \cdot NH \cdot C_6H_4 \cdot CO_2Et$, is treated with diethylamine under pressure at 100°. Ethyl *p*- β -diethylaminoethylaminobenzoate is an oily liquid. The hydrochloride forms white needles, m. p. 156°.

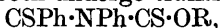
G. W. R.

The Constitution of some Iminosulphides. H. RIVIER and J. SCHALCH (*Helv. Chim. Acta*, 1923, 6, 605—617).—The two isomeric methylthiobenzanilides are readily decomposed by heat without isomerisation in either case. The two benzylthiobenzanilides have now been prepared, and are also found not to be interconvertible by heat. *S-Benzylthiobenzanilide*, $\text{CPh}\cdot\text{NPh}\cdot\text{S}\cdot\text{CH}_2\cdot\text{Ph}$, was prepared by the action of benzyl chloride on an alcoholic sodium hydroxide solution of thiobenzanilide. It crystallises in pale yellow needles, m. p. 53° , and forms a yellow, crystalline *hydrochloride*, m. p. $131\text{--}132^\circ$ (decomp.). *N-Benzylthiobenzanilide* was prepared by the action of phosphorus pentasulphide on benzylbenzanilide in boiling carbon disulphide. It forms yellow crystals, m. p. $121\text{--}122^\circ$, and does not form a hydrochloride.

The constitution, $\text{NPh}\cdot\text{CPh}\cdot\text{S}\cdot\text{CS}\cdot\text{OEt}$, for the "iminoxanthide" obtained by Tschugaev (A., 1902, i, 604) by the action of aromatic iminochlorides on an alkali xanthate has been criticised by Jamieson (A., 1904, i, 396), who suggested the symmetrical formula



The latter formula has now been confirmed by preparing such compounds in three different ways. The same compound is given by (1) Tschugaev's method; (2) the action of an ester of chlorothiocarbonic acid, $\text{OR}\cdot\text{CSCl}$, on the sodium salt of a thioanilide, and (3) by the action of an ester of phenyliminochlorocarbonic acid, $\text{NPh}\cdot\text{CCl}\cdot\text{OR}$, on lead dithiobenzoate. If Tschugaev's formula were correct, the first and third methods should give two isomeric substances, $\text{NPh}\cdot\text{CPh}\cdot\text{S}\cdot\text{CS}\cdot\text{OR}$ and $\text{CSPh}\cdot\text{S}\cdot\text{C}(\text{NPh})\cdot\text{OR}$. It is to be supposed that these both undergo transformation into



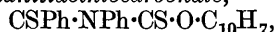
and the product should be called a dithiodiacylanilide. The two new methods for their preparation allow substances in which R is an aromatic radicle to be obtained. Tschugaev's compound, which is now called *ethyl thiobenzanilidothiocarbonate*, is found to be dimorphous, one form being garnet and the other bright red. By the first method were prepared *ethyl α -thiobenzonaphthalidothiocarbonate*, $\text{CSPh}\cdot\text{N}(\text{C}_{10}\text{H}_7)\cdot\text{CS}\cdot\text{OEt}$, red prisms, m. p. 142° , from α -benzonaphthalide, and *ethyl β -thiobenzonaphthalidothiocarbonate*, red crystals, m. p. $123\text{--}124^\circ$, from β -benzonaphthalide and potassium ethylxanthate.

Phenyl thiobenzanilidothiocarbonate, from phenyl chlorothiocarbonate and thiobenzanilide, forms bright red needles, m. p. $112\text{--}113^\circ$; *phenyl p-dimethylaminothiobenzanilidothiocarbonate*,



forms red crystals, m. p. $121\text{--}122^\circ$; it dyes silk. *Phenyl β -thiobenzonaphthalidothiocarbonate*, $\text{CSPh}\cdot\text{N}(\text{C}_{10}\text{H}_7^\beta)\cdot\text{CS}\cdot\text{OPh}$, crystallises in bright red needles, m. p. $145\text{--}146^\circ$.

β -Naphthyl chlorothiocarbonate, $\text{CSCl}\cdot\text{O}\cdot\text{C}_{10}\text{H}_7$, was prepared by the action of thiocarbonyl chloride on sodium β -naphthoxide solution; it forms yellow crystals, m. p. $76\text{--}77^\circ$. *Ethyl naphthyl thiocarbonate*, $\text{OEt}\cdot\text{CS}\cdot\text{O}\cdot\text{C}_{10}\text{H}_7$, forms colourless needles, m. p. 67° . *α -Naphthyl chlorothiocarbonate* is difficult to prepare; it boils at $165\text{--}166^\circ/13\text{ mm.}$ and forms a mass of yellow crystals.

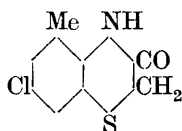
β-Naphthyl thiobenzanilidothiocarbonate,

forms reddish-brown crystals, m. p. 131—132°; *β-naphthyl β-thiobenzonaphthalidothiocarbonate* forms reddish-brown crystals, m. p. 163—164°; *β-naphthyl α-thiobenzonaphthalidothiocarbonate*, bright red crystals, and *α-naphthyl β-thiobenzonaphthalidothiocarbonate*, bright red crystals, m. p. 134—135°. E. H. R.

Polymerisation of Allyl Cinnamylideneacetate. F. F. BLICKE (*J. Amer. Chem. Soc.*, 1923, 45, 1562—1566).—*Allyl cinnamylideneacetate*, b. p. 210°/20 mm., is a light yellow liquid having a high index of refraction. It reacts with bromine in light petroleum solution to give the *hexabromide*, crystals possessing a silky lustre, m. p. 126°. When heated, the ester polymerises to an amorphous, amber-like material having the same composition as the original ester. The polymerised ester is readily hydrolysed to an amorphous acid, having the same composition as cinnamylideneacetic acid. When the amorphous acid is heated with barium hydroxide a mixture of liquid compounds, evidently hydrocarbons, is produced with elimination of carbon dioxide. The analysis of the mixture gives figures not very far removed from those required for phenylbutadiene. W. S. N.

Preparation of Arylthioglycolic [Arylthiolacetic] Acids.

FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 360425; from *Chem. Zentr.*, 1923, ii, 407).—Diazo-compounds of *o*-amino-arylthiolacetic acids are treated with ethyl alcohol and copper. Arylthiolacetic acids, $\text{R} \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$, are thereby obtained without accompanying formation of hydroxy- or alkoxy-compounds. The reaction takes place usually in the presence of sulphuric acid. *Phenylthiolacetic acid* is obtained from 2-aminophenylthiolacetic acid; 4-chlorophenylthiolacetic acid from 4-chloro-2-amino-1-phenylthiolacetic acid; *s*-5-chloro-*m*-tolylthiolacetic acid by the action of sulphur monochloride on *o*-toluidine, reduction of the products of reaction with zinc dust or sodium hyposulphite, and treatment with monochloroacetic acid. Treatment of the sodium salt of 5-chloro-2-amino-*m*-tolylthiolacetic acid with acids gives 7-chloro-3-keto-5-methyldihydro-1 : 4-isobenzthiazine (annexed formula); it forms small needles, m. p. 238°. G. W. R.



Preparation of Halogen Alkyl Esters of Aromatic *o*-Hydroxycarboxylic Acids. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 360491; from *Chem. Zentr.*, 1923, ii, 479).—*o*-Hydroxybenzoic acid or its acyl compounds, or its homologues and derivatives, are esterified by known methods with iodohydrins, or esters, chlorinated or brominated in the alcohol group, are treated with iodides. *Iodoethyl salicylate*, a colourless liquid, b. p. 180—183°/20 mm., is obtained by heating chloroethyl salicylate with sodium iodide in alcoholic solution or by esterification of ethylene iodohydrin either with salicyloyl chloride in the presence of benzene

or pyridine, or with salicylic acid in the presence of hydrogen chloride, or by heating sodium salicylate with ethylene chloroiodide. By acetylation, it gives *iodoethyl o-acetoxybenzoate* (crystals, m. p. 37—38°) which may also be obtained from *chloroethyl o-acetoxybenzoate* (crystals, m. p. 62°). α -Iododihydroxypropane gives with *o*-acetoxybenzoyl chloride the *ester* of propenyl- α -iodohydrin, a thick, yellow oil. *Di-iodopropyl o-acetoxybenzoate* is a viscid, yellow oil. *Chloroethyl 4-hydroxy-m-toluate*, an oil with b. p. 136—139°/10 mm., from 4-hydroxy-*m*-toluic acid and ethylene chlorohydrin, gives, with sodium iodide and amyl alcohol, *iodoethyl 4-hydroxy-m-toluate*, b. p. 166—169°/10 mm. The latter, by acetylation, gives *iodoethyl 4-acetoxy-m-toluate*, a yellow oil decomposing on distillation. G. W. R.

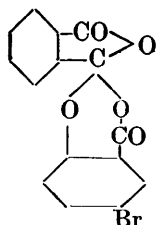
Di-iodohydrin Salicylate. WINCENCY HUMNICKI (*Istý Zjazd Chemików Polskich*, 1923, 62).—*Di-iodohydrin salicylate* is prepared by the iodination of glycerol in the presence of salicylic acid. The same ester can probably be prepared by the direct esterification of salicylic acid with di-iodohydrin. R. T.

Substituted Salicylic Acids. II. H. P. KAUFMANN (*Ber. Deut. pharm. Ges.*, 1923, 33, 120—132).—To decide between the two formulæ possible for the compound obtained by the action of *s*-*o*-phthalyl chloride on sodium or disodium salicylate (A., 1922, i, 252), use is made of the reaction discovered by Pfeiffer (A., 1914, i, 551; 1917, i, 205), who found that both maleic and phthalic anhydrides, which contain the quinonoid linking, $O:\dot{C}:\dot{C}:\dot{C}:\dot{C}:O$, give with aromatic hydrocarbons, phenols and amides, more or less deep colorations obeying the regularities determined for the quinhydrone. Further, phthalaldehyde, which contains the above grouping, dissolves in dimethylaniline giving an orange-yellow coloration, whereas phthalide, which lacks such grouping, remains colourless with this reagent (A., 1919, i, 62). Since it is found that the above compound, m. p. 158·5°, gives no coloration with the solvents used by Pfeiffer, the phthalyl chloride used in its formation must react in its asymmetric form, the compound itself having the structure II (A., 1922, i, 253); it is proposed to call it salicylic acid phthalidylidene-ether-ester.

The latter exhibits extremely high stability and resists hydrolysis, being decomposed only by energetic reducing agents. Its 5-bromo- and 3:5-dibromo-derivatives may be prepared by using the corresponding derivatives of salicylic acid instead of the latter itself. The 5-nitro-derivative gives on reduction the 5-amino-derivative, which shows the usual reactions for primary amines, but is only sparingly soluble in hydrochloric acid. Diazotisation of the amino-compound and coupling of the diazo-salt with aniline and with β -naphthol yields red or cocoa-brown colouring matters.

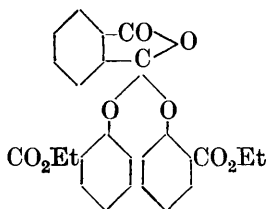
The reaction between *o*-phthalyl chloride and salicylic acid is not altered by substitution in the former, but proceeds quite differently when esters of salicylic acid are used. In this case, two mols. of the ester react with the phthalyl chloride in the asymmetric

configuration, giving esters of phthalaldisalicylic acid. In preparing these derivatives, it is found that esters of the salicylic acids react with difficulty with phthalyl chloride, whereas the sodium salts of the esters react more rapidly. With terephthalyl or isophthalyl chloride, two molecules of the salicylic acids or their esters always react.



5-Bromosalicylic acid phthalidylidene-ether-ester (annexed formula) forms crystals, m. p. 176° , and the corresponding 3:5-dibromo-compound, crystals, m. p. 217° .

5-Nitrosalicylic acid phthalidylidene-ether-ester, $C_{15}H_7O_7N$, is obtained as a white, sandy compound, m. p. 214.5° ; the 5-amino-compound, $C_{15}H_{19}O_5N$, melts gradually with decomposition, and on diazotisation yields with aniline the reddish-brown compound, $C_{15}H_7O_5N:N:NHPh$, and with β -naphthol the cocoa-brown compound, $C_{15}H_7O_5N:N:N \cdot C_{10}H_6 \cdot OH$, neither of which has a definite melting point.



Ethyl o-phthalaldisalicylate (annexed formula) forms crystals, m. p. 56° ; the *phenyl* ester, $C_{34}H_{22}O_8$, crystals, m. p. 112° , and the β -*naphthyl* ester, $C_{42}H_{26}O_8$, white crystals, m. p. 78° .

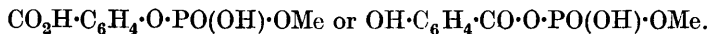
Terephthalaldisalicylic acid, CO_2H CO_2H

is a white, amorphous compound, decomposing at $180-190^{\circ}$; its *ethyl* ester, $C_{26}H_{22}O_8$, crystallises in nodular masses, m. p. 165° , and its *phenyl* ester, $C_{34}H_{22}O_8$, in white needles, m. p. $189-190^{\circ}$; its β -*naphthyl* ester, $C_{42}H_{26}O_8$, forms crystals, m. p. 80° .

Ethyl isophthalaldisalicylate, $C_{26}H_{22}O_8$, forms colourless needles, m. p. 90° ; the *phenyl* ester, a pale yellow oil, and the β -*naphthyl* ester, $C_{42}H_{26}O_8$, crystals, m. p. 130° .

T. H. P.

Monomethylorthophosphosalicylic Ester. ÉMILE GAUTRELET (*Compt. rend.*, 1923, 176, 1770-1772).—The interaction of 3 mols. of monomethyl orthophosphate with 3 mols. of sodium salicylate results in the formation of 1 mol. of trisodium phosphate, 1 mol. of methyl salicylate and 2 mols. of methylorthophosphosalicylate, which, according as the temperature is higher or lower, has the constitution



The former substance forms short, colourless, rhombic crystals, m. p. 113° , and gives in solution scarcely any coloration with ferric chloride. The latter substance forms long needles, m. p. 98° , and gives a violet coloration with ferric chloride. The therapeutic value of the two isomerides is identical, however, their action being both antipyretic and analgesic.

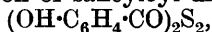
G. F. M.

Iodosalicylic Acids. P. BRENANS and C. PROST (*Compt. rend.*, 1923, 176, 1626—1629; cf. Goldberg, A., 1879, 928; Miller, T., 1882, 41, 398).—5-Iodosalicylic acid, $\text{OH}\cdot\text{C}_6\text{H}_3\text{I}\cdot\text{CO}_2\text{H}$, was prepared by treating the hydrochloride of 5-aminosalicylic acid with sulphuric acid, diazotising, and adding hydriodic acid. It forms white needles, m. p. 198° ; the acetyl derivative crystallises in needles, m. p. 166° ; the ethyl ester (cf. Schmitt, *Z. für Chemie*, 1864, 322), prepared by boiling the acid with absolute alcohol containing 15% of sulphuric acid, forms long, colourless needles of aromatic odour, m. p. $70\text{--}71^\circ$. The isomeride 3-iodosalicylic acid, $\text{OH}\cdot\text{C}_6\text{H}_3\text{I}\cdot\text{CO}_2\text{H}$, prepared similarly from the sulphate of the corresponding amino-acid, crystallises in needles, m. p. 199° , yields an *acetyl* derivative, white plates, m. p. 135° , and an *ethyl* ester which was obtained as a colourless oil. The two acids on addition of iodine yield the same 3:5-di-iodosalicylic acid, $\text{OH}\cdot\text{C}_6\text{H}_2\text{I}_2\cdot\text{CO}_2\text{H}$, white needles, m. p. 228° , *acetyl* derivative, hard, white plates, m. p. 153° . H. J. E.

Acetylation with Acetic Anhydride and Sulphuric Acid. O. FERNÁNDEZ and C. TORRES (*Anal. Fis. Quím.*, 1923, 21, 22—32).—The authors have used acetic anhydride in the presence of small quantities of sulphuric acid for the preparation of a number of acetyl compounds. For example, in the preparation of *o*-acetoxybenzoic acid, 30 g. of salicylic acid are treated with 44.4 g. of acetic anhydride, 15 drops of strong sulphuric acid being then added to the mixture. The authors describe the acetylation of resorcinol, pyrogallol, *o*- and *p*-nitrophenols, morphine, and quinine.

G. W. R.

Preparation of Thiolsalicylic Acid. CHEMISCHE FABRIK VON FRIEDRICH HEYDEN (D.R.-P. 365212; from *Chem. Zentr.*, 1923, ii, 251—252).—An alcoholic solution of an alkali hydro-sulphide is allowed to act on salicyloyl chloride or an acyl-salicyloyl chloride. *Thiolsalicylic acid*, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{SH}$, forms white crystals, m. p. 33° , with an odour like phosphorus. With ferric chloride, a reddish-violet coloration is obtained which disappears with precipitation of salicyloyl disulphide,



m. p. 129° . The alkali and alkaline-earth salts readily decompose, giving sulphur and hydrogen sulphide.

G. W. R.

Brominated Lactones from Benzylidenecampholic Acid. H. RUPE and A. SULGER (*Helv. Chim. Acta*, 1923, 6, 435—442).—It was hoped, by elimination of 2 mols. of hydrogen bromide from $\alpha\beta$ -dibromobenzylcampholic acid (Rupe and Blechschmidt, A., 1918, i, 223), to obtain a compound containing the acetylenic linking, but instead, by the action of alcoholic potassium hydroxide, only 1 mol. of hydrogen bromide was eliminated, with formation of α -bromo- α -phenyl- β -hydroxycamphol-1-carboxylic acid- δ -lactone, $\text{CO}\langle\text{C}_8\text{H}_{14}\rangle\text{CH}\cdot\text{CHPhBr}$, which has m. p. 141° , not 139° , as previously given. The lactone forms the *magnesium*

salt of α -bromo- β -hydroxy- α -phenylhomocampholic acid when treated carefully with magnesium oxide and water. When reduced with sodium amalgam, the lactone is converted into benzylidenecampholic acid. This unusual reaction is probably due to the intermediate formation of β -hydroxy- α -phenylhomocampholic acid, which readily loses water, forming benzylidenecampholic acid. When the lactone is boiled with an excess of magnesium oxide for a long time, the δ -lactone of α - β -dihydroxy- α -phenylcamphol-1-carboxylic acid is formed, white needles, m. p. 156°.

When benzylidenecampholic acid is exposed for a long time to bromine vapour, at first the dibromo-additive compound is formed, but later hydrogen bromide is eliminated with formation of an isomeric lactone. This compound appears to be α -bromo-3-hydroxy- α -phenylcamphol-1-carboxylic acid- γ -lactone (I); it crystallises in long, glistening needles, m. p. 206°, and differs considerably from the δ -lactone in solubility. When boiled with magnesium oxide and water it gives a crystalline compound, m. p. 135°, free from bromine, which has not yet been further examined. When reduced with sodium amalgam it gives benzylidenecampholic acid. By boiling alcoholic potassium hydroxide it is converted into a crystalline product, m. p. 188°, which is assumed to be α -phenyl- α :3-dihydroxycamphol-1-carboxylic acid. Alkalis do not remove bromine from the δ -lactone in this way.

E. H. R.

Hydroxynaphthoic Acids. II. CARLTON BUTLER and FRANK ALBERT ROYLE (T., 1923, 123, 1649—1657).

The Formation of Derivatives of Tetrahydronaphthalene from γ -Phenyl Fatty Acids. III. The Influence of Substituents on Ring Closure. ARTHUR JOHN ATTWOOD, ARNOLD STEVENSON, and JOCELYN FIELD THORPE (T., 1923, 123, 1755—1766).

Ring-chain Tautomerism. VI. The Mechanism of the Keto-cyclol Change in the Propane Series. ERIC WILLIAM LANFEAR and JOCELYN FIELD THORPE (T., 1923, 123, 1683—1689).

A Simple Preparation of Pyromellitic Acid. HENRI DE DIESBACH, VICTOR SCHMIDT, and EUGÈNE DECKER (*Helv. Chim. Acta*, 1923, 6, 548—549).—When technical xylene is brominated in the cold, a solid fraction is obtained consisting of a mixture of 4:6-dibromo-*m*-xylene, 2:5-dibromo-*p*-xylene, and 4:5-dibromo-*o*-xylene. By heating this mixture with cuprous cyanide and pyridine at 200°, a mixture of the nitriles of α - and β -cumidic acids is obtained, m. p. 148—150°. The dibromo-*o*-xylene gives dimethylphthalimide, which remains in the mother-liquor. Hydrolysis of the mixed nitriles with boiling 70% sulphuric acid gives a mixture of α - and β -cumidic acids which are oxidised by potassium permanganate to pyromellitic acid.

E. H. R.

The Molecular Weight of Benzaldehyde-Copper and the Formation of Benzaldehyde-Copper-Pyridine. FRITZ SCHAAF (*Helv. Chim. Acta*, 1923, 6, 535—538).—The molecular weight of benzaldehyde-copper (A., 1922, i, 1029) was determined cryoscopically in camphor, and was found to correspond with the formula $C_{14}H_{12}O_2Cu$. The solubility of the compound in the usual solvents is too low for molecular-weight determinations by the ebullioscopic method. The density of the compound is $d_4^{20} 1.4552$. In hot pyridine, it dissolves with a blue colour, and from the solution, on cooling, there separate deep blue silky needles of *benzaldehyde-copper-pyridine*, $2C_{14}H_{12}O_2Cu \cdot 5C_5H_5N$. This is stable in air, is decomposed by acids and alkalis, but is soluble in ammonium hydroxide. When heated at 150° , it loses pyridine, leaving a residue of pure benzaldehyde-copper. Similar compounds appear to be formed with other organic bases, such as aniline, quinoline, and collidine, in which benzaldehyde-copper dissolves, forming green or blue solutions. E. H. R.

The Catalytic Reduction of Acid Chlorides. VI. The Preparation of Unsaturated Aldehydes. KARL W. ROSENMUND, FRITZ ZETSCHE, and G. WEILER (*Ber.*, 1923, 56, [B], 1481—1487; cf. A., 1922, i, 431 and previous abstracts).—The authors' method of preparing aldehydes from acid chlorides has been extended to unsaturated aldehydes. Satisfactory and uniform results are only obtained when pure palladium preparations are used in conjunction with suitable addenda. Less pure catalysts, including such as are quite suitable for other reductions, appear to cause the production of greater proportions of complex products and less aldehyde. Care is also necessary with regard to the addenda, since freshly prepared "sulphured quinoline" is more uniform in its action than older specimens. On the other hand, crystalline thioquinanthrene gives uniformly good results.

Acetylvannillyl chloride, colourless crystals, m. p. 57° (corresponding *amide*, m. p. 175° ; *anilide*, m. p. 160 — 161°), is reduced by hydrogen in the presence of xylene, palladised barium sulphate, and sulphured quinoline to vanillin, m. p. 80° , the yield being 82.5% of that theoretically possible. Under similar conditions, phenoxyacetaldehyde is produced in 72% yield from phenoxyacetyl chloride and anisaldehyde from anisyl chloride in 81% yield. Cinnamyl chloride is preferably treated with hydrogen under diminished pressure, whereby cinnamaldehyde is formed, the yield being in the most favourable cases 60% of that theoretically possible; β -phenylpropaldehyde does not appear to be formed to an appreciable extent. *o*-Chlorocinnamic acid is converted by thionyl chloride into *o*-chlorocinnamoyl chloride, b. p. 155 — $160^\circ/12$ mm., m. p. 40° (corresponding *anilide*, m. p. 176°), which is transformed further into *o*-chlorocinnamaldehyde, colourless needles, m. p. 150° (*oxime*, needles, m. p. 96° after softening at 92° ; *acetate* of oxime, m. p. 71 — 72°). The aldehyde is also prepared by the condensation of *o*-chlorobenzaldehyde with acetaldehyde in the presence of diethylamine. Reduction of the

oxime with sodium amalgam in the presence of glacial acetic acid gives γ -o-chlorophenyl-*n*-propylamine which is isolated as the *hydrochloride*, m. p. 167°.

Salicyloxyacetyl dichloride, b. p. 174°/17 mm., m. p. 60° (corresponding *anilide*, m. p. 171—172°), could not be reduced in a satisfactory manner. H. W.

Preparation of Nucleus-halogenated Di(dichloromethyl) Benzenes and Dichloromethyltrichloromethylbenzenes. LEOPOLD CASSELLA & Co., (D.R.-P. 360414; from *Chem. Zentr.*, 1923, ii, 406).—*o*-, *m*-, and *p*-Xylenes are first chlorinated in the nucleus at low temperatures and in darkness, and then in the side-chain at higher temperatures (120—130°) in light. The products give, on heating with strong sulphuric acid, dialdehydes and aldehyde carboxylic acids. *Dichloro-1:3-di(dichloromethyl)benzene*, $C_6H_2Cl_2(CHCl_2)_2$, is a colourless liquid, b. p. 312—313°/760 mm., obtained from dichloro-*m*-xylene. By the action of strong sulphuric acid at 90—100°, *dichloroisophthalaldehyde*, $C_6H_2Cl_2(CHO)_2$, crystals, m. p. 145°, is obtained. *Trichloro-1:3-di(dichloromethyl)benzene*, $C_6HCl_3(CHCl_2)_2$, is a colourless liquid, b. p. 330—331°/760 mm. It gives with strong sulphuric acid *trichloroisophthalaldehyde*, $C_6HCl_3(CHO)_2$, crystals, m. p. 172°. Other compounds mentioned are: *Tetrachloro-1:3-di(dichloromethyl)benzene*, crystals, m. p. 83°; b. p. 359—360°/760 mm.; *tetrachloroisophthalaldehyde*, crystals, m. p. 197°; *chloro-1:3-di(dichloromethyl)benzene*, b. p. 291—292°/760 mm.; *chloroisophthalaldehyde*, m. p. 119°; *dichloro-1:4-di(dichloromethyl)benzene*, b. p. 313—316°/760 mm.; *dichloroterephthalaldehyde*, m. p. 150°; *trichloro-1:2-di(dichloromethyl)benzene*, b. p. 322—324°/760 mm.; *trichlorophthalaldehyde*, m. p. 152°; *trichloro-1:4-di(dichloromethyl)benzene*, b. p. 331—333°/760 mm.; *trichloroterephthalaldehyde*, m. p. 178°; 2:3:5:6-*tetrachloro-1:4-di(dichloromethyl)benzene*, b. p. above 360°, m. p. 168°; 2:3:5:6-*tetrachloroterephthalaldehyde*, m. p. 200°; *dichloro-1-dichloromethyl-3-trichloromethylbenzene*, b. p. 321—322°/760 mm.; *dichlorobenzaldehyde-m-carboxylic acid*, nacreous leaflets, m. p. 160°; *trichloro-1-dichloromethyl-3-trichloromethylbenzene*, a thick, colourless oil, b. p. 339—340°/760 mm.; *trichlorobenzaldehyde-m-carboxylic acid*, leaflets, m. p. 214°; *dichloro-1-dichloromethyl-4-trichloromethylbenzene*, b. p. 322—324°/760 mm.; *dichlorobenzaldehyde-p-carboxylic acid*, m. p. 185°; *trichloro-1-dichloromethyl-4-trichloromethylbenzene*, m. p. 120°; *trichlorobenzaldehyde-p-carboxylic acid*, m. p. 216°. G. W. R.

Decomposition of Aromatic Ketones. ALPHONSE MAILHE (*Bull. Soc. chim.*, 1923, [iv], 33, 632—637).—The decomposition of aromatic ketones in contact with copper turnings at 550—600° takes place in a manner identical with that of aliphatic ketones (cf. A., 1922, i, 985), scission into three fragments occurring, with formation of carbon monoxide and the two residues attached to it. The aromatic residue by reaction with hydrogen is liberated as an aromatic hydrocarbon, whilst the alkyl group by loss of hydrogen is resolved into an unsaturated hydrocarbon and a

certain quantity of methane. Certain of the ketones studied showed considerable stability and were recovered almost unchanged. This was particularly the case where the ketonic group was attached directly to the nucleus, as, for example, in the case of acetophenone and benzophenone. On the other hand, decomposition occurred with much greater facility with ketones in which the aromatic nucleus was separated from the ketonic group by one or more methylene groups, as in benzyl methyl ketone, cinnamyl ethyl ketone, or dibenzyl ketone. G. F. M.

Witt's Method of Diazotisation. WALTER FUCHS (*Rec. trav. chim.*, 1923, 42, 511—512).—Commenting on a recent paper by Elion (this vol., i, 390), who claimed that Witt's process of diazotisation (addition of a mixture of a base and potassium metabisulphite to nitric acid) did not proceed uniformly but gave nitro-derivatives as by-products, Fuchs points out that Elion used too great an excess of nitric acid. In the case, for instance, of the preparation of 3:5-dibromoacetophenone from 4-amino-3:5-acetophenone, Elion obtained only a 70% yield and about 30% of a nitrated by-product, whereas by using only about one-fifth of the amount of nitric acid the yield of the dibromoacetophenone is practically quantitative. F. A. M.

Witt's Method of Diazotisation. L. ELION (*Rec. trav. chim.*, 1923, 42, 513—515; cf. preceding abstract).—A reply to Fuchs's criticisms. The author denies that the relative amount of nitric acid used is a decisive factor, but emphasises the importance of the concentration of the acid. Thus, if 3:5-dibromo-4-aminobenzoic acid is treated with nitric acid (*d* 1.40) no action occurs, but if the experiment be repeated with acid of *d* 1.48 there is an immediate violent evolution of carbon dioxide, the carboxyl being replaced by a nitro-group. This also occurs even in the presence of potassium metabisulphite. In the same way, 3:5-dibromo-4-aminoacetophenone is also readily converted into the same 3:5-dibromo-1-nitro-4-aminobenzene, but of course without evolution of carbon dioxide. Elion disputes Fuchs's claim to have obtained quantitative yields of nitrogen-free product from 3:5-dibromo-4-aminoacetophenone by Witt's method. F. A. M.

Action of Alcoholic Potassium Hydroxide on Ketones.
VIII. The Replacement of Bromine by Hydrogen in Bromobenzophenones and their Derivatives. P. J. MONTAGNE (*Rec. trav. chim.*, 1923, 42, 499—510; cf. A., 1920, i, 394; this vol., i, 227).—Previous work has shown that when 2-bromobenzophenone is heated with alcoholic potassium hydroxide benzhydrol is formed, but with 3- and 4-bromobenzophenones the bromine atoms are practically unattacked, the products being respectively 3- and 4-bromobenzhydrols (cf. A., 1913, i, 55). Again, with 3:5-dibromobenzophenone the CO-group is reduced but the bromine is only partly replaced. It has now been found that 3:5-dibromo-4-hydroxybenzophenone remains unaltered when heated with alcoholic potash and 2'-bromo-4-hydroxybenzophenone (prepared by
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boiling 2-bromo-4-ethoxybenzophenone with acetic and hydrobromic acids as colourless crystals, m. p. 114° , b. p. $260^{\circ}/10$ mm.) was only slightly attacked by hot alcoholic potash.

On treating 3:5-dibromo-4-aminobenzophenone for two days with alcoholic potash, two products were obtained: 3:5-dibromo-4-aminobenzhydrol (m. p. 149.5°) and 3-bromo-4-aminobenzophenone. 4-Aminobenzophenone remained unchanged after four days' treatment, as also did 3-bromo-4-aminobenzophenone after two days (prepared by brominating aminobenzophenone in acetic acid as colourless crystals, m. p. $157-158^{\circ}$, b. p. $241^{\circ}/11$ mm.). 3:5-Dibromo-4-aminobenzhydrol is unattacked by hot alcoholic potash.

F. A. M.

The Formation of Six-membered Carbon Rings. FRITZ MAYER and GEORG STAMM (*Ber.*, 1923, 56, [B], 1424-1433).—The formation of six-membered carbon rings by the action of aluminium chloride on γ -phenyl-*n*-butyryl chloride and its homologues formed by the introduction of methyl groups into the nucleus or side chain has been investigated. With the parent substance, the yield of ketone is only 10% of that theoretically possible, whereas when a methyl group is present in very varied position the yield rises to between 70% and 76%.

Methylsuccinic acid is obtained conveniently in 93% yield by the hydrogenation under somewhat increased pressure of citraconic anhydride dissolved in water in the presence of palladous chloride and animal charcoal.

The requisite acid chlorides are obtained by the interaction of the acids at the atmospheric temperature with thionyl chloride which is purified by two distillations followed by distillation from quinoline and finally from linseed oil. They are allowed to react with aluminium chloride in the presence of light petroleum, b. p. $70-80^{\circ}$, which has been purified by agitation with fuming sulphuric acid (containing about 20% SO_3), then with water, followed by desiccation with calcium chloride and distillation over sodium.

Phenylbutyryl chloride gives 1-keto-1:2:3:4-tetrahydronaphthalene, b. p. $133-135^{\circ}/14$ mm. 1-Keto-7-methyl-1:2:3:4-tetrahydronaphthalene, b. p. $143-145^{\circ}/15$ mm., m. p. $35-36^{\circ}$ (semicarbazone, m. p. $226-228^{\circ}$), is obtained in 72% yield from γ -*p*-tolyl-*n*-butyryl chloride.

The action of benzene on methylsuccinic anhydride leads to the production of a mixture of β -benzoyl- α -methylpropionic acid, m. p. $139-140^{\circ}$, and β -benzoyl- β -methylpropionic acid, m. p. $56-59^{\circ}$ after previous softening. The former acid is transformed by Clemmensen's method into γ -phenyl- α -methyl-*n*-butyric acid, which is converted into 1-keto-2-methyl-1:2:3:4-tetrahydronaphthalene, b. p. $135-137^{\circ}/16$ mm. (semicarbazone, m. p. $200-201^{\circ}$), in 70% yield. In a similar manner, methylsuccinic anhydride and toluene in the presence of aluminium chloride give a mixture of β -*p*-toluoyl- α -methylpropionic acid, colourless leaflets, m. p. $169-171^{\circ}$ [oxime, slender, colourless needles, m. p. $141-142^{\circ}$ (decomp.)], and β -*p*-toluoyl-*n*-butyric acid, m. p. $63-65^{\circ}$ (oxime, m. p. $139-$

141°). The constitution of the former acid is established by its syntheses from *p*-tolyl bromomethyl ketone and ethyl isosuccinate in the presence of sodium and alcohol. γ -*p*-Tolyl- α -methyl-*n*-butyric acid, m. p. 54—55°, b. p. 183—184°/15 mm. (ethyl ester, b. p. 149—151°/14 mm.), is obtained from the corresponding toluoyl acid by the action of amalgamated zinc and hydrochloric acid. The corresponding chloride has b. p. 145—146°/15 mm., and the amide has m. p. 150—151°. The chloride gives 1-*keto*-2 : 7-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene, b. p. 145—147°/15 mm. (semicarbazone, m. p. 220—221°), the yield being 75% of that theoretically possible. β -*p*-Toluoyl-*n*-butyric acid is transformed successively into ethyl γ -*p*-tolyl- β -methyl-*n*-butyrate, b. p. 149—151°/14 mm.; γ -*p*-tolyl- β -methyl-*n*-butyric acid, b. p. 180—181°/15 mm.; γ -*p*-tolyl- β -methyl-*n*-butyryl chloride, b. p. 141—143°/15 mm., and 1-*keto*-3 : 7-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene, b. p. 150°/15 mm., m. p. 52—53° (semicarbazone, m. p. 203—205°).

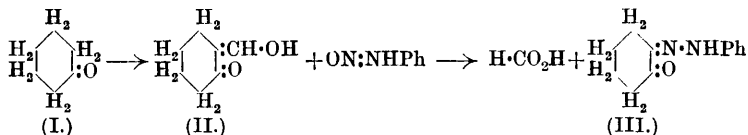
γ -Phenyl- Δ^8 -butenoic acid, colourless leaflets, m. p. 75—78°, prepared from ethyl β -benzoylpropionate and magnesium methyl iodide, is catalytically hydrogenated in the form of its sodium salt to γ -phenylvaleric acid, b. p. 169—170°/14 mm., the chloride of which is transformed into 1-*keto*-4-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene, b. p. 145—160° (semicarbazone, colourless leaflets, m. p. 210°). In a similar manner, γ -*p*-tolylvaleric acid, b. p. 178—180°/15 mm., is converted successively into the chloride, b. p. 145—155°/16 mm., and 1-*keto*-4 : 7-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene, b. p. 145—152°/15 mm. (semicarbazone, colourless leaflets, m. p. 194—195°).

The condensation of citraconic anhydride with benzene in the presence of aluminium chloride leads to the formation of small yields of a mixture of β -benzoyl- α -methylacrylic acid, colourless needles, m. p. 150° after softening at 120° (the acid is identified by its hydrogenation to β -benzoyl- α -methylpropionic acid) and β -benzoyl- Δ^8 -butenoic acid, slender needles, m. p. 100—102° after softening at 80°. In a similar manner, toluene and citraconic anhydride yield β -*p*-toluoyl- α -methylacrylic acid, m. p. 138—139°, and β -*p*-toluoyl- Δ^8 -butenoic acid, colourless leaflets, m. p. 94—95°; the constitutions of these acids are established by their reduction to the corresponding saturated acids. H. W.

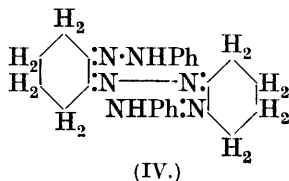
The Isomerism of the Oximes. XII. Hydrochlorides. OSCAR LISLE BRADY and FREDERICK PERCY DUNN (T., 1923, 123, 1783—1803).

Derivatives of cycloHexan-1 : 2-dione. SAMUEL COFFEY (*Rec. trav. chim.*, 1923, 42, 528—532).—Attempts to prepare cyclohexanedione by condensing cyclohexanone in large excess with aldehydes gave in all cases well crystallised, yellow 2 : 6-dibenzylidene derivatives, of which the following are new : 2 : 6-dipiperonylidene cyclohexanone, m. p. 187—188°; 2 : 6-di-*m*-nitrobenzylidene cyclohexanone, lustrous, golden needles, m. p. 191—192°; 2 : 6-di-*anisylidene* cyclohexanone, which melts at 162° to a turbid, anisotropic liquid showing the characteristic properties of liquid crystals

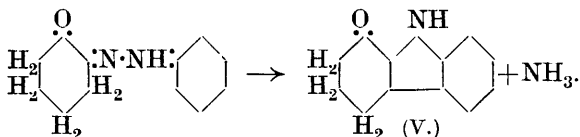
and clearing sharply at 172°. The monophenylhydrazone of *cyclohexan-1 : 2-dione* was made in the following manner : *cyclohexanone* (I) and amyl formate were condensed together by Borsche's method (A., 1910, i, 880) to give hydroxymethylenecyclohexan-1 : 2-one (II) which condensed with diazotised aniline to give the monophenylhydrazone of *cyclohexan-1 : 2-dione* (formula III), which



forms lustrous, reddish-brown scales, m. p. 183—185°. It is sparingly soluble in most organic solvents. Further treatment with phenylhydrazine yielded the osazone of *cyclohexan-1 : 2-dione*, forming long, yellow needles, m. p. 153—154°, which had been obtained by Kötze (A., 1913, i, 1201) by the action of phenylhydrazine on 2-hydroxycyclohexanone. With hydrazine hydrate, the monophenylhydrazone gave a colourless, unstable, oily product, probably the hydrazone-phenylhydrazine of the diketone. On the addition of a little dilute acetic acid, a crimson precipitate was at once produced consisting of the ketazine (*cyclohexandione-ketazine-2 : 2'-diphenylhydrazone*) (IV). Treatment of the monophenylhydrazone of *cyclohexandione* with a mixture of acetic and hydrochloric acids led to the formation not of the free diketone but of



1-ketotetrahydrocarbazole (formula V) by Fischer's indole synthesis,



After recrystallisation from 50% alcohol or acetic acid, the substance formed flat needles several cm. long, m. p. 169—170°; it is stable to dilute acids and alkalis, and could not be acetylated or benzoylated. The *phenylhydrazone* is oily and unstable, and the *oxime* was obtained as a glassy mass. The *semicarbazide* formed crystals melting at about 228—230°. On heating with alcoholic hydrazine hydrate, the lemon-yellow *ketazine*, C₂₄H₂₂N₄, m. p. 258—260°, was formed; it is sparingly soluble in most common solvents.

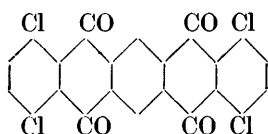
F. A. M.

The Dibenzoylxylenes and Dinaphthanthracenediquinones. HENRI DE DIESBACH [with WERNER PERRIG, MELCHIOR BETSCHART, and KARL STREBEL] (*Helv. Chim. Acta*, 1923, 6, 539—548).—A new synthesis of linear dinaphthanthracenediquinone is described which consists in condensing the acid chloride of α - or β -cumidic acid with benzene to obtain dibenzoylxylenes, oxidising the methyl groups to carboxyl groups, and heating with sulphuric acid to form

the diquinone. New syntheses of α - and β -cumidic acids are described. By heating 2 : 5-dibromo-*p*-xylene with cuprous cyanide and pyridine in an autoclave at 200° for eight hours, 2 : 5-dicyano-*p*-xylene was obtained, colourless needles, m. p. 209.5—210°. It is converted quantitatively by boiling 70% sulphuric acid into β -cumidic acid. β -Cumidoyl chloride forms long needles, m. p. 116°. 4 : 6-Dibromo-*m*-xylene, when heated in the same manner with cuprous cyanide, gives 4 : 6-dicyano-*m*-xylene, crystallising in long, colourless needles, m. p. 144—145°, which is readily hydrolysed to α -cumidic acid. When the crude chloride of this acid is heated with benzene and aluminium chloride, 4 : 6-dibenzoyl-*m*-xylene is formed, colourless needles, m. p. 104°. At the same time, there is formed 5-benzoyl-2 : 4-dimethylbenzoic acid, crystallising in small prisms, m. p. 149—150°. Instead of benzene, *p*-dichlorobenzene can be condensed with α -cumidoyl chloride, when there is formed 4 : 6-di(2' : 5'-dichlorobenzoyl)-*m*-xylene, colourless needles, m. p. 133—134°, and at the same time 5(2' : 5'-dichlorobenzoyl)-2 : 4-dimethylbenzoic acid, m. p. 180°. With *p*-dimethoxybenzene, α -cumidoyl chloride condenses to form 4 : 6-di(2'-hydroxy-5'-methoxybenzoyl)-*m*-xylene, long, greenish-yellow prisms or needles, m. p. 139—140°. During this condensation, two methoxy-groups are hydrolysed.

β -Cumidoyl chloride condenses with benzene in presence of aluminium chloride, forming 2 : 5-dibenzoyl-*p*-xylene, hexagonal prisms, m. p. 160°, and 4-benzoyl-2 : 5-dimethylbenzoic acid, colourless, prismatic needles, m. p. 151—152°. The diketones prepared from β -cumidic acid are less soluble and more difficult to burn than those from α -cumidic acid. 2 : 5-Di(2' : 5'-dichlorobenzoyl)-*p*-xylene crystallises in spangles, m. p. 182°, and 4(2' : 5'-dichlorobenzoyl)-2 : 5-dimethylbenzoic acid forms small prisms, m. p. 193°. When condensed with toluene, β -cumidoyl chloride gives 2 : 5-di-*p*-toluoyl-*p*-xylene, colourless prisms, m. p. 162°, and with anisole, 2 : 5-di-*p*-anisoyl-*p*-xylene, colourless prisms, m. p. 177°.

The above diketones are oxidised by nitric acid (*d* 1.15), at 200°, to dibenzoylbenzenedicarboxylic acids. Thus 4 : 6-dibenzoyl-*m*-xylene gives the known 4 : 6-dibenzoylisophthalic acid, and 2 : 5-dibenzoyl-*p*-xylene gives 2 : 5-dibenzoylterephthalic acid, and these are readily converted into dinaphthantracenediquinone (cf. Philippi, A., 1911, i, 793). By oxidising 4 : 6-di(2' : 5'-dichlorobenzoyl)-*m*-xylene, 4 : 6-di(2' : 5'-dichlorobenzoyl)isophthalic acid was obtained, crystallising in spangles, m. p. 264—266° (decomp.). Its dimethyl ester forms a crystalline powder, m. p. 178°. When



the acid is heated with sulphuric acid monohydrate it is converted into 1 : 4 : 8 : 11-tetrachloro-5 : 7 : 12 : 14-dinaphthanthracenediquinone (annexed formula), crystallising in greenish-yellow needles, decomposing at about 340°. It forms a violet-blue hydro-sulphite vat, but the sodium salt of the reduction product is almost insoluble, and, unlike the unsubstituted diphthaloylbenzene, does not oxidise in air.

E. H. R.

Purpurogallin. J. HERZIG (*Annalen*, 1923, 432, 99—114).—The action of ethyl-alcoholic potash on tetramethylpurpurogallin gives a *trimethylethylpurpurogallin*, m. p. 114—116°, the reverse change not being effected by means of methyl-alcoholic potassium hydroxide. A second *trimethylethylpurpurogallin*, m. p. 105—107°, is produced by the action of alkali and ethyl sulphate on trimethylpurpurogallin. Warm concentrated sulphuric acid converts trimethylpurpurogallin or tetramethylpurpurogallin into *dimethylpurpurogallin*, orange-red needles, m. p. 193—195°, which gives a *diacetate*, white crystals, m. p. 180—181°. The trimethylethyl ether, m. p. 114—116°, gives a *monomethylpurpurogallin*, m. p. 193—194°, whilst the isomeric ether, m. p. 105—107°, gives a mixture, m. p. 158—162°, of monomethyl ether and dimethyl ether. The action of diazomethane on this mixture, on the dimethyl ether, m. p. 193—195°, or on the monomethyl ether, m. p. 193—194°, gives the same trimethylpurpurogallin, m. p. 179° (Perkin and Steven, T., 1903, 83, 196). It is concluded that purpurogallin, as distinct from any possible isomeride, is the parent substance of all the above-mentioned compounds.

The alkaline reduction of tetramethylgalloflavin gives an amorphous substance in the formation of which one methoxyl has become hydrolysed, which contains the free hydroxyl and carboxyl groups which form the lactone ring in *isogalloflavin*. Trimethylpurpurogallin behaves similarly when reduced by means of alkali hydroxide and zinc dust, giving an amorphous product, which has not been obtained pure, but which is certainly a dimethyl ether; it is converted by means of diazomethane into a compound having a methoxyl content corresponding with the trimethyl ether. Similarly, the dimethyl ether, m. p. 193—195°, is converted into a monomethyl ether, which likewise gives a trimethyl derivative with diazomethane.

When air is led through a dilute alkaline solution of purpurogallin, a green coloration appears, but eventually gives place to a reddish-brown shade. A pure product has not, however, been isolated from this experiment (but cf. Perkin and Steven, *loc. cit.*). W. S. N.

The Phenanthrene Series. XXXIV. The Preparation of 2-Hydroxymorpholquinone [2:3:4-Trihydroxyphenanthraquinone] from 4-Nitrophenanthraquinone. JULIUS SCHMIDT and OTTO SCHAIRER (*Bér.*, 1923, 56, [B], 1331—1337).—3:4-Dihydroxyphenanthraquinone is the only product of the degradation of the opium alkaloids which has been obtained from phenanthraquinone, but its preparation is not easy owing to difficulties in the preparation of 3-nitrophenanthraquinone (cf. Schmidt and Söll, A., 1908, i, 995). In the hope of ultimately obtaining morpholquinone or a derivative thereof more readily, the preparation of 4-nitrophenanthraquinone (Schmidt and Austin, A., 1904, i, 69) has been re-examined without thereby effecting any improvement in the method. 2:3:4-Trihydroxyphenanthraquinone has, however, been obtained in small yield from 4-hydroxyphenanthraquinone.

Phenanthraquinyll monoacetate crystallises in almost colourless,

matted needles, m. p. 181—182° [Goldschmidt and Schmidt (A., 1922, i, 1149) gave m. p. 170° (decomp.)]; it is readily converted by boiling acetic anhydride into phenanthraquinyl diacetate, m. p. 202°. Under widely varied conditions, neither of the substances could be converted by nitric acid into 4-nitrophenanthraquinone. 2 : 7-Dinitro-9 : 10-diacetoxyphenanthrene, m. p. about 280° (decomp.), can, however, be readily prepared by the action of nitric acid (*d* 1.45) on the diacetate in the presence of acetic acid and acetic anhydride.

2 : 3-Dinitro-4-hydroxyphenanthraquinone, pale red, crystalline leaflets, m. p. 248° (decomp.), is obtained by the action of nitric acid on 4-hydroxyphenanthraquinone, only small quantities of which should be taken for each experiment. The corresponding acetate forms reddish-brown crystals, m. p. 233° (decomp.); the monoxime, orange-coloured crystals, decomp. 214—215°, is described. The hydroxy-compound is conveniently identified by converting it into 2 : 3-dinitro-4-hydroxyphenanthraphenazine, $\text{HO} \cdot \text{C}_6\text{H}(\text{NO}_2)_2 \cdot \text{C} \cdot \text{N} > \text{C}_6\text{H}_4$, slender, pale brown needles, m. p. 240° (decomp.). The constitution of 2 : 3-dinitro-4-hydroxyphenanthraquinone is established by its oxidation by potassium dichromate and sulphuric acid to phthalic acid from which it follows that the three substituents are attached to the same benzenoid nucleus; the presence of the nitro-groups in the 2 : 3-position is deduced as a result of the authors' experience that the nitro-group never enters in position 1. The dinitro-compound is reduced by tin and hydrochloric acid to 2 : 3-diamino-4-hydroxyphenanthraquinone, which is diazotised with some difficulty and subsequently converted into 2 : 3 : 4-trihydroxyphenanthraquinone, a brownish-red powder, m. p. 185°, in small yield. 2 : 3 : 4-Trihydroxyphenanthraphenazine forms small, brown crystals, m. p. about 255° (decomp.).
H. W.

A New Class of Free Organic Radicles. IV. ROLAND SCHOLL, HEINRICH DEHNERT, and HANS SEMP (*Ber.*, 1923, 56, [B], 1633—1638).—Knowledge of the 1-aryloxanthronyls has been gained previously mainly as a result of experiments with 1-*p*-chlorobenzoyloxanthronyl. In the present communication the preparation of a series of 1-arylanthraquinones and their conversion into 1-aryloxanthronyls are described.

1-Arylanthraquinones are obtained from anthraquinone-1-carboxyl chloride by the Friedel-Crafts method. The formation of blue by-products, undoubtedly oxanthronyls, is invariably observed, and is attributed to the dehydrogenating action of anhydrous aluminium chloride on aromatic nuclei in which the anthraquinone-1-carboxyl chloride functions as catalyst. The formation of the blue substances is favoured by increasing mobility of the hydrogen atoms of the aromatic compound which is used and by rise in temperature during the reaction. The most favourable conditions for the production of the ketones are obtained when carbon disulphide is used as solvent and the temperature is kept as low as

possible. The oxanthronyls are obtained by reducing the 1-aroyle-anthraquinones with zinc dust and glacial acetic acid to 1-aroyle-anthraquinols and disproportionation or dehydrogenation of the latter by hydrochloric acid.

The following individual substances are described: *m*-xylyl 1-anthraquinonyl ketone, $C_6H_4:(CO)_2:C_6H_3\cdot CO\cdot C_6H_3Me_2$, prisms, capped by pyramids, m. p. 191—192°; 1-anisoylanthraquinone, m. p. 205° (Schaarschmidt, A., 1915, i, 566, gives m. p. 269°); *p*-di-phenylyl 1-anthraquinonyl ketone, $C_6H_4:(CO)_2:C_6H_3\cdot CO\cdot C_6H_4Ph$, small, pale yellow needles, m. p. 234°; $C_6H_4 \begin{array}{c} \diagup CO \\ \diagdown C \end{array} \begin{array}{c} \diagup C_6H_3\cdot C \cdot Ph \\ \diagdown OH \end{array}$ 1-benzoyl-9-oxanthronyl (annexed formula), bluish-violet needles with copper reflex, m. p. 192—193°; 1-*p*-toluoyl-9-oxanthronyl, bluish-violet needles or rodlets, m. p. 182—183°; 1-*m*-xyloyl-9-oxanthronyl, dark violet-blue, metallic needles, m. p. 171—172°; 1-anisoyl-9-oxanthronyl, needles, m. p. 167—168°; 1-*p*-phenylbenzoyl-9-oxanthronyl, m. p. 216—217°; 1- α -naphthoyl-9-oxanthronyl, m. p. 198—199°.

Internally complex hydroketyls have also been obtained in the naphthalene series. H. W.

Preparation of Inactive Menthol. RHEINISCHE KAMPFER-FABRIK G. M. B. H. (Brit. Pat. 189450).—By treatment with hydrogen at 5—30 atmospheres and 200° in presence of finely divided nickel, cobalt, platinum, or palladium, thymol yields a mixture of inactive menthol and liquid isomenthol. The latter is dehydrogenated to menthone by heating at 200° with copper oxide in presence of alkali, and the menthone hydrogenised to inactive menthol in the same manner as thymol. T. S. W.

π -Chlorosulphoxidecamphor and *iso*Ketopinic Acid [*Nor*- π -camphor-7-carboxylic Acid]. E. WEDEKIND and R. STÜSSER (Ber., 1923, 56, [B], 1557—1561; cf. Wedekind, Schenk, and Stüsser, this vol., i, 346).—In the previous communication, the conversion of Reyhler's acid into 10-chlorosulphoxidecamphor has been described and the hypothesis has been put forward that the process is applicable to all sulphonyl chlorides in which the sulphonyl residue is present in a methyl group. Confirmation of this view is found in the behaviour of π -camphorsulphonic acid.

π -Chlorosulphoxidecamphor (annexed formula), m. p. about 190° (decomp.), is prepared by the action of $CH_2-CMe-CO$ pyridine on π -camphorsulphonyl chloride; $\begin{array}{c} | \\ Me\cdot C\cdot C(SO)Cl \\ | \end{array}$ it gives a normal *phenylhydrazone*, small, $CH_2-CH-CH_2$ yellow needles, m. p. 167—168°. It is oxidised by potassium permanganate in alkaline solution to *isoketopinic acid* (*nor*- π -camphor-7-carboxylic acid) (annexed formula), m. p. 245°, which can also be prepared by means of nitric acid (*d* 1.34); the corresponding *phenylhydrazone* has m. p. 200° (decomp.).

Attempts to sulphonate other cyclic ketones by Reyhler's method are also described; menthone and fenchone

are, however, almost unaffected, whilst *cyclohexanone* and *carvone* do not yield crystalline sulphonc acids.

Fluorene is transformed by sulphuric acid and acetic anhydride quantitatively into fluorene-2-sulphonic acid in place of the desired fluorene-9-sulphonic acid. On the other hand, *sodium fluorene-9-sulphonate* can be prepared in small yield by the action of boiling, concentrated sodium hydrogen sulphite solution on 9-chloro-fluorene. Attempts to transform the salt by means of phosphorus pentachloride into fluorene-9-sulphonyl chloride were not successful, since the drastic conditions necessary for the change cause the primarily formed chloride to decompose with evolution of sulphur dioxide and production of 9-chlorofluorene. H. W.

Preparation of Basic Derivatives of Camphorimide.

MARGARET FREIFRAU VON AXTER (D.R.-P. 362379; from *Chem. Zentr.*, 1923, ii, 480—481).—The imido-hydrogen of camphorimide is replaced by basic groups of the composition $\cdot C_nH_{2n} \cdot NRR'$ (where R=alkyl or hydrogen and R'=alkyl). These basic compounds may be obtained by treating camphorimide in the presence of sodium ethoxide with halogen substituted bases such as chlorotriethylamine, $NEt_2 \cdot C_2H_4Cl$, or by treating halogen alkyl imides of camphoric acid of the composition $C_8H_{14} \begin{smallmatrix} CO \\ < \\ CO \end{smallmatrix} N \cdot C_nH_{2n}X$ with primary or secondary amines, or by heating camphoric acid (or its anhydride) with *as*-dialkylated diamines of the composition $NH_2 \cdot C_nH_{2n} \cdot NRR'$, or camphor dialkylaminoalkylamidic acids are changed into basic imides by way of α - or β -camphor *isodialkyl*-aminoalkylamides of the composition $C_8H_{14} \begin{smallmatrix} CO \\ | \\ O \end{smallmatrix} > C \cdot N \cdot C_nH_{2n} \cdot NRR'$.

Camphor- β -diethylaminoethylimide, $C_8H_{14} \begin{smallmatrix} CO \\ < \\ CO \end{smallmatrix} N \cdot C_2H_4 \cdot NEt_2$, forms blunt needles, m. p. 87—88°. The *hydrochloride* has m. p. 91—93°. It is prepared by the action of chlorotriethylamine on camphorimide or of *as*-diethylethylenediamine on camphoric anhydride, or by heating *camphor- β -diethylaminoethylamidic acid*, $CO_2H \cdot C_8H_{14} \cdot CO \cdot NH \cdot C_2H_4 \cdot NEt_2$, or by heating camphor- β -bromoethylimide with diethylamine at 100—120°. Camphordiethylaminoethylamidic acid is obtained by gentle heating of a solution of camphoric anhydride and diethylethylenediamine in benzene; it forms needles in star-shaped clusters, m. p. 172—173° (decomp.). Camphor- β -bromoethylimide is a viscid, colourless oil, b. p. 185—190°/12 mm.; it is prepared by the action of ethylene bromide on camphorimide. When heated in alcoholic or benzene solution with methylamine, it gives *camphor- β -methylaminoethylimide*, $C_8H_{14} \begin{smallmatrix} CO \\ < \\ CO \end{smallmatrix} N \cdot C_2H_4 \cdot NHMe$, a basic oil (cf. A., 1922, i, 254).

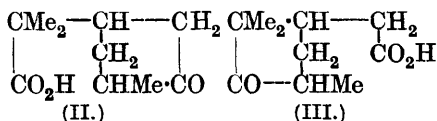
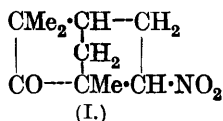
G. W. R.

Preparation of Methylenecamphor. HANS RUPE and WALTER KUSSMAUL (Swiss Pat. 87757; from *Chem. Zentr.*, 1923, ii, 527).—Camphylcarbinol is heated with 70—80% sulphuric
f f*

acid, for example, at 100°. The products of reaction are then poured on to ice and extracted with ether. The reaction proceeds according to the equation $C_8H_{14} \begin{smallmatrix} <CH \cdot CH_2 \cdot OH \\ CO \end{smallmatrix} = C_8H_{14} \begin{smallmatrix} <C \cdot CH_2 \\ CO \end{smallmatrix} + H_2O$. *Methylenecamphor* is obtained after removal of the ether by distillation as a white, wax-like mass with a strong odour of camphor; it has m. p. 43.5–44°, and b. p. 82–84°/10 mm.

G. W. R.

The Action of Nitric Acid on Fenchone. S. S. NAMETKIN [with (MLLE) K. D. LUBOVCOVA and (MLLE) V. A. CHOCHRIAKOVA] (*J. Russ. Phys. Chem. Soc.*, 1922, **54**, 169–176).—By the action of dilute nitric acid on fenchone, Kononov (A., 1904, i, 257) prepared, in addition to the well-known tertiary-4-nitrofenchone, a secondary nitrofenchone, m. p. 88°, $[\alpha]_D -42.88^\circ$; and it is now shown that these substances are also accompanied by *isocamphoronic* and α -dimethyltricarballic acids, both of which Gardner and Cockburn (T., 1898, **73**, 708) have obtained by the oxidation of fenchone by means of nitric acid. Now *isocamphoronic* acid is doubtless produced by the further degradation of the secondary nitrofenchone and for this reason the formula (I) is assigned to this substance.



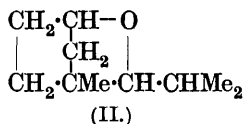
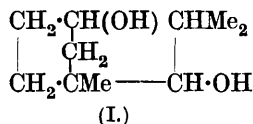
(III.)

The nitroketone is shown to be analogous to α -nitrocamphor (Lowry, T., 1898, **73**, 986; 1903, **83**, 953) in its behaviour towards ferric chloride and permanganate and it is concluded that it is a true nitro-compound. The action of bromine on a solution of the nitroketone in alkali leads to a *bromonitrofenchone*, $C_{10}H_{14}O_3NBr$, forming colourless plates from alcohol, m. p. 53°, stable to heat in the presence of an indifferent solvent. On reduction with zinc and acetic acid, or tin and hydrochloric acid, the nitro-ketone passes into a *keto-acid*, $C_{10}H_{16}O_3$, which is probably a mixture of stereoisomerides, because it has no sharp melting point (73–76°, clears 79–80°); the *semicarbazone* decomposes without melting at 188°. The structure of the acid is most probably represented by formula (II) although the alternative formula (III) is also possible.

G. A. R. K.

Kononov's "Hydroxyfenchone." II. S. S. NAMETKIN and (MLLE) V. A. CHOCHRIAKOVA (*J. Russ. Phys. Chem. Soc.*, 1922, **54**, 163–168; cf. A., 1916, i, 217).—It has already been shown (*loc. cit.*) that the compound $C_{10}H_{16}O_2$ obtained by Kononov (A., 1904, i, 257) by the reduction of 4-nitrofenchone is a monocyclic diketone, formed by the fission of one ring in the bicyclic system present in fenchone. It is now shown that on reduction the diketone passes into a *glycol*, b. p. 151–152°/11 mm.,

$[\alpha]_D +44.54^\circ$ (acetyl derivative, oil, b. p. $152-153^\circ/12$ mm., n_D^{20} 1.4530, d_4^{20} 1.0189); the glycol very readily passes into an oxide when dehydrated with dilute sulphuric acid and for this reason the formula (I) is suggested for the glycol, the oxide being represented by (II),

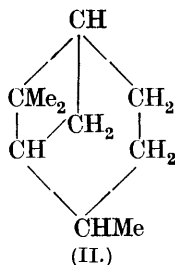
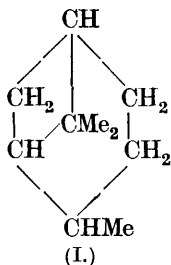


The oxide is a colourless liquid with an odour reminiscent of cineole, b. p. $171-172^\circ/749$ mm., d_4^{20} 0.8985, n_D^{20} 1.4478.

It is pointed out that the great stability usually shown by the bicyclic system of fenchone is profoundly affected by the replacement of the tertiary hydrogen atom by a nitro-group, fission readily taking place under the influence of mild reagents; this fission appears to occur in the neighbourhood of the -CMe_2 -group, as in the splitting of fenchone by the action of sodamide (Semmler, A., 1906, i, 681).

G. A. R. K.

The Stereochemistry of Alicyclic Compounds. I. Dihydropinenes. S. S. NAMETKIN (*J. Russ. Phys. Chem. Soc.*, 1922, 54, 177—194).—A short account of this work has already appeared (this vol., i, 588). It has been shown that the catalytic reduction of *l*-pinene by a modification of Sabatier and Senderens's method leads to a perfectly individual dihydrocompound which has been named pinane (this vol., i, 692). It is now found that when either *d*-pinene (partly racemised) isolated by careful fractionation from Russian turpentine (b. p. $154.5-155^\circ$ [corr.], d_4^{20} 0.8597, n_D^{20} 1.4663, $[\alpha]_D +24.9^\circ$) or inactive pinene, prepared by the regeneration of the nitrosochloride of *d*-pinene (Tilden, T., 1904, 85, 763) are similarly hydrogenated, the product consists of a mixture of two hydrocarbons; it boils within a range of several degrees and the physical properties do not agree with those of pinane. The dihydro-compound was then prepared from *d*-pinene by converting the latter into pinocamphone and treating its *hydrazone*, a colourless oil, b. p. $134-135^\circ/22$ mm., d_4^{20} 0.9917, n_D^{20} 1.5155, either with potassium hydroxide (Kijner, A., 1911, i, 679), or sodium ethoxide (Wolff, A., 1912, i, 988). The first preparation of the hydrocarbon, *pinocamphane*, had b. p. $164.5-165^\circ/763$ mm., d_4^{20} 0.8551, n_D^{20} 1.4609, $[R_L]_D$ 44.33 (calc. 43.98); the second had b. p. $163.5-164^\circ/747$ mm., d_4^{20} 0.8558, n_D^{20} 1.4611, $[R_L]_D$ 44.31; pinocamphane is thus an individual hydrocarbon distinct from pinane in its physical properties (cf. *loc. cit.*). It is suggested that both hydrocarbons are normal hydrogenation products of pinene and that a mixture of the two is produced from *d*- or *r*-pinene by the Sabatier-Senderens method. It is shown that two dihydropinenes are possible; corresponding with the *d*- and *l*-forms of pinene and formulated thus:



Actually, formula (I) probably represents pinocamphane and (II) is assigned to pinane, by analogy with *isobornylane* and *fenchane* (A., 1916, i, 269); in the latter case the hydrocarbon (*fenchane*) possessing no substituents on the carbon atom forming the bridge shows an exaltation of the molecular refraction as compared with *isobornylane* (0.26) and the same difference is observed in the refractions of pinane and pinocamphane.

It is clear that the reduction of either the racemic or optically impure *d*-pinene should lead to a mixture of the two hydrocarbons; the individual *l*-pinene gives only one of them, owing presumably to the selective addition (*cis* or *trans*) of hydrogen to the double linking, such selective additions having been observed in some cases of hydrogenation of triple bonds.

The results obtained by Zelinski (A., 1911, i, 997), who used a higher temperature for the reduction of pinene, are probably attributable to partial isomerisation of the latter. G. A. R. K.

Action of Phosphorus Pentachloride on Pinene. LÉONCE BERT (*Bull. Soc. chim.*, 1923, **33**, 787—790).—When phosphorus pentachloride acts on pinene in the cold, hydrogen chloride is liberated and the other products of the reaction are, besides phosphorus trichloride, *p*-cymene (in about 13% yield), an unstable liquid pinene dichloride, a stable solid pinene dichloride, m. p. 183°, a dark yellow resin, and much tarry matter. H. H.

Curious Case of Separation of Optical Antipodes by Distillation and by Crystallisation. GEORGES DUPONT and L. DESALBRES (*Compt. rend.*, 1923, **176**, 1881—1884).—In the fractional distillation of various pine oils, inactive pinene distils over in the first fractions. Similarly, on freezing the distillates, active pinene separates, the inactive variety being concentrated in the mother-liquors. The presence of inactive pinene decreases the velocity of crystallisation of the active compound, apparently acting simply as a foreign substance, since no evidence could be obtained for the existence of a racemic compound in the liquid state. No explanation is forthcoming to account for the distillation effect. E. E. T.

Action of a Saturated Solution of Hydrogen Chloride in Acetic Acid on Oil of Turpentine. R. HUERRE (*J. Pharm. Chim.*, 1923, [vii], **27**, 441—448).—When 1 part of turpentine is gradually added to 4 parts of a saturated solution of hydrogen

chloride in glacial acetic acid a reaction occurs which is accompanied by a considerable rise of temperature, and on allowing the reaction product to evaporate spontaneously at a temperature below 15° a separation into two layers occurs, the upper layer consisting of a terpene monohydrochloride boiling with slight decomposition between 150° and 200° , and having $\alpha_D -10^{\circ}$ in 5% ethyl acetate solution. The hydrogen chloride is very firmly retained in this compound and is only very partly eliminated by aqueous or alcoholic potassium hydroxide, but more readily by sodium acetate and acetic acid. The lower acetic acid layer of the above reaction product on further spontaneous evaporation below 15° deposits crystals which were identified as terpin, and were obtained pure and anhydrous by recrystallisation from boiling ethyl acetate.

G. F. M.

The Preparation of *d*- and *l*-Limonene in the Pure Condition. JULIUS VON BRAUN and GEORG LEMKE (*Ber.*, 1923, **56**, [B], 1562—1563).—The authors' previous experience has shown that bromine atoms attached to vicinal carbon atoms are very readily and smoothly removed by the action of magnesium in the presence of ether. The method has been applied to the isolation of *d*- and *l*-limonene from the corresponding pure tetrabromides. *d*-Limonene prepared in this manner and finally purified by distillation over sodium has b. p. $176-176.4^{\circ}$, d_4^{20} 0.8411, $[\alpha]_D^{20} +126^{\circ} 8.4'$ in substance, $[\alpha]_D^{20} +117^{\circ} 27'$ when dissolved in chloroform. *l*-Limonene has b. p. $176-176.4^{\circ}$, d_4^{20} 0.8422, $[\alpha]_D^{20} -122^{\circ} 6'$ in substance.

H. W.

Researches on Phellandrenes. I. HENRY GEORGE SMITH, ERIC HURST, and JOHN READ (*T.*, 1923, **123**, 1657—1670).

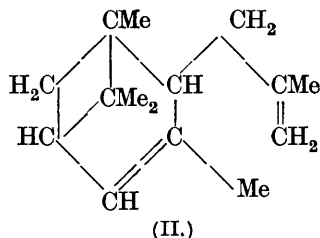
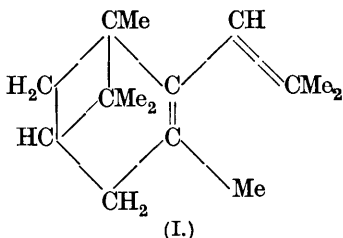
The Conversion of Sabinol into Thujene. GEORGE GERALD HENDERSON and ALEXANDER ROBERTSON (*T.*, 1923, **123**, 1713—1717).

A New Method of Preparing Camphene. H. PARISELLE (*Compt. rend.*, 1923, **176**, 1901—1902).—By effecting the conversion of pinene into its hydrochloride in two stages, in order to minimise heating the material, the yield is increased to 75—85% of that theoretically possible. The use of sodium phenoxide for converting the hydrochloride into camphene is to be avoided, since the product cannot be freed from phenol or from unchanged hydrochloride. Using a mixture of crude *meta*- and *para*-cresols instead of phenol, an 88% conversion into camphene (b. p. $51-53^{\circ}/17$ mm.) can be effected [cf. *J.S.C.I.*, 1923, Aug.].

E. E. T.

Caryophyllene. ERNST DEUSSEN (*Z. angew. Chem.*, 1923, **36**, 348—349; cf. *Annalen*, 1912, **388**, 155).—Oil of cloves contains both inactive α -caryophyllene and the laevorotatory β -isomeride, whereas the sesquiterpene in oil of hops, formerly known as humulene, has been identified as α -caryophyllene. The latter gives a well-defined α -nitrosochloride (m. p. 177°) and α -nitrosite

(m. p. 161°), whilst the β -isomeride gives a blue, crystalline β -nitrosite (m. p. 115°) possessing a very high specific rotation, $[\alpha]_D^{20} +1666^{\circ}$ (in ligroin). The blue α -caryophyllene nitrosite is optically inactive and melts at 116° . β -Caryophyllene is readily converted, by the action of nitrous acid, into a γ -isomeride, which forms a dihydrochloride identical with that of the β -isomeride. Neither the purified caryophyllene from oil of cloves nor γ -caryophyllene gives additive compounds with picric acid or *o*-nitrophenol, but the former yields well-defined additive products with mercurous sulphate and, in particular, with mercuric acetate below 0° . The products with the latter are converted into halides by means of potassium halides, and these compounds have the formula $\text{OH}\cdot\text{Hg}\cdot\text{C}_{15}\text{H}_{24}\text{X}$. They do not give the ionic reactions of mercury until treated with dilute hydrochloric or sulphuric acid. Treatment of the mercury additive compounds with potassium cyanide gives the corresponding cyanide, which is readily soluble in ether and is precipitated by light petroleum. The behaviour of caryophyllene towards sulphur, whereby a mixture of hydrocarbons, $\text{C}_{15}\text{H}_{18}$, $\text{C}_{14}\text{H}_{16}$ (?), $\text{C}_{10}\text{H}_{14}$, is produced, argues against its molecule containing a naphthalene skeleton. Reasons are given for regarding β -caryophyllene as being of the terpinolene type (I) and the γ -isomeride of the limonene type (II) (cf. Semmler, A., 1912, i, 120).



α -Caryophyllene must also contain two adjacent tertiary carbon atoms.

W. T. K. B.

A Sesquiterpene Alcohol from Elemi Oil. H. JANSCH and P. FANTL (*Ber.*, 1923, 56, [B], 1363—1370).—The constituents of higher boiling point of elemi oil contain a bicyclic, singly unsaturated, tertiary sesquiterpene alcohol, $\text{C}_{15}\text{H}_{26}\text{O}$, which is designated α -elemol. The substance, elemol (now termed β -elemol) isolated by Semmler and Futung Liao (A., 1916, i, 492; cf. Semmler, A., 1908, i, 557) is not present as such in elemi oil, but is a secondary product derived from α -elemol.

The elemi oil is submitted to fractional distillation under diminished pressure and the portion, b. p. 140 — $150^{\circ}/10$ mm., is thoroughly drained after it has solidified. It is purified by being repeatedly alternately spread on porous clay and distilled, whereby ultimately α -elemol, $\text{C}_{15}\text{H}_{26}\text{O}$, slender, almost odourless needles, m. p. 46° , b. p. 142 — $143^{\circ}/10$ mm., $\alpha_D^{20} -2.73^{\circ}$ (50 mm. tube), $d_{20}^{25} 0.94112$, $n_D^{25} 1.49788$, is obtained. It is converted by benzoyl chloride in the presence of pyridine into β -elemyl benzoate, b. p.

210—215°/10 mm., n_D^{18} 1.5408, d_4^{18} 1.0346, which is hydrolysed by alcoholic alkali to β -elemol, b. p. 143—144°/10 mm., d_4^{18} 0.9419, n_D^{18} 1.5070; these compounds are identical with those described by Semmler and Futung Liao (*loc. cit.*). The tertiary nature of the hydroxy-group of α -elemol is established by its conversion by zinc dust at about 200° into *elemene*, $C_{15}H_{26}$, a colourless liquid, b. p. 115—119°/10 mm., d_4^{17} 0.8830, n_D^{17} 1.4950. α -Elemol is readily oxidised by permanganate or chromic acid and glacial acetic acid to ill-defined, acidic products; it is violently oxidised by nitric acid to (?) dinitro-dihydrocuminic acid, $C_{10}H_{12}O_6N_2$, decomp. above 155° after darkening at about 140°. The presence of one double bond in α -elemol is established by its hydrogenation in dry ethereal solution in the presence of spongy platinum to *dihydro- α -elemol*, $C_{15}H_{28}O$, m. p. 46°, b. p. 150—151°/11 mm. The action of bromine on α -elemol in the presence of chloroform does not lead to the isolation of a homogeneous product. H. W.

Russian Essential Oils. I. GEORGI VASILIEVITSCH FIGULEVSKI (*J. Russ. Phys. Chem. Soc.*, 1920, 51, 60—71).—The investigation of the following oils is described: oil from *Pinus silvestris* (needles), *Abies sibirica* (needles and twigs), *Juniperus communis* (needles and twigs), *Mentha piperita*, and turpentine.

Two samples of pine needle oil were examined, both derived from the Viatka region (N.E. Russia). The first had d_4^{15} 0.9155, $[\alpha]_D$ -2.08°, $[\alpha]_d$ -2.68°, $[\alpha]_c$ -3.40°, $[\alpha]_h$ -3.96°, $[\alpha]_h/[\alpha]_c$ 1.90; acid number 7.48, saponification value 46.57 (calculated as bornyl acetate); after repeated fractionation the lowest fractions are dextrorotatory and possess a low rotatory dispersion; this may be due to the presence of β -pinene in addition to α -pinene which was identified. Camphene could not be definitely identified, but was isolated (as isobornyl acetate) from the second sample examined; this had d_4^{14} 0.9224, $[\alpha]_c$ +3.84°, $[\alpha]_d$ +4.94°, $[\alpha]_e$ +6.54°, $[\alpha]_h$ 8.06°, $[\alpha]_h/[\alpha]_c$ 2.10, acid number 6.31, saponification value 44.91. The results obtained on fractionating the oil were similar to those above, the low fractions being dextrorotatory, but with a much higher rotation than those from the first sample; the higher fractions show lævorotation. α -Pinene is present, the presence of β -pinene could not be definitely established, but is probable owing to the anomalously low rotatory dispersion of some of the fractions. Both oils show a high ester content.

Two samples of Siberian fir-needle oil from *A. sibirica* were examined, one from the Viatka, the other from the Archangel district; they had almost identical physical properties, agreeing with those in the literature. Fractionation of these oils shows that with rise in boiling point the rotation and rotatory dispersion diminish. A sample of juniper oil (from *J. communis*, origin unknown) had d_4^{15} 0.9258, acid number 10.71, saponification value 55.33 and was very feebly lævorotatory. On fractionation it gave dextrorotatory low fractions, the higher fractions being lævo-rotate. The anomalous rotatory dispersion of the lowest (pinene) fraction points to the presence of nopinene.

Two samples of peppermint oil, one from the Pottava and the other from the Kursk district (Southern Russia) had almost identical properties; the first showed d_4^{20} 0.9113, $[\alpha]_c$ -21.96° , $[\alpha]_d$ -27.66° , $[\alpha]_e$ -35.14° , $[\alpha]_f$ -41.84° , $[\alpha]_g$ 1.91 ; the free menthol content of the samples was high, being $[\alpha]_c$ 43.58 and 45.30, respectively.

Two samples of pine turpentine from the Viatka district were examined; the first, "red" turpentine, was purified by steam distillation (1) and had the following properties, those of the second, "colourless" sample (2), being shown for comparison:

(1)	d_4^{20} 0.8978,	$[\alpha]_c + 7.20^\circ$,	$[\alpha]_d + 9.36^\circ$,	$[\alpha]_e + 12.40^\circ$,	$[\alpha]_f 15.24^\circ$,	$[\alpha]_g/[\alpha]_c$ 2.12
(2)	d_4^{20} 0.8827,	$+ 5.16^\circ$,	6.66° ,	8.80° ,	10.66° ,	2.07

The acid numbers were 2.48 and 2.15, respectively. The results of fractional distillation and the rotations of the fractions are also given.
G. A. R. K.

Russian Essential Oils. II. G. V. PIGULEVSKI and (MILE) V. S. NIKITINA (*J. Russ. Phys. Chem. Soc.*, 1920, **51**, 72—80).—Specimens of the following oils were examined: caraway, pennyroyal, laurel, thuja, spruce, and *Pinus densiflora*.

Of the three specimens of caraway oil from Kharkov district, two were obtained from the seeds and had the usual properties, the carvone content being from 47 to 56%; the third specimen was obtained from the crushed pulp and showed a higher density (0.9451), somewhat lower rotation ($[\alpha]_D + 65.34^\circ$), and a very high carvone content (79%).

The oil of pennyroyal which came from the Caucasus had the usual properties, the pulegone content being 75%.

The oil of the Caucasian spruce (*Picea orientalis*) obtained from the dry needles has the following properties: d_4^{20} 0.9325, $[\alpha]_c$ -28.39° , $[\alpha]_d$ -36.38° , $[\alpha]_e$ -47.42° , $[\alpha]_f$ -58.10° , $[\alpha]_g/[\alpha]_c$ 2.05; the acid number is 2.17, the saponification value 97.95 (=26.42% bornyl acetate). Fractionation shows a comparatively small percentage of low-boiling hydrocarbons (α - and β -pinene and camphene) compared with the oil of *P. vulgaris*; the ester content, on the other hand, is higher.

The oil of the Caucasian fir (*Abies nordmanniana*) obtained from the dry needles had d_4^{20} 0.9410, $[\alpha]_c$ -29.66° , $[\alpha]_d$ -38.12° , $[\alpha]_e$ -49.68° , $[\alpha]_f$ -60.82° , $[\alpha]_g/[\alpha]_c$ 2.05; acid number 3.06, saponification value 107.03 (=28.6% bornyl acetate), the values being similar to those for Siberian fir oil (cf. preceding abstract).

The specimens of Caucasian thuja oils were obtained from *Thuja gigantia* (i), *T. dolabrata* (ii), and *T. compacta* (iii). Their properties were:

	$[\alpha]_c$	$[\alpha]_d$	$[\alpha]_e$	$[\alpha]_f$	$[\alpha]_g/[\alpha]_c$	Density.	Solubility in 80% alcohol.
(i)	-1.68°	-3.14°	-5.90°	-9.22°	5.49	d_4^{20} 0.9260	1 : 0.6
(ii)	$+12.98^\circ$	$+16.00^\circ$	$+19.64^\circ$	$+22.48^\circ$	1.73	d_4^{20} 0.9204	1 : 0.6
(iii)	$+2.24^\circ$	$+2.60^\circ$	$+2.80^\circ$	$+2.40^\circ$	1.07	d_4^{20} 0.9568	1 : 0.6

The acid numbers and saponification values were (i) 5.96 and 32.03, (ii) 3.17 and 25.67, (iii) 6.85 and 43.40.

The oil of the Caucasian pine (*Pinus densiflora*) was prepared from the dry needles (i) in a yield of 0.37% and cones (ii) in a yield of 0.22%. The properties of two samples were :

	$[\alpha]_c$	$[\alpha]_d$	$[\alpha]_e$	$[\alpha]_f$	$[\alpha]_f/[\alpha]_c$	Density.	Solubility in 80% alcohol.
(i)	-29.98°	-38.34°	-49.75°	-60.81°	2.03	d_{15}^{20} 0.9124	1 : 7
(ii)	-23.72°	-30.28°	-39.28°	-47.44°	2.00	d_{15}^{20} 0.9602	

The acid numbers and saponification values were (i) 1.50 and 91.21, (ii) 7.60 and 103.04; sample (ii) has thus the higher density and percentage of esters. The oil is characterised by the high ester content.

The oil from laurel leaves (*Laurus nobilis*) of Caucasian origin is shown to be similar to the Crimean oil, and does not differ greatly from other European oils.

G. A. R. K.

Russian Essential Oils. III. G. V. PIGULEVSKI and U. A. PLOTNITZKI (*J. Russ. Phys. Chem. Soc.*, 1920, **51**, 81—86).—The preparation of the following oils from plants grown in the Crimea is described :

Hyssopus officinalis, *Salvia officinalis*, *Cupressus sempervirens*, and *Juniperus excelsa* M.R. (*J. sabina* var. *taurica* Pall.). The preparation of turpentine from the resin of *Pinus silvestris* and *P. taurica* was also carried out and the yield from the latter is shown to be comparable with that of French turpentine from *P. maritima*. Samples of this turpentine have $[\alpha]$ -32.11° and -32.53°, $[\alpha]_f/[\alpha]_c$ 1.95 and 2.01; whilst the turpentine from *P. silvestris* is also laevorotatory ($[\alpha]_d$ -17.48° and -13.94°, $[\alpha]_f/[\alpha]_c$ 1.74 and 1.59).

G. A. R. K.

Russian Essential Oils. IV. G. V. PIGULEVSKI and (MME) S. S. FICHTENHOLZ (*J. Russ. Phys. Chem. Soc.*, 1920, **51**, 87—95).—The properties of hyssop, savin, and cypress oils prepared by Pigulevski and Plotnitzki (preceding abstract) are described.

Several samples of hyssop oil were examined and the properties of oils from blue-, red-, and white-flowered varieties are compared. The effect of keeping the raw material before subjecting it to distillation is discussed. The properties of the oils do not differ greatly from those of French oils. The greater part of the oil distils between 203° and 217° and this fraction shows the highest rotation.

A sample of savin oil (from the needles and young twigs of *Juniperus sabina* var. *taurica*) had d_{15}^{20} 0.8896, $[\alpha]_c$ +23.16°, $[\alpha]_d$ +29.20°, $[\alpha]_e$ +37.24°, $[\alpha]_f$ +44.52°, $[\alpha]_f/[\alpha]_c$ 1.92, acid number 2.67, ester value 14.32 before and 44.55 after acetylation; the properties of a second sample were very similar.

The results of fractionation of the oil, and the effect due to the age of the needles from which it is derived, are also discussed.

The oil obtained from cypress twigs and needles shows properties

agreeing with those of French oils but the ester value is higher (26.11 before and 82.21 after acetylation); the results of fractionation are described.

G. A. R. K.

Physico-chemical Studies on Caoutchouc. I. The Viscosity-Concentration Formula for Caoutchouc Solutions.

KEIICHI SHIMADA (*J. Chem. Ind. Japan*, 1923, 26, 705—708).—Viscosities of benzene solutions (0.03—0.47%) of caoutchouc at 15° have been determined by means of Ostwald's viscosimeter. The viscosities conform to Arrhenius's viscosity formula, $\log \eta/\eta_0 = \textcircled{a}C$, where η is the viscosity of the solution, η_0 that of the solvent, and C the concentration of the system. The presence of resin in raw caoutchouc is without effect on the relation between viscosity and concentration.

K. K.

Higher Terpene Compounds. X. Isomerism Phenomena among the Pine Resinic Acids of the Abietic Acid Group.

L. RUZICKA and H. SCHINZ (*Helv. Chim. Acta*, 1923, 6, 662—673).—Modern American colophony is prepared from the crude resin at a comparatively low temperature, not exceeding 150°, and the abietic acid prepared from it is difficult to crystallise and is *d*-rotatory. By distillation at 0.3 mm. and crystallisation it gives the *l*-rotatory abietic acid previously described, m. p. 158° (Ruzicka and Meyer, A., 1922, i, 547). It is a general rule that the abietic acid of low temperature colophony undergoes inversion at about 250°, and a second inversion, becoming again *d*-rotatory, at 300°. The first inversion is also brought about by boiling acetic acid. French colophony has sometimes a small positive, sometimes a negative rotation. The former may be accounted for by the isomerisation of *l*-pimaric acid, which is present in French white resin (galipot), during the preparation of the colophony. When distilled in a high vacuum it behaves similarly to American colophony, but unlike the latter does not decompose into hydrocarbon when distilled at 12 mm. The abietic acid obtained has, after recrystallisation, m. p. 159—161°, $[\alpha]_D -59^\circ$ to 63° , and appears identical with that from American colophony.

From a natural Swiss pine resin, care being taken not to heat above 60°, an abietic acid was obtained forming rectangular, colourless crystals, m. p. 142—144°, $[\alpha]_D -138^\circ$ in alcohol. By catalytic reduction this gave a tetrahydro-derivative, m. p. 168—170°, $[\alpha]_D +19^\circ$. Crystallographically this acid appears to be related to the so-called *l*-pimaric acid. After boiling with acetic acid and recrystallising it had m. p. 162—164°, $[\alpha]_D -92^\circ$, and was closely similar crystallographically to the high temperature abietic acid from American colophony, forming hemimorphic monoclinic crystals. The angles of the crystals are very similar to those of a number of different abietic acids of m. p. from 155° to 180° and $[\alpha]_D$ from $+3^\circ$ to -180° . It seems probable that the abietic acids may form a wide range of mixed crystals.

E. H. R.

Higher Terpene Compounds. XI. *d*-Pimaric Acid and the Classification of the Pine Resin Acids. L. RUZICKA and FR. BALAS (*Helv. Chim. Acta*, 1923, 6, 677—691).—To throw

further light on the chemical relationship between the *d*-pimaric acid of French white resin (galipot), and the abietic acid of American colophony, attempts have been made to elucidate the constitution of the former. According to Tschugaev and Teearu (A., 1913, i, 726), by catalytic hydrogenation it takes up two atoms of hydrogen, and it is probably a tetracyclic compound containing a single unsaturated bond. The molecular refractions of methyl and ethyl *d*-pimarate, however, agree with the values calculated on the assumption that the molecule contains two double bonds. Methyl *d*-pimarate has d_D^{19} 1.030, n_D^{19} 1.5208, and ethyl *d*-pimarate d_D^{14} 1.013, n_D^{14} 1.5151. In each case the determinations were made on the supercooled liquid. It was confirmed that only a dihydro-derivative of *d*-pimaric acid could be obtained by hydrogenation, but an *ozonide* was obtained, m. p. 90° (decomp.), having the formula $C_{20}H_{28}O_2 \cdot O_9$ or $C_{20}H_{30}O_2 \cdot O_9$, which might be a triozone of the unchanged *d*-pimaric acid or of a dehydro-acid, $C_{20}H_{28}O_2$. The dihydro-*d*-pimaric acid obtained by hydrogenation had m. p. 239–240°, $[\alpha]_D +14.5^\circ$ in 0.5% alcoholic solution; a less pure fraction had m. p. 225–228° and it appears that a mixture of dihydro-acids is formed. The acid, m. p. 239–240°, crystallises in rhombic plates, $[a : b : c = 0.681 : 1 : 1.892]$, and is morphologically very close to *d*-pimaric acid, $[a : b : c = 0.7056 : 1 : 1.8936]$. By dehydrogenation of *d*-pimaric acid with sulphur at 250°, a hydrocarbon was obtained, $C_{16}H_{14}$, which appears to be a *dimethylphenanthrene*, m. p. 86°. It forms a *picrate*, yellow needles, m. p. 131–132°, and *styphnate*, m. p. 159°. When oxidised with chromic acid, it gives a *quinone*, $C_{16}H_{12}O_2$, red needles, m. p. 166°, which condenses with *o*-phenylenediamine to form a *quinoxaline*, needles, m. p. 194°. The pine resinic acids, $C_{20}H_{30}O_2$, can now be definitely divided into two groups, the abietic acid group, the members of which, when dehydrogenated, give retene, and the new group of which *d*-pimaric acid is the first representative.

A number of improvements in the methods of preparation of *d*- and *l*-pimaric acids from galipot are described. E. H. R.

Higher Terpene Compounds. XII. Fichtelite and the Stereochemistry of Hydrogenated Phenanthrene Derivatives. L. RUZICKA, FR. BALAS, and H. SCHINZ (*Helv. Chim. Acta*, 1923, 6, 692–697).—Although fichtelite has generally been recognised as a hydrogenated retene the relationship has never been proved. Retene has now been obtained from fichtelite by heating it with sulphur at 180–250° during twenty hours. It is pointed out that the formula of fichtelite is still uncertain, the choice lying between $C_{18}H_{32}$ and $C_{19}H_{34}$. The molecular refraction does not distinguish between the two.

With regard to the stereochemistry of hydrogenated phenanthrene derivatives, it is pointed out that when the two carbon atoms common to two rings are united by a double bond the two rings must lie in a plane, but when the bond between these two carbon atoms is single, the two rings are in different planes. In the case of a three-ring system such as phenanthrene, when the system is fully hydro-

generated the three rings will all lie in different planes and *cis-trans*-isomerism becomes possible. In the case of dodecahydrophenanthrene derivatives containing different substituents in the two outer rings, another kind of isomerism becomes possible due to the fact that the one double bond may be situated between the first and second or the second and third rings. The isomerism, sometimes of a labile nature, of retene and abietic acid derivatives may be due to these factors. E. H. R.

The Synthesis of Æsculin. E. GLASER and M. KRAUS (*Biochem. Z.*, 1923, **138**, 182—191).—When æsculetin is dissolved in cold potassium or sodium hydroxide solution and treated with an acetone solution of tetra-acetylbromoglucose, according to Mauthner's method (A., 1910, i, 677; 1911, i, 647; 1912, i, 570; 1914, i, 195), *æsculetintetra-acetylglucoside*, $C_9H_5O_4 \cdot C_6H_7O_5Ac_4$, is obtained, in 50% yield, as white, compact, prismatic crystals, m. p. 181—182°, $[\alpha]_D^{20} - 21^\circ$ in methyl alcohol ($c = 466$). Æsculin (æsculetinglucoside), $C_9H_5O_4 \cdot C_6H_{11}O_5 \cdot 2H_2O$, was obtained in 60% yield from the tetra-acetylglucoside by hydrolysis with baryta or, preferably, alcoholic ammonia, as white needles, m. p. 205°, $[\alpha]_D^{20} - 146^\circ$ in methyl alcohol ($c = 0767$). It loses $1\frac{1}{2}$ mols. H_2O at 100° and the rest of its water of crystallisation at its melting point. Synthetic æsculin gives all the reactions of the natural product but does not show fluorescence. It is suggested that the fluorescence of the natural glucoside is due to the presence of traces of impurities or decomposition products. J. P.

The Synthesis of Protocatechualdehyde Glucoside. E. GLASER and S. UEBERALL (*Biochem. Z.*, 1923, **138**, 192—197).—*Protocatechualdehydetetra-acetylglucoside*, $C_7H_5O_3 \cdot C_6H_7O_5Ac_4$, obtained by Mauthner's method (cf. preceding abstract), forms white needles, m. p. 179—180°, $[\alpha]_D^{20} - 49.5^\circ$ in ethyl alcohol ($c = 677$). Hydrolysis with baryta (used in preference to alcoholic ammonia) gave *protocatechualdehydegucoside*, $C_7H_5O_3 \cdot C_6H_{11}O_5$, in 50% yield. It forms white, hygroscopic needles, m. p. 73—74°, $[\alpha]_D^{20} - 36.2^\circ$ in water ($c = 2.405$), and is hydrolysed by emulsin. Evidence is adduced in favour of the view that the glucose residue is attached to the *p*-hydroxyl group of protocatechualdehyde. J. P.

Constituents of *Monotropa hypopitys*, L. ; Preparation of a New Glucoside, Monotropein. MARC BRIDEL (*Compt. rend.*, 1923, **176**, 1742—1744).—The prolonged action of emulsin on an alcoholic extract of *Monotropa hypopitys* resulted in an inversion of the rotation and a large increase in the percentage of reducing sugars. At the same time a blue colouring matter was developed. This behaviour pointed to the presence of a glucoside, *monotropein*, which was eventually isolated in the form of colourless and odourless prisms with a pronounced acid taste. The glucoside decomposes hydrogen carbonates with evolution of carbon dioxide and has $[\alpha]_D^{20} + 130.44^\circ$. It is hydrolysed by 3% sulphuric acid with formation of a black precipitate similar to that given by aucubin, but the two glucosides are by no means identical. Emulsin hydrolyses

monotropein with formation of the above-mentioned blue substance. The darkening of the plant on drying is to be attributed to the presence of the glucoside.

G. F. M.

Preparation of Verbenalin. J. D. RIEDEL, AKT. GES. (D.R.-P. 358873; from *Chem. Zentr.*, 1923, ii, 337).—Extracts from plant material are purified by precipitation with solutions of salts of the alkaline earths or of heavy metals. The glucoside is then precipitated from the filtrate with ammonia and lead acetate. The aqueous solution obtained after decomposition of the precipitate is concentrated and the glucoside extracted by an organic solvent such as ethyl acetate. *Verbenalin* forms colourless prisms, m. p. 179—180° (uncorr.).

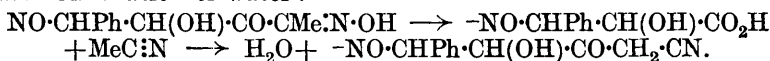
G. W. R.

Theory of Vegetable Tanning. I. Dehydration of Lyophilic Sols and Gels by Tannins and its Bearing on the Theory of Vegetable Tanning. H. G. BUNGENBERG DE JONG (*Rec. trav. chim.*, 1923, 42, 437—472).—The investigations described deal with the following points: (1) whether the disperse phase in an aqueous solution of tannic acid has a capillary electric charge; (2) the mechanism of the precipitation of lyophilic bio-colloids with tannic acid; (3) the dehydration of an agar sol by tannic acid; (4) the rehydration of colloids dehydrated with tannic acids; (5) the character of some commercial tannic extracts; (6) the dehydration of gels with special reference to the theory of vegetable tanning.

The following results were obtained: (1) No capillary electric charge could be found with carefully purified tannic acid either by means of viscosimetry or cataphoresis. (2) In general, impure lyophilic bio-colloids are precipitated with tannin whether they are negatively charged (colloid carbohydrates) or positively charged (proteins). Specially purified lyophilic colloids, however, are not usually precipitated with tannin. (3) On addition of tannin to sols of specially purified agar or gelatin, the latter change into hydrophobic systems of which the capillary electric charge remains unaltered; considerable dehydration was indicated by viscosimetric measurements. (4) With impure lyophilic colloids the presence of electrolytic impurities frequently causes the capillary electric charge to fall below the critical value so that directly after dehydration precipitation by the tannin begins. Similarly with specially purified proteins precipitation takes place in the neighbourhood of the isoelectric point since here also the charge is below the critical value. (5) The dehydrations are connected with the adsorption of the tannin by the lyophilic particles and it is suggested that polar molecules are in general adsorbed in an orientated state in accordance with the views of Langmuir and Harkins. Hence after the adsorption the surface of the particles consists of feebly lyophilic phenolic groups so that there is little further opportunity for hydration. (6) On heating or on the addition of organic liquids miscible with water, rehydration occurs to a greater or lesser extent, as was found in making viscosimetric measurements with an agar sol. The degree of rehydration varies

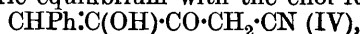
with the nature of the lyophilic sol. (7) Viscosimetric measurements with an agar sol showed that the addition of sodium hydroxide also causes rehydration, but in this case there are no individual differences with lyophilic bio-colloids as the rehydration is equally complete in all cases, due to the neutralisation of the adsorbed tannin whilst the sodium tannate so formed is not adsorbed. (8) Commercial tanning extracts have, like tannin, a dehydrating effect on lyophilic colloids. In some of these extracts charged lyophilic colloids are present as an impurity which are dehydrated by the excess of tannin after cooling the extract. The behaviour of the extracts on heating, cooling, adding alcohol or sodium hydroxide, etc., agrees with this point of view. (9) Tannin has, like alcohol, a dehydrating effect on gels of lyophilic bio-colloids as seen in the case of agar. (10) Vegetable tannin is in the first place a physical dehydration of the lyophilic gel elements as a result of the adsorption of tannin. F. A. M.

Action of Nitrous Gases on Unsaturated Compounds. The Action of Nitrogen Trioxide on the Monoxime of Benzilidenediacetyl. OTTO DIELS (*Annalen*, 1923, 432, 1—45).—The action of nitrogen trioxide on benzilidenediacetyl monoxime in dry ethereal solution leads to the formation of the bisnitroso-compound, $N_2O_2[CHPh\cdot CH(OH)\cdot CO\cdot CH_2\cdot CN]_2$, m. p. 118—120° (decomp.), in the formation of which two $-O\cdot NO$ groups in the initial product must become hydrolysed to hydroxyl groups, and the compound thus produced must then undergo a Beckmann interconversion of the "second type" (Werner and Piguet, A., 1905, i, 66; Diels and Stern, A., 1907, i, 480), with elimination of acetonitrile, which then condenses with the residual molecule with elimination of water:

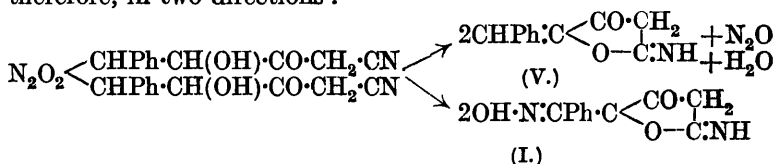


The bisnitroso-compound is insoluble in the usual solvents in the cold, but on warming with neutral solvents, whereby an unstable, green nitroso-compound is apparently first produced, with glacial acetic acid, or with moist or dry acetone, or by treatment with cold pyridine, it passes, with evolution of gas, into a bright yellow compound (see below). If boiling moist acetone is used, the oxime (I), pale yellow crystals, m. p. 158° (decomp.), is also formed; this may be hydrolysed to the ketone, $COPh\cdot CH<\begin{smallmatrix} CO\cdot CH_2 \\ O-C:NH \end{smallmatrix}$ (II), transparent, rod-like crystals, m. p. 152—153° (decomp.), by means of concentrated hydrochloric acid.

$\beta\gamma$ -Diketo- δ -phenylvaleronitrile, $CH_2Ph\cdot CO\cdot CO\cdot CH_2\cdot CN$ (III), intensely yellow, rod-like, monoclinic holohedral crystals, m. p. 138—139° (decomp.), is most conveniently prepared by the action of ice-cold pyridine on the bisnitroso-compound. The reactions of this substance, referred to hereunder as "the yellow compound," are interpreted on the assumption that the diketo-nitrile (III) exists in tautomeric equilibrium with the enol form,



and that the compound may also react as the imino-lactone (V). The decomposition of the bisnitroso-compound proceeds, therefore, in two directions :



the nature of the solvent determining which kind of decomposition will predominate.

Oxidation of the yellow compound in chloroform solution by means of ozone, and decomposition of the ozonides by means of boiling water, gives benzoic acid and dibenzylidene diperoxide, derived, through benzaldehyde, from the benzylidene part of the molecule (IV); the remainder of the molecule is completely destroyed.

The reduction of the yellow compound by means of zinc dust and hydrochloric acid in aqueous methyl-alcoholic solution gives *γ*-hydroxy-β-keto-δ-phenylvaleronitrile, $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{OH})\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CN}$ (VI), colourless, glistening needles, m. p. 104–105°, for which, however, the formula $\text{CH}_2\text{Ph}\cdot\text{C} < \begin{array}{l} \text{C}(\text{OH})\cdot\text{CH}_2 \\ \text{O}-\text{C:NH} \end{array}$ (VII) is preferred,

the keto form of which, $\text{CH}_2\text{Ph}\cdot\text{CH} < \begin{array}{l} \text{CO}\cdot\text{CH}_2 \\ \text{O}-\text{C:NH} \end{array}$ (VIII), may also

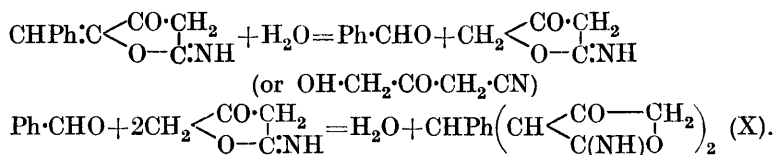
be capable of existence. This reduction product gives a *benzoate*, stout crystals, m. p. 54·5°, and dissolves unchanged in concentrated hydrochloric acid. It is decomposed by boiling with dilute aqueous alkali hydroxide, with evolution of ammonia; it reduces Fehling's solution or ammoniacal silver nitrate in the cold. In contrast to the yellow compound (see below), the reduction product does not form an additive compound with aniline or phenylhydrazine. When it is heated at 140°, carbon monoxide and toluene are evolved; the residue from this experiment, or the reduction product itself, gives phenylacetic acid, when oxidised by means of ozone. The reduction product spontaneously undergoes oxidation, accompanied by liquefaction, in contact with air, or rapidly in an atmosphere of oxygen; phenylacetic acid (the chief product), benzaldehyde, benzyl alcohol, acetic acid, and an indefinite nitrogenous residue are formed, the main reaction probably being: $(\text{VII}) + \text{O}_2 + 2\text{H}_2\text{O} = \text{CO}_2 + \text{NH}_3 + \text{CH}_2\text{Ph}\cdot\text{CO}_2\text{H} + \text{Me}\cdot\text{CO}_2\text{H}$.

When the yellow compound is boiled with benzene for three hours, an equivalent quantity of carbon monoxide is evolved, with formation of a *compound*, $\text{C}_{29}\text{H}_{35}\text{O}_3\text{N}_2$, white, matted crystals, m. p. 189° (decomp.), together with a viscous, reddish-orange gum. The action of hydrochloric acid and acetic acid at 150° on the compound $\text{C}_{29}\text{H}_{35}\text{O}_3\text{N}_2$ gives a *compound*, $\text{C}_{24}\text{H}_{21}\text{O}_2\text{N}$, elongated prisms, m. p. 175°, which is gradually decomposed by boiling with concentrated potassium hydroxide solution, but without the evolution of ammonia.

The yellow compound forms additive compounds with methyl or ethyl alcohol, aniline, *o*-phenylenediamine, or phenylhydrazine. Since these products are colourless, it is suggested that addition occurs at the double bond of the individual (VIII). The compound, $C_{12}H_{13}O_3N$, from methyl alcohol, gradually dissociates, when kept in a vacuum. The compound, $C_{17}H_{16}O_2N_2$, m. p. 121—122° (decomp.), from aniline, and the compound, $C_{17}H_{17}O_2N_3$, m. p. 118—119°, from *o*-phenylenediamine, behave as salts, being decomposed in the presence of acids, with reproduction of the yellow compound. The compound,
$$\begin{array}{c} \text{NHPh}\cdot\text{NH} \\ \text{CH}_2\text{Ph} \end{array} > \text{C} \begin{array}{l} \text{CO}\cdot\text{CH}_2 \\ \text{O}-\text{C}\cdot\text{NH} \end{array} \quad (\text{IX}), \text{ m. p.}$$

123—124°, from the yellow compound and phenylhydrazine in cold alcoholic solution, breaks down, in boiling toluene solution, with evolution of carbon monoxide, and formation of the phenylhydrazone of phenylacetic acid, $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{NH}\cdot\text{NHPh}$.

At higher temperatures, strong amine bases are able to cause the elimination of benzaldehyde from the yellow compound. Thus benzaldehydephenylhydrazone is formed when the yellow compound and phenylhydrazine are boiled in alcoholic solution. When the yellow compound is boiled with aqueous alcoholic ammonia, free benzaldehyde is formed, together with a compound (X), m. p. 175°, which reduces cold ammoniacal silver nitrate or warm Fehling's solution, is insoluble in acids, but soluble in cold dilute alkali, and is decomposed, with elimination of ammonia, by means of warm, dilute alkali. It is evidently formed according to the scheme :



It gives a *diacetyl* derivative, m. p. 96°, and an *additive* compound, white, matted crystals, m. p. 207°, with one molecule of phenyl-carbimide. The same compound is produced, together with benzylidene-ethylamine, by the action of aqueous ethylamine on the yellow compound.

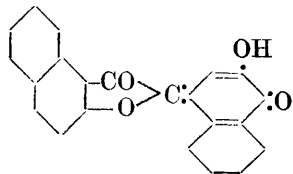
The yellow compound, reacting in the open-chain form (III), shows certain characteristic properties of nitriles. Thus, when fused with phosphorus pentachloride, it forms a colourless *additive* compound, which is soluble in ether, but is dissociated in the presence of water. A pale yellowish-red *additive* compound is likewise formed when the yellow compound and acetyl chloride are boiled with zinc chloride. Moreover, when the yellow compound and resorcinol are treated, in ethereal solution, in the presence of zinc chloride, with anhydrous hydrogen chloride, a colourless *additive* compound, white needles or prisms, m. p. 200—203°, $+\text{CH}_3\cdot\text{CN}$, colourless prisms, m. p. 150° (decomp.), is produced. The colourless reduction product (VI), or (VII) (VIII), does not undergo this reaction, presumably owing to the greater stability

of the imino-lactone phase (VII), or (VIII). The existence of the nitrile radicle in the yellow compound is also indicated by its behaviour when gently warmed with glacial acetic acid. Carbon monoxide is rapidly evolved, with formation of $\beta\gamma$ -diketo- δ -phenyl-valeric acid, white, matted needles, m. p. 168° , copper salt, hard, green prisms, methyl ester, b. p. $105-110^\circ/0.6$ mm. During the production of this acid, a small quantity of phenylacetic acid is also formed; hence the generation of carbon monoxide. The diketo-acid gives benzaldehyde, and benzoic, oxalic, and acetic acids, when oxidised by means of ozone. It is decomposed by boiling with 95% formic acid into acetic and phenylpyruvic acids. A similar fission occurs when the acid is warmed with aqueous phenylhydrazine acetate, with production of phenylpyruvic acid phenylhydrazone. The action of boiling anhydrous formic acid on the yellow compound is very similar; phenylpyruvic acid is produced, but partly decomposes, with elimination of carbon monoxide, and formation of phenylacetic acid.

A somewhat complicated reaction occurs when the yellow compound is boiled with a mixture of acetic acid and hydrochloric acid. Carbon monoxide, and some carbon dioxide, are eliminated, with production of phenylacetic acid and a *dibasic acid*, $C_{20}H_{18}O_5N$, glistening, matted leaflets, m. p. 204° (decomp.), *acid pyridine* salt, m. p. 182° , *acid aniline* salt, m. p. $187-188^\circ$ (decomp.), in the formation of which three molecules of the yellow compound obviously participate. Its constitution has not, however, been elucidated.

The prolonged action of aqueous-ethereal hydrochloric acid on the yellow compound gives oxalic acid, whilst with boiling acetic anhydride, phenylacetic anhydride is produced. W. S. N.

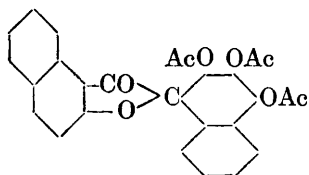
The Autoxidation of 1-Acetyl- β -naphthol. K. FRIES and H. EHLERS (*Ber.*, 1923, 56, [B], 1304-1308).—It has been shown previously that 2-acetyl- α -naphthol undergoes a peculiar autoxidation in alkaline solution when the amount of alkali does not exceed a certain limit (cf. Fries and Leue, A., 1922, i, 462). Similar observations are now recorded with the isomeric 1-acetyl- β -naphthol which yields acetic acid and a substance, $C_{22}H_{12}O_4$, to which, on account of its synthesis and reactions, the annexed constitution is assigned.



An improved method for the preparation of 1-acetyl- β -naphthol is described in detail (cf. Fries and Frelstedt, A., 1921, i, 423).

When a solution of 1-acetyl- β -naphthol in the requisite amount of aqueous sodium hydroxide solution is evaporated to dryness in an open dish, the compound, $C_{22}H_{12}O_4$ (see above), is obtained as slender, brilliant red needles, m. p. 308° after darkening at 260° ; the *carbethoxy*-derivative crystallises in reddish-brown needles, m. p. 243° . The parent substance is decomposed by boiling aniline into 4:5-benzocumaran-3-one and anilino- β -naphthaquinone. It

is produced synthetically from 4 : 5-benzocumaran-3-one and 3-hydroxy-1 : 4-naphthaquinone-4-anil in the presence of boiling glacial acetic acid or, less advantageously, from 4 : 5-benzocumaran-3-one



and β -naphthaquinone in boiling alcoholic solution; the production of smaller amounts of blue and green substances is also observed (cf. this vol., i, 829). The compound, $C_{22}H_{12}O_4$, is converted by acetic anhydride containing a little concentrated sulphuric acid into the triacetate (annexed formula), colourless

needles, m. p. 223° , which loses acetic anhydride at 150° and passes into the yellow monoacetate.

4 : 5-Benzocumaran-3-one is conveniently prepared by the successive action of phosphorus pentachloride and aluminium chloride on the β -naphthyl ether of glycollic acid in the presence of benzene.

4-Bromo-2-acetyl- α -naphthol is unaffected by oxygen in the presence of an equivalent amount of aqueous sodium hydroxide solution or by lead peroxide in the presence of boiling glacial acetic acid. It is converted by nitric acid (*d* 1.5) and glacial acetic acid into 4-nitro-2-acetyl- α -naphthol, yellow needles, m. p. 159° . Under similar conditions, 4-bromo-2-ethyl- α -naphthol is transformed into 2 ethyl-1 : 4-naphthaquinone.

H. W.

Thioflavanones, Thiochromanones, and Thiochromanols.

F. ARNDT [with W. FLEMMING, E. SCHOLZ, and V. LÖWENSOHN] (*Ber.*, 1923, 56, [B], 1269—1279).—The recent publications of Krollpfeiffer and Schäfer (this vol., i, 343) and of Zahn (this vol., i, 375) have caused the authors to publish an account of work which is not quite completed.

β -*p*-Tolylthiol- β -phenylpropionic acid, $C_6H_4Me \cdot S \cdot CHPh \cdot CH_2 \cdot CO_2H$, colourless needles, m. p. 106° , is prepared in 63% yield by the action of a mixture of saturated solutions of hydrogen bromide and hydrogen chloride in glacial acetic acid on cinnamic acid and *p*-thiocresol at 100° ; it is purified by means of its sparingly soluble sodium salt. β -Phenylthiol- β -phenylpropionic acid, coarse, colourless needles, m. p. 85 — 86° , is prepared in an analogous manner. Ring closure with the *p*-tolyl acid is effected by heating it on the water bath with phosphoryl chloride whereby 6-methylthioflavanone, $C_6H_4Me \cdot \begin{smallmatrix} CO \cdot CH_2 \\ | \\ S \cdot CHPh \end{smallmatrix}$, colourless needles, m. p. 96° , is

obtained. The reaction can also be effected by the action of phosphoric oxide in the presence of boiling benzene, but, in this case, 6-methylthioflavone, $C_6H_4Me \cdot \begin{smallmatrix} CO \cdot CH \\ | \\ S \cdot CPh \end{smallmatrix}$, m. p. 149 — 150°

(Ruhemann [A., 1913, i, 1374] gives m. p. 153 — 154°) is also produced by some unexplained process of oxidation. Thioflavanone crystallises in coarse, colourless needles, m. p. 55 — 56° . 6-Methylthioflavanone condenses with benzaldehyde in the presence of hydrogen chloride to yield 3-benzylidene-6-methylthioflavanone, m. p. 108 — 109° , identical with the product described previously

by von Auwers and Arndt (A., 1909, i, 668). 3-Benzylidenethioflavanone forms pale yellow crystals, m. p. 132—133°. The phenylhydrazone of 6-methylthioflavanone crystallises in long, colourless needles, m. p. 206°.

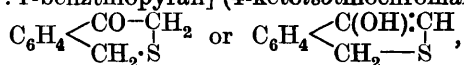
The conversion of the thioflavanones into thioflavanols has not yet been successfully accomplished. The conversion of the former into oximino-derivatives by amyl nitrite and hydrochloric acid or other agents does not take place to an appreciable extent under mild conditions, whereas under more drastic treatment oxidative elimination of benzoic acid occurs with formation of the thionaphthenquinone, $C_6H_4Me \begin{smallmatrix} CO \\ \diagup \quad \diagdown \\ S \end{smallmatrix} CO$, pale red needles, m. p. 145—146°. The change gives another example of the tendency of the thionaphthen ring to contraction. On the other hand, the thioflavanones condense smoothly with nitrosobenzene or *p*-nitrosodimethylaniline, whereby 6-methylthioflavanol-*p*-dimethylaminoanil, $C_6H_4Me \begin{smallmatrix} CO \cdot C \cdot N \cdot C_6H_4 \cdot NMe_2 \\ \diagup \quad \diagdown \\ S - CHPh \end{smallmatrix}$, lustrous, brownish-red leaflets, m. p. 166—167°, thioflavanol-*p*-dimethylaminoanil, m. p. 124—125°, and two stereoisomeric forms of 6-methylthioflavanolanil, m. p. 91—92°, and yellow needles, m. p. 172—173°, are isolated. Fission of the *p*-dimethylaminoanils could not be effected, whereas the simpler anils regenerated the thioflavanones.

β -*p*-Tolylthiolpropionic acid, $C_6H_4Me \cdot S \cdot CH_2 \cdot CH_2 \cdot CO_2H$, lustrous crystals, m. p. 70°, is obtained in almost quantitative yield by the action of *p*-tolylthiol dissolved in aqueous sodium hydroxide solution on β -chloropropionic acid (the preparation of the latter is described in detail). β -Phenylthiolpropionic acid crystallises in colourless leaflets, m. p. 58°. Ring closure of the substituted propionic acids is simply and almost quantitatively effected by concentrated sulphuric acid, whereby 6-methylthiochromanone, $C_6H_3Me \begin{smallmatrix} CO \cdot CH_2 \\ \diagup \quad \diagdown \\ S - CH_2 \end{smallmatrix}$, colourless, crystalline leaflets, m. p. 41°, and thiochromanone, colourless leaflets, m. p. 28°, are obtained. The benzylidene derivative of 6-methylthiochromanone crystallises in coarse, yellow needles, m. p. 119.5°; it yields an additive product with hydrogen chloride, needles, m. p. 164°. The *p*-dimethylaminoanils of 6-methylthiochromanol, brownish-red crystals, m. p. 193°, and of thiochromanol, m. p. 142°, are described. Fission of the respective anils by boiling sulphuric acid (50—60%) leads to the production of 6-methylthiochromonol, $C_6H_3Me \begin{smallmatrix} CO \cdot C \cdot OH \\ \diagup \quad \diagdown \\ S - CH \end{smallmatrix}$, coarse, pale yellow crystals, m. p. 167—168°, and thiochromanol, transparent, pale yellow needles, m. p. 172°.

Attention is directed to the advantages of vacuum sublimation as a means of purifying organic compounds and various forms of apparatus are described in detail. H. W.

4-Hydroxyhomothionaphthen (4-Ketoisothiochroman). RUDOLF LESSER and ALICE MEHLÄNDER (*Ber.*, 1923, 56, [B], 1642—1648).—The preparation of 4-hydroxyhomothionaphthen

[4-hydroxy-2:1-benzthiopyran] (4-ketoisothiochroman),



is described. The substance does not usually resemble β -hydroxythionaphthen in its behaviour, and reacts generally in the ketonic form.

S-Benzylthiolacetic acid, $\text{CH}_2\text{Ph}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, m. p. 62—63°, after previous softening, is obtained by the condensation of benzyl mercaptan with chloroacetic acid or as its ethyl ester, b. p. 156—157°/11 mm., by use of ethyl chloroacetate. The barium salt, $(\text{C}_9\text{H}_9\text{O}_2\text{S})_2\text{Ba}\cdot 2\text{H}_2\text{O}$, lustrous, colourless platelets and the copper salt (+2H₂O), pale bluish-green needles, are described. The acid is converted by thionyl chloride into *benzylthiolacetyl chloride*, a colourless, viscous liquid, b. p. 144—145°/11 mm. The latter substance is converted by aluminium chloride in the presence of nitrobenzene into 4-hydroxy-2:1-benzthiopyran, colourless leaflets, m. p. 60—61° after previous softening. The corresponding *oxime*, $\text{C}_9\text{H}_9\text{ONS}$, crystallises in pale yellow needles, m. p. 134—135°; it yields a sparingly soluble *sodium* salt. The *benzoyl* derivative of the oxime, $\text{C}_{16}\text{H}_{13}\text{O}_2\text{NS}$, forms colourless needles, m. p. 147—148°. 4-Hydroxy-2:1-benzthiopyran yields a *p*-nitrophenylhydrazone, red needles, m. p. 214°, and a *ketazine*, $\text{C}_9\text{H}_8\text{S}\cdot\text{N}\cdot\text{N}\cdot\text{S}_9\text{H}_8\text{S}$, slender, yellow needles, m. p. 229° after previous softening and darkening. *Benzeneazo*-4-hydroxy-2:1-benzthiopyran crystallises in pale red needles or rodlets, m. p. 139°. The action of *p*-nitroso-dimethylaniline on 4-hydroxy-2:1-benzthiopyran in alcoholic solution in the presence of potassium hydroxide leads to the formation of *p*-dimethylaminophenylbishydroxy-2:1-benzthiopyranylamine, $(\text{C}_6\text{H}_4 \begin{array}{l} \text{CH}_2-\text{S} \\ \text{C}(\text{OH}) \end{array}) (\text{C}_2\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2)$, m. p. 175—176°; the *sodium* and *calcium* salts are described. *Bromo*-4-hydroxy-2:1-benzthiopyran, $\text{C}_9\text{H}_7\text{OBrS}$, unstable, colourless, rhombohedral crystals, m. p. 89—90°, is obtained by the action of bromine on the naphthen dissolved in carbon disulphide.

o-Cyanobenzylthiolacetic acid, well-defined plates, m. p. 118—119°, is prepared by the action of ω -thiolacetic acid on *o*-cyanobenzyl chloride in the presence of potassium hydroxide in aqueous-alcoholic solution; the corresponding *amide*, $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$, crystallises in colourless needles, m. p. 112—113°. *o*-Carboxy-benzylthiolacetic acid, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, colourless needles, m. p. 146—147°, is prepared by the action of aqueous sodium hydroxide solution (20%) on the corresponding nitrile; it is converted by boiling acetic anhydride and potassium acetate into 4-acetoxy-2:1-benzthiopyran, pale yellow crystals, m. p. 94—95°, which is converted by sodium hydroxide solution into 4-hydroxy-2:1-benzthiopyran.

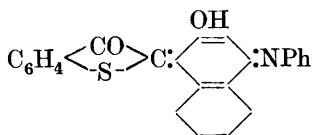
Benzylthiolacetic acid dissolved in glacial acetic acid is oxidised by hydrogen peroxide (30%) to *benzylsulphoneacetic acid*, $\text{CH}_2\text{Ph}\cdot\text{SO}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, lustrous platelets, m. p. 137—138° after slight previous softening; the *ammonium* salt, *silver* salt, colourless needles and the dihydrated *copper* salt are described. The

chloride forms colourless crystals, m. p. 95° (indefinite); the *amide*, colourless leaflets, m. p. 177—178°, and the *anilide*, pale yellow, slender needles, m. p. 171°, were prepared. The action of aluminium chloride on the chloride in the presence of nitrobenzene causes total decomposition of the sulphone. H. W.

Dinaphthathiophen. I. The Action of Sulphuric Acid on Dinaphthathiophen. K. DZIEWOŃSKI and M. PROKOPCZUK (*1²²⁹ Zjazd Chemików Polskich*, 1923, 56).—The sulphonation of dinaphthathiophen, $C_{24}H_{12}S$, is shown to be a reaction of extreme complexity. The nature of the products depends on the conditions of the process, and the products consist of sulphonic acids, oxidation, polymerisation, and condensation products of the various compounds formed, the following substances being isolated: $C_{24}H_{12}O_6S_3$, $C_{24}H_{12}O_9S_4$, $C_{48}H_{20}O_3S_3$, $C_{48}H_{18}O_5S_3$, $C_{72}H_{24}O_{12}S_6$, $C_{92}H_{40}O_{22}S_7$. These are intensely coloured substances, the colours ranging from orange to black, and appear to be sulphonic acids, quinone-sulphonic acids, and sulphonosulphonic acids. They have the property of dyeing animal fibres, in some cases without the use of a mordant. R. T.

Indigoid Compounds from 3-Hydroxy-1:4-naphthaquinone-4-anil and Benzocumaranonones or Oxythionaphthen. K. FRIES and H. EHLERS (*Ber.*, 1923, 56, [B], 1308—1319).—During the synthesis of the products obtained by the autoxidation of 2-acetyl- α -naphthol (Fries and Leue, A., 1922, i, 462) and 1-acetyl- β -naphthol (Fries and Ehlers, this vol., i, 825), the formation of minor amounts of blue and green compounds is invariably observed. The nature of these products has been elucidated and a series of analogous substances prepared.

The condensation of 3-hydroxythionaphthen with 2-hydroxy-1:4-naphthaquinone-4-anil in the presence of boiling glacial acetic acid leads to the formation of 3-hydroxy-4-keto-1-(oxythionaphthenylidene)dihydronaphthalene (Sachs and Ohlm, A., 1914, i, 552), red needles, m. p. 224°. With anilino- β -naphthaquinone in the presence of alcohol and acetic anhydride, hydroxythionaphthen gives 2-thionaphthen-2'-hydroxynaphthalene-1'-indolignone-4'-anil [4-anilino-2-hydroxy-1-(oxythionaphthenylidene)dihydronaphthalene] (annexed formula), dark red leaflets, m. p. 242°. 3-Hydroxythionaphthen and 2-anilino-1:4-naphthaquinone-4-anil yield 3-anilino-4-keto-1-(thionaphthenylidene)dihydronaphthalene, long, dark blue needles, m. p. 234°, which

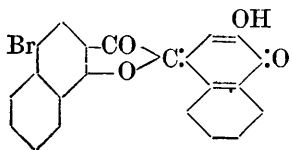


is converted by alcoholic potassium hydroxide solution into aniline and the corresponding 3-hydroxy-compound (described above); it can also be obtained by acting on the latter with aniline.

4-Anilino-1-keto-2-(thionaphthenylidene)dihydronaphthalene, greenish-blue or bronzy needles, m. p. about 224° (decomp.), is prepared from hydroxythionaphthen and 2-methoxy-1:4-naphthaquinone-4-anil in the presence of boiling glacial acetic acid; the corresponding *acetyl* derivative crystallises in pale red, lustrous

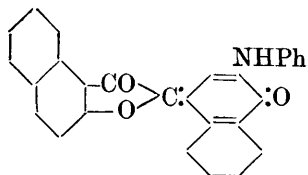
needles, m. p. 174°. The parent substance is converted by boiling aniline into 2-anilino-1:4-naphthaquinone-4-anil.

5-Bromo-6:7-benzocumaran-3-one and anilino- β -naphthaquinone yield 3-hydroxy-4-keto-1-(5'-bromo- $\alpha\beta$ -benzcumaronylidene)dihydronaphthalene (annexed formula), lustrous red needles, m. p. 310° (decomp.) after incipient darkening at 285°. The corresponding 3-anilino-derivative crystallises in blue needles, m. p. 270° (decomp.).

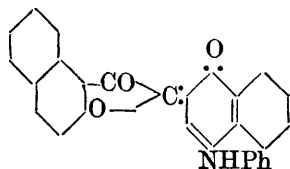


glacial acetic acid solution

4:5-Benzocumaranone and 3-anilino-naphthaquinoneanil react in boiling glacial acetic acid solution to yield 3-anilino-4-keto-1-($\alpha\beta$ -benzcumaronylidene)dihydronaphthalene (annexed formula), blue needles, m. p. 280° (decomp.), and the green substance identical with that derived from benzocumaranone and 3-methoxy-1:4-naphthaquinone-4-anil.

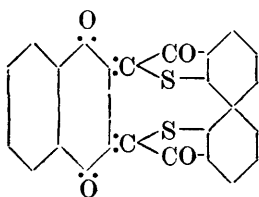


yield 4-anilino-1-keto-2-($\alpha\beta$ -benzcumaronylidene)dihydronaphthalene



4:5-Benzocumaran-2-one and 3-methoxy-1:4-naphthaquinone-4-anil (annexed formula), slender, dark green needles, m. p. about 280° (decomp.). 4-Anilino-1-keto-2-(5'-bromo- $\alpha\beta$ -benzcumaronylidene)dihydronaphthalene crystallises in slender, green needles, decomp. 232°.

2:3-Dichloro-1:4-naphthaquinone condenses very readily with hydroxythionaphthen in alcoholic solution in the presence of a little alkali hydroxide; the primary product of the action is very readily converted by atmospheric oxygen into the substance, $C_{26}H_{12}O_4S_2$ (annexed constitution), slender, almost black needles, m. p. above 360°. In a similar manner, 2:3-dichloro-1:4-naphthaquinone and benzocumaranone give the compound, $C_{34}H_{16}O_6$, slender, dark violet needles, m. p. above 360°. 2-Chloro-3-anilino-1:4-naphthaquinone gives the substance, $C_{24}H_{13}O_3NS$, dark red needles, m. p. above 360°, with hydroxythionaphthen and the compound, $C_{28}H_{15}O_4N$, slender, brilliant red needles, m. p. above 360°, with 4:5-benzocumaran-2-one.

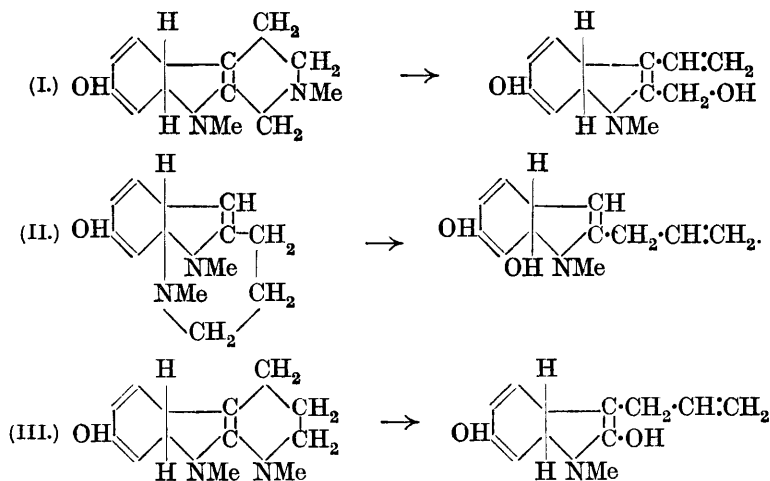


Method of Preparation of some Crystalline Alkaloidal Bismuthic Iodides. MAURICE FRANÇOIS and LOUIS GASTON BLANC (*Bull. Soc. chim.*, 1923, [iv], 33, 640—654).—Details are given of the methods of preparation and analysis of numerous crystalline alkaloidal bismuthic iodides (cf. A., 1922, i, 851) of which a general description has already been given. An accurate estimation of the alkaloid, the iodine, and the bismuth in these

H. W.

compounds was achieved by dissolving the substance in a solution of sodium tartrate containing an excess of sodium hydroxide. The iodine was thereby converted into alkali iodide and was estimated as silver iodide, the bismuth dissolved as sodium bismuthyl tartrate, and was estimated by precipitation from this solution as sulphide and weighing as oxide, whilst the alkaloid was extracted in the usual way with an immiscible organic solvent. In the preparation of the compounds the general method (*loc. cit.*) is followed with such modifications in detail as are necessitated by reason of their different solubilities. Full particulars are given of the preparation and composition of the bismuthic-iodides of caffeine, theobromine, nicotine, sparteine, arecoline, pilocarpine, atropine, quinine, morphine, codeine, and also of aniline $(\text{BiI}_3)_4(\text{NH}_2\text{Ph.HI})_3$, pyridine and quinoline, of analogous composition. In general, the bismuthiodides of the monoacidic alkaloids have the constitution $(\text{BiI}_3)_4(\text{Alk.HI})_3$, whilst the diacid alkaloids form compounds of the type $(\text{BiI}_3)_3\text{Alk.HI}$.
G. F. M.

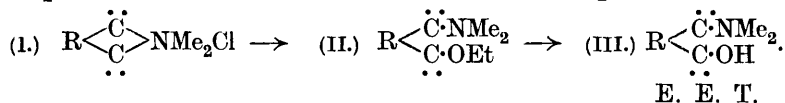
The Constitution of Eserine. MAX POLONOVSKI and MICHEL POLONOVSKI (*Compt. rend.*, 1923, **176**, 1896—1898).—The existence of an ethylenic linking in the pyrrole nucleus in etherseroline, and the ready formation, by the latter, of a methiodide, can only be explained by assuming the presence of a hydroindole structure (see below). The authors suggest provisionally three formulæ (I, II, and III) for eseroline, which agree better with its chemical behaviour than formulæ hitherto proposed for that substance. The degradation of eseroline to etherseroline, according to each formula, can be probably represented by the following schemes :



E. E. T.

Eseretholemethine and its Alcoholate. MAX POLONOVSKI and MICHEL POLONOVSKI (*Compt. rend.*, 1923, **177**, 127—129; cf. this vol., i, 700).—Eseretholemethine, hitherto regarded as an

anhydro-base, actually behaves as if a free hydroxyl group were present. Thus hydriodic acid readily converts it into eserethole methiodide, and all of its derivatives contain one molecule of water which cannot in every case be considered simply as solvent of crystallisation. This view is supported by experiments on the conversion of the methine into the hydrochloride. If eserethole methochloride (I) is treated with alcoholic sodium ethoxide (1 mol.), in absence of water, an *ethoxide* (II) is formed (an oil, $[\alpha]_D +114^\circ$), which is sparingly soluble in water, but, on heating in aqueous suspension, is converted into the methine (III), m. p. 89° :



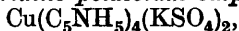
E. E. T.

Some Bases of the Tropacocaine Type derived from ψ -Pelletierine. GEORGES TANRET (*Compt. rend.*, 1923, 176, 1659—1662).—*n*-Methylgranatoline was obtained from ψ -pelletierine by reduction with sodium and absolute alcohol and was used as a starting point in the work described. *Benzoylmethylgranatoline*, $\text{NMe} \cdot \text{C}_7\text{H}_{12} \cdot \text{CH} \cdot \text{OBz}$, was obtained by the action of a benzene solution of benzoyl chloride at 100° (cf. Ciamician and Silber, A., 1894, i, 154) and is an almost colourless oil, b. p. $230^\circ/24 \text{ mm.}$, yielding a *sulphate*, m. p. 181° , a *nitrate*, m. p. 227° , and a *methiodide*, m. p. above 300° . It has marked physiological properties, and experimental detail with respect to these is given. *Cinnamoylmethylgranatoline*, prepared by means of cinnamoyl chloride, readily forms crystals, m. p. $62\text{--}63^\circ$. *p*-Nitrobenzoylmethylgranatoline, from *p*-nitrobenzoyl chloride, forms pale yellow crystals, m. p. $149\text{--}150^\circ$, and yields a *hydrochloride*, white needles. *p*-Aminobenzoylmethylgranatoline was obtained from the nitro-derivative by reduction with iron and acetic acid, and forms white crystals, m. p. $194\text{--}196^\circ$. The general conclusion is drawn from a study of the local anæsthetic properties of these substances that the double piperidine ring of homotropacocaine yields derivatives of more marked action than those obtained from the piperidine-pyrrolidine nucleus of tropacocaine.

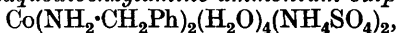
H. J. E.

Complex Ammonium Salts. G. SPACU and R. RIFAN (*Bul. Soc. Stiinte Cluj*, 1922, 1, 473—496; from *Chem. Zentr.*, 1923, i, 674—676; cf. this vol., i, 96, and ii, 72).—The following complex salts are described: *copper tetrapyridine ammonium sulphate*, $\text{Cu}(\text{C}_5\text{NH}_5)_4(\text{NH}_4\text{SO}_4)_2$, a blue, crystalline powder prepared from anhydrous pyridine and copper ammonium sulphate; it is unstable in air, losing pyridine on exposure. *Copper hexamine ammonium sulphate*, $\text{Cu}(\text{NH}_3)_6(\text{NH}_4\text{SO}_4)_2$, is a blue, crystalline powder formed by the action of dry ammonia on the copper tetrapyridine ammonium sulphate; it is unstable in air. *Copper triaquotribenzylamine ammonium sulphate*, $\text{Cu}(\text{NH}_2 \cdot \text{CH}_2\text{Ph})_3(\text{H}_2\text{O})_3(\text{NH}_4\text{SO}_4)_2$, a blue powder obtained by the action of benzylamine on copper ammonium sulphate, and *copper tribenzylamine ammonium sulphate*, $\text{Cu}(\text{NH}_2 \cdot \text{CH}_2\text{Ph})_3(\text{NH}_4\text{SO}_4)_2$.

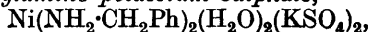
obtained similarly, using excess of benzylamine, are both stable in air. *Copper tetrapyridine potassium sulphate*,



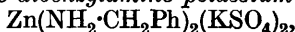
prepared by the action of anhydrous pyridine on copper potassium sulphate, is a blue, crystalline powder. *Copper tribenzylamine potassium sulphate*, $\text{Cu}(\text{NH}_2\cdot\text{CH}_2\text{Ph})_3(\text{KSO}_4)_2$, a blue, crystalline powder stable in air. *Cobalt tetra-aquodipyridine ammonium sulphate*, $\text{Co}(\text{C}_5\text{NH}_5)_2(\text{H}_2\text{O})_4(\text{NH}_4\text{SO}_4)$, a red, crystalline powder, unstable in air. *Cobalt diaquodibenzylamine ammonium sulphate*,



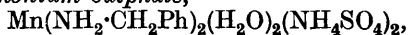
a red, crystalline powder. *Nickel aquopentapyridine potassium sulphate*, $\text{Ni}(\text{C}_5\text{NH}_5)_5\cdot\text{H}_2\text{O}\cdot(\text{KSO}_4)_2$, a green, crystalline powder. *Nickel diaquodibenzylamine potassium sulphate*,



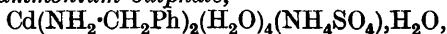
a brown, crystalline powder, stable in air. *Zinc tetra-aquodipyridine ammonium sulphate*, $\text{Zn}(\text{C}_5\text{NH}_5)_2(\text{H}_2\text{O})_4(\text{NH}_4\text{SO}_4)_2$, a white, crystalline powder, unstable in air. *Zinc tetra-aquodipyridine potassium sulphate*, $\text{Zn}(\text{C}_5\text{NH}_5)_2(\text{H}_2\text{O})_4(\text{KSO}_4)_2$, a colourless, crystalline powder unstable in air. *Zinc dibenzylamine potassium sulphate*,



a white, crystalline powder stable in air. *Manganese diaquodibenzylamine ammonium sulphate*,



a white, crystalline powder, stable in air. *Cadmium tetra-aquodibenzylamine ammonium sulphate*,



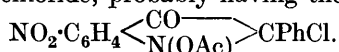
a white, amorphous powder, stable in air.

G. W. R.

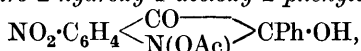
Preparation of the Homologues of Isatin. Preparation of 5-Bromo-7-methylisatin. (Mlle) MARCELLE RESSY and ANDRÉ P. ORTODOCU (*Bull. Soc. chim.*, 1923, [iv], 33, 637—640).—5-Bromo-7-methylisatin was synthesised from *o*-toluidine on the lines of Staudinger's synthesis of isatin from aniline. *o*-Toluidine was acetylated, and the acetyl-*o*-toluidide, m. p. 107°, gave on bromination acetyl-*p*-bromo-*o*-toluide, m. p. 156·7°. The corresponding benzoyl compound melted at 115°. On hydrolysis of either of these compounds, *p*-bromo-*o*-toluidine was obtained, m. p. 57°. Condensation of the hydrochloride of this base with hydroxylamine hydrochloride and chloral hydrate gave a yellow product, the dibromodi-*o*-tolylamidine of the oxime of glyoxalic acid, which on hydrolysis was converted into oximinoacetyl-bromo-*o*-toluidide, $\text{C}_6\text{H}_3\text{MeBr}\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}\cdot\text{NOH}$, m. p. 181°. On warming this substance with sulphuric acid, a violet-blue solution was obtained from which water precipitated the desired 5-bromo-7-methylisatin, crystallising in long, red prisms, m. p. 240°. Its phenylhydrazone melts at 252°, and its oxime at 249°. Its colour is much deeper than that of either isatin or methylisatin owing to the accumulation of auxochromes and the increased molecular weight. G. F. M.

Additive Compounds of the Isatogens. P. RUGGLI, A. BOLLIGER, and W. LEONHARDT (*Helv. Chim. Acta*, 1923, 6, 594—604; cf. A., 1921, i, 811).—When 6-nitro-2-phenylisatogen is boiled

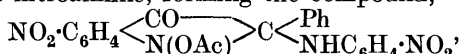
with acetyl chloride a yellow additive compound is formed with one mol. of acetyl chloride, probably having the formula



It crystallises in large, transparent prisms decomposing between 145° and 160° and is very sensitive to moisture, by which it is decomposed into its constituents. By ice, it is decomposed with formation of 6-nitro-2-hydroxy-1-acetoxy-2-phenylisatogen,

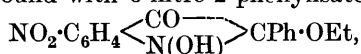


yellow needles, decomposing at 125° . This compound, which is more stable than the acetyl chloride compound, cannot be prepared directly from its constituents. The acetyl chloride compound reacts with *p*-nitroaniline, forming the compound,



m. p. 214° . In the same way, it reacts with methyl alcohol, forming a compound, m. p. 164.5° , and with ethyl alcohol, forming a compound, m. p. 144.5 — 145° ; in each case the chlorine atom attached to carbon is probably replaced by the alkyloxy group. Acetic anhydride also forms an additive compound when boiled with 6-nitro-2-phenylisatogen, but the reaction is incomplete. The compound forms yellow needles, m. p. 195 — 198° , when heated quickly; it probably has the formula $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \left\langle \begin{array}{c} \text{CO} \\ \text{N(OAc)} \end{array} \right\rangle \text{CPh} \cdot \text{OAc}$.

Cold ethyl alcohol saturated with hydrochloric acid also forms an additive compound with 6-nitro-2-phenylisatogen,



yellow needles, decomposing at 80 — 90° into its constituents. This is isomeric with the compound formed with ethyl alcohol at higher temperatures (A., 1919, i, 221). The oxime of isonitrophenylisatogen previously described is now found to be identical with the *N*-oxime of the quinonoid form. E. H. R.

3-Hydroxyquinoline Derivatives from the *N*-Benzylidene Compounds of *o*-Aminophenylacetic Acid. A. KLIEGL and ADOLF SCHMALENBACH (*Ber.*, 1923, 56, [B], 1517—1520).—In a recent communication (A., 1922, i, 545), Neber has described the preparation of 3-hydroxy-2-*o*-nitrophenylquinoline by the action of heat on *o*-nitrobenzylidene-*o*'-aminophenylacetic acid. The authors' failure to effect ring closure with a number of apparently similarly constituted substances has caused them to doubt the identity of the compound isolated by Neber. They find that the primary products of the action of heat on *o*-nitrobenzylidene-*o*'-aminophenylacetic acid are *o*-nitrobenzaldehyde and oxindole, and that these substances react further with the ultimate formation of 3-*o*-nitrobenzylideneoxindole, $\text{NH} \left\langle \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{CO} \end{array} \right\rangle \text{C} \cdot \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$.

Pyruvilidene-o-hydrazinobenzoic acid, $\text{COMe} \cdot \text{CH} \cdot \text{N} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$, long, yellow needles, decomp. about 215° after softening at 200° ,

is prepared by the action of diazotised anthranilic acid on acetoacetic acid. It could not be caused to undergo ring closure by the action of heat. It is converted by phenylhydrazine into the *phenylosazone*, $C_{16}H_{16}O_2N_4$, yellow crystals, m. p. about 215° (decomp.) after softening at 200° , which is transformed by boiling glacial acetic acid into aniline and 1-o-carboxyphenyl-3-methyl-1 : 2 : 5-triazole, $\begin{matrix} CH=N \\ CMe:N \end{matrix} > N \cdot C_6H_4 \cdot CO_2H$, a crystalline powder, m. p. about 275° (decomp.) after darkening at about 240° . H. W.

5 : 6 : 7 : 8-Tetrahydroquinolines and their Derivatives. II.

JULIUS VON BRAUN, WALTER GMEIN, and ADAM SCHULTHEISS (*Ber.*, 1923, **56**, [B], 1338—1347).—It has been shown recently (this vol., i, 136) that whereas quinoline itself is readily hydrogenated to 1 : 2 : 3 : 4-tetrahydroquinoline, certain of its derivatives become similarly hydrogenated to a greater or less extent in the benzenoid portion of the molecule. The influence of substituents on the course of the hydrogenation has therefore been systematically investigated with the methylquinolines. The presence of a methyl group in positions 6, 7, or 8 causes the exclusive formation of 1 : 2 : 3 : 4-tetrahydro-compounds, and this is also probably true in the case of 5-methylquinoline, which, however, has not been examined. 3- and 4-Methylquinolines give a mixture of 33% of the 5 : 6 : 7 : 8- and 66% of the 1 : 2 : 3 : 4-tetrahydro-derivatives, whereas 2-methylquinoline yields 4% of the 5 : 6 : 7 : 8 and 96% of the 1 : 2 : 3 : 4-tetrahydro-compounds. The introduction of more methyl groups into the pyridine nucleus of the molecule causes the formation of a greater proportion of the 5 : 6 : 7 : 8-tetrahydro-substances.

The methylquinolines are hydrogenated under pressure in the presence of nickel, tetra- or deca-hydronaphthalene being used as solvents. The temperature is raised gradually until hydrogen commences to be absorbed, after which it is usually maintained approximately constant until reduction is complete. The secondary and tertiary bases in the products are separated from one another by exhaustive treatment with benzoyl chloride.

8-Methylquinoline yields exclusively 8-methyl-1 : 2 : 3 : 4-tetrahydroquinoline, b. p. $126\text{--}129^\circ/12$ mm. (benzoyl derivative, m. p. 108° ; nitroso-compound, m. p. 51°). 7-Methylquinoline gives as sole product 7-methyl-1 : 2 : 3 : 4-tetrahydroquinoline, b. p. $130\text{--}132^\circ/12$ mm. (benzoyl derivative, m. p. $70\text{--}72^\circ$; *picrate*, m. p. $153\text{--}154^\circ$; *hydrochloride*, m. p. 175° ; the acetyl derivative is a liquid).

4-Methylquinoline yields a mixture of 4-methyl-1 : 2 : 3 : 4-tetrahydroquinoline, b. p. $130^\circ/12$ mm. (benzoyl derivative, m. p. 129°) and 4-methyl-5 : 6 : 7 : 8-tetrahydroquinoline, a colourless liquid, b. p. $122^\circ/11$ mm. (*hydrochloride*, m. p. $203\text{--}204^\circ$; *picrate*, m. p. 170° ; *methiodide*, m. p. 183° after darkening at 179°). The latter substance is smoothly reduced by sodium and alcohol to 4-methyldecahydroquinoline, a colourless liquid, b. p. $105^\circ/11$ mm. (*hydrochloride*, m. p. 205° ; *picrate*, m. p. 159° ; *phenylthiocarbamide* derivative, m. p. 105° ; *methiodide*, $C_{12}H_{24}NI$, m. p. 235°).

3-Methylquinoline is obtained conveniently from *o*-aminobenzaldehyde and propaldehyde at 120—130°. It is hydrogenated to a mixture of 3-methyl-1:2:3:4-tetrahydroquinoline, a colourless liquid, b. p. 116—118°/10 mm. (benzoyl derivative, m. p. 84°; hydrochloride, m. p. 207°; picrate, m. p. 155°; the nitroso-compound is a liquid) and 3-methyl-5:6:7:8-tetrahydroquinoline, b. p. 126—127°/17 mm. (the hydrochloride does not solidify; chloroplatinate, decomp. 219°; picrate, m. p. 171°; methiodide, m. p. 162°). Sodium and alcohol convert the latter compound into 3-methyldecahydroquinoline, b. p. 125—127°/15 mm., m. p. 70—71° (picrate, m. p. 75°; hydrochloride, m. p. 218° after softening at 210°; the nitroso- and benzoyl derivatives are liquid).

2-Methylquinoline yields 2-methyl-1:2:3:4-tetrahydroquinoline, b. p. 115—116°/12 mm., and 2-methyl-5:6:7:8-tetrahydroquinoline, a colourless liquid, b. p. 101—104°/12 mm., d_4^{16} 1.0000 (picrate, lemon-yellow needles, m. p. 154°; hydrochloride, m. p. 164°; very hygroscopic methiodide, m. p. 118°). Temperature and concentration of the solution appear to have little influence on the course of the hydrogenation.

2:3-Dimethylquinoline, m. p. 68°, is obtained by Pfitzinger's method by the decarboxylation of 2:3-dimethylcinchonic acid derived from isatin and methyl ethyl ketone. The crude acid contains small amounts of 2-ethylcinchonic acid, m. p. 174°, since, when converted into its silver salt and subsequently treated with methyl iodide, it gives a readily separable mixture of methyl 2:3-dimethylcinchonate, m. p. 120—121°, and methyl 2-ethylcinchonate, b. p. 176—178°/13 mm., m. p. 38°. The dimethyl derivative is hydrogenated to a mixture of 2:3-dimethyl-1:2:3:4-tetrahydroquinoline, a mobile liquid, b. p. 127—128°/13 mm., d_4^{15} 1.0048 (benzoyl derivative, slender, colourless crystals, m. p. 94—95°; hydrochloride, m. p. 154°; picrate, m. p. 161°; nitroso derivative, yellow platelets, m. p. 56°) and 2:3-dimethyl-5:6:7:8-tetrahydroquinoline, m. p. 38°, b. p. 125—126°/14 mm. (very hygroscopic hydrochloride, m. p. 192°; picrate, m. p. 169°; methiodide, m. p. 117°). The latter base is transformed by sodium and alcohol into 2:3-dimethyldecahydroquinoline, a mobile liquid, b. p. 95—97°/11 mm., d_4^{15} 0.9152 (the picrate and nitroso-compounds are liquid; the hydrochloride does not melt below 280°; methiodide, m. p. 199°).

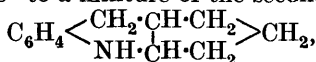
2:4-Dimethylquinoline gives 2:4-dimethyl-1:2:3:4-tetrahydroquinoline, b. p. 125—127°/12 mm., and, mainly, 2:4-dimethyl-5:6:7:8-tetrahydroquinoline, b. p. 122—123°/12 mm. (picrate, m. p. 144°; hydrochloride, m. p. 195°; methiodide, m. p. 163° after darkening at 157°). 2:4-Dimethyldecahydroquinoline has b. p. 96—97°/12 mm. (picrate, m. p. 141—145°; hydrochloride, slender needles; methiodide, m. p. 210° after softening at 200°; the nitroso-derivative is a yellow liquid). H. W.

5:6:7:8-Tetrahydroquinolines and their Derivatives.

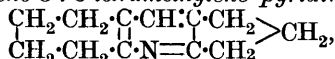
III. Tricyclic Compounds. JULIUS VON BRAUN, ADOLF PETZOLD, and ADAM SCHULTHEISS (*Ber.*, 1923, 56, [B], 1347—1350).—The presence of methyl groups in the pyridine portion of

the quinoline molecule has been shown (preceding abstract) to cause catalytic hydrogenation to occur to a greater extent in the benzenoid portion of the molecule. The same effect is observed when the substituents are themselves united in a ring, as is shown by experiments with tetrahydroacridine and 2 : 3-trimethylenequinoline.

Tetrahydroacridine, m. p. 54°, which is readily prepared from isatin and cyclohexanone, is hydrogenated at 150° to a mixture of *as*-octahydroacridine, $C_6H_4 \begin{smallmatrix} \text{CH}_2 \\ \text{NH} \end{smallmatrix} > C_6H_{10}$, m. p. 84°, b. p. 183°/12 mm. (*benzoyl* derivative, m. p. 104°) and *s*-octahydroacridine, $C_6H_8 \begin{smallmatrix} \text{CH} \\ \text{N} \end{smallmatrix} > C_6H_8$, colourless crystals, m. p. 69°, b. p. 175°/17 mm. (the *hydrochloride* is liquid; *chloroplatinate*, red needles, m. p. 199—200°; *picrate*, m. p. 195°; *methiodide*, m. p. 159°). The symmetrical octahydro-base is reduced by sodium and alcohol to *perhydroacridine*, $C_6H_{10} \begin{smallmatrix} \text{CH}_2 \\ \text{NH} \end{smallmatrix} > C_6H_{10}$, b. p. 140°/14 mm., m. p. 80° (the *hydrochloride* does not melt below 300°; *picrate*, m. p. 167°; *nitroso*-derivative, m. p. 217°; *methiodide*, $C_{15}H_{28}NI$, m. p. 266°).
2 : 3-Trimethylenequinoline, from isatin and cyclopentanone, is hydrogenated at 170° to a mixture of the secondary base,



b. p. 169—171°/18 mm. (*benzoyl* derivative, m. p. 157°; *hydrochloride*, m. p. 143°; *picrate*, m. p. 154°; *nitroso*-derivative, m. p. 154°) and 2 : 3-trimethylene-5 : 6-tetramethylene pyridine,



b. p. 160—161°/17 mm. (*hydrochloride*, m. p. 91°; *picrate*, yellow needles, m. p. 160°). Reduction with sodium and alcohol converts the base into the *perhydrogenated amine*, $C_{12}H_{21}N$, a colourless, mobile liquid, b. p. 140—142°/17 mm. (*picrate*, small, yellow needles, m. p. 171°; *hydrochloride*, decomp. 255—258°; the *nitroso*-derivative could not be caused to crystallise). H. W.

5-Methyl-1 : 2 : 3 : 4-tetrahydroquinoline and its Fission.

JULIUS VON BRAUN and THEO KÜHLEIN (*Ber.*, 1923, 56, [B], 1351—1352).—The replacement of the chlorine atom in 8-chloro-5-methylquinoline by hydrogen cannot be effected smoothly by hydriodic acid or tin and hydrochloric acid. The base is, however, quantitatively converted by sodium and alcohol into 5-methyl-1 : 2 : 3 : 4-tetrahydroquinoline, b. p. 130—131°/14 mm. (*hydrochloride*, m. p. 228°; *picrate*, m. p. 156°; *nitroso*-derivative, m. p. 66—67°; *benzoyl* compound, m. p. 121°). The *benzoyl* derivative is converted by phosphorus pentachloride into 3-methyl-2- γ -chloropropylbenzanilide, m. p. 102—103°. H. W.

Pictet's Synthesis of Tetrahydroisoquinoline. HEISABURO KONDO and ELI OCHIAI (*J. Pharm. Soc. Japan*, 1923, No. 495, 313—319).—Pictet and Spengler (*A.*, 1911, i, 750) synthesised tetrahydroisoquinoline by warming a mixture of phenylethylamine and aldehyde in the presence of concentrated hydrochloric

acid. The authors find that as pointed out by Decker and Becker, (A., 1913, i, 291), the reaction is not simple. Phenylethylamine hydrochloride (100 g.) is dissolved in 600 g. of concentrated hydrochloric acid, heated on a water-bath, 100 g. of dimethoxymethane are gradually added, and the mixture is heated during ten hours. After heating under reduced pressure to remove hydrochloric acid the residue is dissolved in water, rendered alkaline with sodium hydroxide, and extracted first with ether and then with chloroform. The former extract on fractionation yielded (1) 49 g. distilling between 70° and $120^{\circ}/6$ mm. (mainly $84^{\circ}/6$ mm.), and (2) 18 g. distilling between 200° and $250^{\circ}/6$ mm. (mainly $210^{\circ}/6$ mm.). When treated with sodium nitrite and reduced with tin and hydrochloric acid, (1) yielded β -phenylethyl chloride and a small quantity of tetrahydroisoquinoline. The fraction (1) is therefore composed mainly of unchanged phenylethylamine with a small quantity of tetrahydroisoquinoline. When acidified with hydrochloric acid and concentrated, (2) yielded white crystals of *di*-(β -phenylethylamino)-methane hydrochloride, m. p. above 300° . It forms double salts with chloroplatinic acid, dichromate, mercuric chloride, etc., all melting above 280° . The *chloroaurate*, yellow needles, has m. p. $118-120^{\circ}$. The free base, $\text{CH}_2(\text{NH}\cdot\text{C}_2\text{H}_4\text{Ph})_2$, forms white needles, m. p. $150-151^{\circ}$, gives Liebermann's secondary amine reaction and easily absorbs carbon dioxide. The *diacetyl* derivative, silky needles, has m. p. 190° . From the chloroform solution a base was also obtained as a yellowish-brown, amorphous powder, which is identical with that obtained by heating a mixture of phenylethylamine hydrochloride, methylal, and hydrochloric acid in a sealed tube at 130° , but its nature is not yet clear. K. K.

The Relative Stability of Cyclic Bases. IX. JULIUS VON BRAUN (*Ber.*, 1923, 56, [B], 1570—1573).—It has been shown previously (A., 1916, i, 421) that the introduction of methyl groups into the 2-, 3-, or 4-positions of tetrahydroquinolinium chloride has little influence on the stability of this compound towards sodium amalgam. Similar observations are now recorded with the methylated 3-ethyl- and 3-amyl-tetrahydroquinolinium chlorides, from which it follows that the stability of the ring is not greatly influenced by the magnitude of the alkyl residue. When chlorides which contain two different alkyl groups attached to the nitrogen atom are acted on by sodium amalgam, it is found that it is the smaller of the two groups which is removed; this is established experimentally in the case of *N*-ethylhexahydrocarbazole methochloride.

The quaternary methiodide of 3-ethyltetrahydroquinoline is converted into the corresponding chloride, which is reduced by sodium amalgam; the product is treated with formaldehyde and hydrochloric acid, whereby ultimately α -phenyl- β -dimethylamino-methyl-*n*-butane, $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{CH}_2\cdot\text{NMe}_2)\cdot\text{CH}_2\text{Me}$, b. p. $112-114^{\circ}/12$ mm., is obtained in 70% yield. It forms a non-crystalline *hydrochloride*, a *picrate*, thick, rhombic rods, m. p. 132° , and a *methiodide*, m. p. $155-160^{\circ}$, according to the rate of heating. In a

similar manner, the quaternary methiodide of 3-amyltetrahydroquinoline is converted into α -phenyl- β -dimethylaminomethylheptane, $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{CH}_2\cdot\text{NMe}_2)\cdot\text{C}_5\text{H}_{11}$, b. p. $147\text{--}149^\circ/11$ mm. (the *picrate*, m. p. 97° , the non-crystalline *hydrochloride*, and the *methiodide*, m. p. 95° , are described).

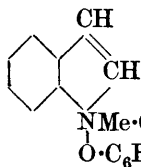
Ethylhexahydrocarbazole methiodide is converted into the corresponding chloride and reduced with sodium amalgam; the mixture of bases is treated with formaldehyde and hydrochloric acid, whereby the *compound* (annexed formula), m. p. $89\text{--}90^\circ$ (*dimethiodide*, m. p. $83\text{--}84^\circ$), is obtained in 60% yield. (The identity of the compounds is established by their production from an authentic specimen of ethylhexahydrocarbazole.) The volatile bases which remain after treatment of the crude mixture with formaldehyde are separated by methyl iodide into *o*-cyclohexylmethyl ethylaniline, $\text{C}_6\text{H}_{11}\cdot\text{C}_6\text{H}_4\cdot\text{NMeEt}$, b. p. $147\text{--}149^\circ/12$ mm. (*picrate*, m. p. 164°) and *o*-phenylcyclohexylmethyl ethylamine methiodide, $\text{C}_{16}\text{H}_{26}\text{NI}$, m. p. 186° . H. W.

The Action of Magnesium Propyl Bromide on Quinoline Methiodide. Stereochemistry of Tervalent Nitrogen. JAKOB MEISENHEIMER and MAX SCHÜTZE (*Ber.*, 1923, 56, [B], 1353—1362).—In a recent communication, Freund and Kessler (*A.*, 1919, i, 283) have described several pairs of stereoisomeric 1-methyl-2-alkyltetrahydroquinolines the occurrence of which is attributed to the presence of an asymmetric nitrogen and carbon atom. The authors' experience has led them to the conclusion that the saturated, trivalent nitrogen atom can only function as an asymmetric centre in very unusual cases. Since, moreover, the asymmetry does not disappear according to Freund and Kessler when methyl iodide is added to the isomerides, the authors have repeated the work, which is found to be erroneous. The results obtained are due to the attempt of Freund and Kessler to purify 1-methyl-2-propyl-1:2-dihydroquinoline by distillation under atmospheric pressure; in the circumstances, it becomes decomposed to a very considerable extent into methane and 2-propylquinoline, whilst a small quantity is reduced to the tetrahydro-derivative; the residue remains unchanged or is decomposed in other unexplained directions. Freund and Kessler's 1-methyl-2-propyl-1:2-dihydroquinoline is therefore a mixture of much 2-propylquinoline, little 1-methyl-2-propyl-1:2:3:4-tetrahydroquinoline and other compounds with the unaltered dihydroquinoline.

1-Methyl-2-propyl-1:2-dihydroquinoline, b. p. $152^\circ/13$ mm., is prepared in 60—70% yield according to the method of von Braun and Aust (*A.*, 1915, i, 586); the corresponding *picrate* has m. p. 72° but is so unstable in solution that it cannot be recrystallised. The base is decomposed when boiled under atmospheric pressure, yielding mainly 2-propylquinoline, a pale, greenish-yellow liquid, b. p. $130\text{--}131^\circ/10$ mm., together with small amounts of 1-methyl-2-propyl-1:2:3:4-tetrahydroquinoline, which is identified as the *picrate*, m. p. 123° . 2-Propylquinoline methiodide is a pale yellow,

crystalline powder, m. p. 181°, which is completely decomposed by repeated crystallisation from alcohol. 2-Propyltetrahydroquinoline, b. p. 140—140·5°/10 mm. [von Braun and Aust (*loc. cit.*) give b. p. 152°/20 mm.], is prepared by the reduction of 2-propylquinoline with tin and hydrochloric acid. The hydrochloride, colourless needles, m. p. 221—222° (220°) and the benzoyl derivative, m. p. 102° (97°) are described. (The figures placed within brackets are the data of von Braun and Aust.) The picrate (m. p. 143°) separates from water (+H₂O) as a brown oil which gradually solidifies, m. p. 56—60°, from toluene (+0·5 C₇H₈) in needles, m. p. 115°, and from alcohol or ether in reddish-brown or orange-coloured plates, m. p. 125°. Reduction of 1-methyl-2-propyl-1:2-dihydroquinoline is not smoothly effected by tin and hydrochloric acid (cf. von Braun and Aust, *loc. cit.*), but may be readily performed with sodium and alcohol, thus yielding 1-methyl-2-propyl-1:2:3:4-tetrahydroquinoline, a pale yellow liquid, b. p. 144·5°/10 mm. (151—157°/20 mm.). 1-Methyl-2-propyl-1:2:3:4-tetrahydroquinoline methiodide forms coarse, colourless crystals, which have m. p. 180—200° (decomp.) according to the mode of heating.

1-Methyl-2-propyl-1:2-dihydroquinoline picrate is decomposed in boiling alcoholic solution; one-third of it is transformed into 1-methyl-2-propylquinolinium picrate, yellow needles, the constitution of which is established by its formation from the corresponding methiodide and picric acid, a second third is converted into the indole picrate (? annexed formula), reddish-brown leaflets, m. p. 122°, whereas the remaining third becomes resinified.

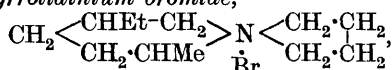


H. W.

Cyclic Di-imines and their Decomposition. II. JULIUS VON BRAUN, GEORG LEMKE, and ANNEMARIE NELKEN (*Ber.*, 1923, 56, [B], 1564—1569).—A comparatively easy method for the preparation of pyrrolidine is based on the interaction of 2-methyl-5-ethylpiperidine (copellidine) with $\alpha\delta$ -dibromobutane, transformation of the product into the corresponding cyclic di-imine, and fission of the latter.

Technical copellidine is a mixture of two racemic, *cis-trans*-isomerides which have been designated copellidine and *isocopellidine*, respectively; for these the authors prefer the designation *A*- and *B*-copellidine, and reserve the term "copellidine" for the mixture of bases. The isomerides are readily separated from one another by utilising the observation that *A*-copellidine hydrochloride, in contrast to the *B*-isomeride, is difficultly soluble in acetone. For the present purpose, the mixture of bases may be employed, but the experimental difficulties are greater than when either of the homogeneous isomerides is used.

A-Copellidylpyrrolidinium bromide,



a very hygroscopic substance, m. p. 195°, is prepared by the action

of *A*-copellidine on $\alpha\delta$ -dibromobutane in boiling alcoholic solution; the corresponding *chloride*, an extremely hygroscopic, crystalline mass, and the *chloroplatinate*, m. p. 242° (decomp.) are described. *B-Copellidylpyrrolidinium bromide* has m. p. $176-177^\circ$; the corresponding *chloride* is extremely hygroscopic; the *chloroplatinate* has decomp. 234° . The bromides are converted by treatment with aqueous ammonia (25%) at 180° during twenty-four hours into a mixture of pyrrolidine (the yield is about 66% of that theoretically possible) and the corresponding di-imine. *A-Methylethylbis-pentamethyleneimine*, $\text{CH}_2 \begin{array}{c} \text{CHEt} \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CHMe} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CH}_2 \end{array}$, is an almost colourless, fairly mobile liquid, b. p. $132-136^\circ/12$ mm. The *hydrochloride* and the *picrate* are non-crystalline. The *picrolonate* has m. p. $174-175^\circ$. The *benzenesulphonyl* derivative could not be caused to crystallise. Treatment of the base with alkali and methyl iodide results in the production of a quaternary iodide which rapidly alters on exposure to air and is therefore converted into the chloride, from which the *chloroplatinate*, $\text{C}_{16}\text{H}_{36}\text{N}_2\text{Cl}_6\text{Pt}$, a yellow, crystalline powder, m. p. 254° , and the *chloroaurate*, m. p. $223-225^\circ$, are prepared. *B-Methylethylbis-pentamethyleneimine* resembles exactly the *A*-compound in appearance, odour, and boiling point. The *hydrochloride*, *picrate*, and *benzenesulphonyl* derivative are non-crystalline; the *picrolonate* has m. p. 144° . The *chloroplatinate* obtained from the hygroscopic, quaternary iodide has m. p. 252° , whereas the *chloroaurate* has m. p. $216-218^\circ$.

H. W.

Displacement of Acyl Groups from Nitrogen to Oxygen in the Cases of Amino-alcohols. MAX BERGMANN and ERWIN BRAND (*Ber.*, 1923, 56, [B], 1280-1283).—The transformation of *ON*-dibenzoylaminopropylene glycol,



into γ -aminopropylene $\alpha\beta$ -dibenzoate hydrochloride,



(cf. Bergmann, Brand, and Dreyer, *A.*, 1921, i, 444), has been examined in greater detail.

The conversion is most conveniently effected by means of thionyl chloride at the atmospheric temperature whereby an intermediate product, probably 2-phenyl-5-benzoxymethylloxazoline hydrochloride, $\text{OBz} \cdot \text{CH}_2 \cdot \text{CH} \begin{array}{c} \text{CH}_2 \cdot \text{N} \\ | \\ \text{O} - \text{CPh} \end{array} \cdot \text{HCl}$, m. p. $130-131^\circ$,

can be isolated. It is transformed by water at 18° into γ -aminopropylene $\alpha\beta$ -dibenzoate hydrochloride or the free base. The following salts of the oxazoline derivative are described: the *hydrogen sulphate*, $\text{C}_{17}\text{H}_{17}\text{O}_4\text{N} \cdot \text{H}_2\text{SO}_4$, m. p. $77-78^\circ$; the *normal sulphate*, m. p. $152-153^\circ$ (decomp.), and the *picrate*, m. p. about 205° .

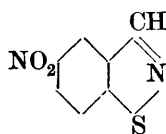
ON-Dibenzoylaminopropylene glycol is transformed by phosphoryl chloride in the presence of anhydrous chloroform into a compound, $\text{C}_{17}\text{H}_{18}\text{O}_6\text{N} \cdot \text{PCl}_2$, needles, m. p. $102-103^\circ$. It is converted by pyridine into the oxazoline derivative.

H. W.

g g*

Derivatives of Benz-4 : 5-isothiazole. K. FRIES and G. BROTHUHN (*Ber.*, 1923, 56, [B], 1630—1633).—Derivatives of benz-4 : 5-isothiazole are obtained by the action of ammonia on arylsulphur halides which contain an aldehydic or ketonic group in the neighbourhood of the sulphur atom.

4 : 4'-Dinitro-2 : 2'-dialdehydodiphenyl disulphide, coarse, pale yellow needles, m. p. 256°, is prepared by the action of sodium disulphide on a solution of 2-chloro-5-nitrobenzaldehyde in alcohol. It is converted by prolonged treatment with a solution of bromine in carbon tetrachloride at 100° into 4-nitro-2-aldehydophenylsulphur bromide, $\text{CHO} \cdot \text{C}_6\text{H}_3(\text{NO}_2) \cdot \text{SBr}$, m. p. 171°, which is transformed by dimethylaniline dissolved in benzene into 4-nitro-2-aldehydo-4'-dimethylaminodiphenyl sulphide, $\text{CHO} \cdot \text{C}_6\text{H}_3(\text{NO}_2) \cdot \text{S} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2$, yellowish-red, prismatic crystals, m. p. 164° [hydrochloride, colourless, cubic crystals, m. p. 197° (decomp.)].



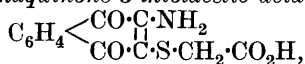
When a solution of the sulphur bromide in benzene is heated with concentrated aqueous ammonia, 5-nitrobenz-4' : 5'-isothiazole (annexed formula), colourless needles, m. p. 149°, is obtained. 4-Nitro-2-aldehydophenylsulphur bromide is converted by aniline in the presence of benzene into 5-nitro-2-phenylbenz-4' : 5'-

isothiazolium bromide, $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \langle \begin{smallmatrix} \text{CH} \\ \text{S} \end{smallmatrix} \rangle \text{NPh} \cdot \text{Br}$, decomp. about 240°, which is transformed by concentrated hydrochloric acid into the corresponding chloride, pale yellow, prismatic crystals, m. p. about 228° (decomp.). H. W.

2 : 3-Dichloro-1 : 4-naphthaquinone. K. FRIES and P. OCHWAT (*Ber.*, 1923, 56, [B], 1291—1304; cf. Fries and Kerkow, A., 1922, i, 577).—The replaceability of the halogen atoms of 2 : 3-dichloro-1 : 4-naphthaquinone by a variety of other groups has been examined; in certain cases one chlorine atom appears to be far more easily displaced than the other, whereas in other cases both atoms are replaced.

3-Chloro-2-amino-1 : 4-naphthaquinone is readily obtained in the pure condition by the gradual addition of concentrated ammonia to a suspension of 2 : 3-dichloro-1 : 4-naphthaquinone in boiling alcohol; the corresponding acetyl derivative forms brownish-red leaflets, m. p. 219°. The amine is converted by boiling acetic anhydride in the presence of a little concentrated sulphuric acid into 2-methyl-ββ-naphthoxazole-4 : 9-quinone, $\text{C}_6\text{H}_4 \langle \begin{smallmatrix} \text{CO} \cdot \text{C} \cdot \text{N} \\ \text{CO} \cdot \text{C} \cdot \text{O} \end{smallmatrix} \rangle \text{CMe}$,

brownish-yellow crystals, m. p. 317° (diacetate, colourless needles, m. p. 222°). It is transformed by the successive action of sodium sulphide and methyl sulphate into 2-amino-3-methylthiol-1 : 4-naphthaquinone, brownish-red needles, m. p. 132°, which loses the methylthiol group under the influence of hydrogen peroxide. 2-Amino-1 : 4-naphthaquinone-3-thiolacetic acid,

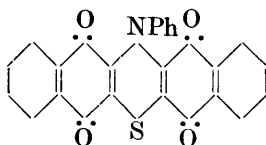


brown leaflets, m. p. 220° (decomp.), is prepared by the addition

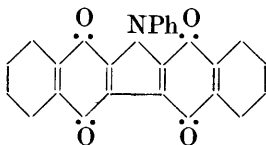
of sodium chloroacetate solution to the sodium salt of amino-thiolnaphthaquinone. When a solution of the acid in glacial acetic acid is boiled it is converted into 3 : 5 : 10-*triketo*-2 : 3-*dihydro-naphthathiazine*, $C_6H_4 \begin{smallmatrix} \text{CO} \cdot \text{C} \cdot \text{NH} \cdot \text{CO} \\ | \quad | \\ \text{CO} \cdot \text{C} \cdot \text{S} - \text{CH}_2 \end{smallmatrix}$, dark brown needles,

m. p. 260° (decomp.), which is converted by zinc dust and boiling acetic anhydride into 3-*keto*-5 : 10-*diacetoxy*-2 : 3-*dihydro*-1 : 4-*naphthathiazine*, $C_6H_4 \begin{smallmatrix} \text{C}(\text{OAc}) \cdot \text{C} \cdot \text{NH} \cdot \text{CO} \\ | \quad | \\ \text{C}(\text{OAc}) \cdot \text{C} \cdot \text{S} - \text{CH}_2 \end{smallmatrix}$, colourless leaflets, m. p. 270° (decomp.).

The addition of 2 : 3-dichloro-1 : 4-naphthaquinone to the product



glacial acetic acid



of the action of sodium sulphide on 3-chloro-2-anilino-1 : 4-naphthaquinone leads to the production of 6-*phenyldinaphthathiazine*-5 : 7 : 12 : 14-*diquinone* (annexed formula), small, brown crystals, which is converted by boiling nitrobenzene or, preferably, by nitric acid (*d* 1.4) in the presence of

into 12-*phenyldibenzcarbazole*-5 : 6 : 11 : 13-*diquinone* (annexed formula), slender, yellow needles, m. p. above 400°. The latter compound is converted by zinc dust and boiling acetic anhydride into 12-*phenyl*-5 : 6 : 11 : 13-*tetra-acetoxydibenzcarbazole*, yellow crystals, m. p. 275° (decomp.). The carbazolediquinone is reduced by an excess of stannous

chloride in the presence of glacial acetic acid to 12-*phenyldibenzcarbazole*-5 : 6-*quinone*, coarse, dark brown, lustrous crystals, m. p. above 360°.

3-*Chloro*-2-*p*-chloroanilino-1 : 4-naphthaquinone, red, prismatic crystals, m. p. 266°, is obtained from 2 : 3-dichloro-1 : 4-naphthaquinone and *p*-chloroaniline and is converted in a similar manner into the following series of derivatives : 6-*p*-chlorophenyldinaphthathiazine-5 : 7 : 12 : 14-*diquinone*, brown, prismatic crystals, m. p. above 360°; 12-*p*-chlorophenyldibenzcarbazole-1 : 6 : 7 : 12-*diquinone*, yellow leaflets, m. p. above 360°; 13-*p*-chlorophenyl-5 : 6 : 11 : 13-*tetra-acetoxydibenzcarbazole*, small, yellow crystals, m. p. above 360°; 12-*p*-chlorophenyldibenzcarbazole-5 : 6-*quinone*, coarse, brown crystals, m. p. above 360°.

2 : 3-*Diazido*-1 : 4-naphthaquinone, $C_6H_4 \begin{smallmatrix} \text{CO} \cdot \text{C} \cdot \text{N}_3 \\ | \quad | \\ \text{CO} \cdot \text{C} \cdot \text{N}_3 \end{smallmatrix}$, m. p. 136°,

appears to be the sole product of the action of sodium azide on a suspension of dichloronaphthaquinone in boiling alcohol, whereas under similar conditions sodium acetate yields 3-*chloro*-2-*acetoxy*-1 : 4-naphthaquinone, slender, yellow needles, m. p. 98°.

2-Amino-3-thiol-1 : 4-naphthaquinone and chloroaminonaphthaquinone yield the compound (annexed formula), brownish-yellow crystals, m. p. above 360°.

g g* 2

o-Nitroaniline, β -aminoanthraquinone, and 3-chloro-2-aminonaphthaquinone could not be caused to react with dichloro- α -naphthaquinone. The latter substance does not appear to react with benzene in the presence of aluminium chloride.

2 : 3-Dichloro-1 : 4-naphthaquinone reacts with *o*-nitrothiophenol to give 2 : 3-di-*o*-nitrophenylthiol-1 : 4-naphthaquinone, slender, cinnabar-red needles, m. p. 253°, which is transformed by stannous chloride in the presence of glacial acetic acid into 1 : 4-dihydroxy-2 : 3-di-*o*-nitrophenylthiolnaphthalene, slender, almost colourless needles, m. p. 233° (diacetate, slender needles, m. p. 217°). The protracted action of stannous chloride and glacial acetic acid on di-*o*-nitrophenylmercaptanaphthaquinone leads to the production of the compound (annexed formula), dark red needles, m. p. above 360° (the additive compound with tin chloride is also described). 3-Anilino-2-*o*-nitrophenylthiol-1 : 4-naphthaquinone, bluish-red leaflets, m. p. 216°, is prepared by the action of the requisite quantity of aniline on the di-*o*-nitrophenylmercapto-derivative.

[With W. PENSE.]—The following substances have been prepared from chloranil: Tetra-*o*-nitrophenylthiol-*p*-benzoquinone, brownish-yellow crystals which explode violently when heated. 2 : 5-Dianilino-3 : 6-di-*o*-nitrophenylthiol-*p*-benzoquinone, m. p. above 360°, obtained by the action of aniline on the preceding compound. 2 : 5-Dichloro-3 : 6-diazido-*p*-benzoquinone, coarse, prismatic crystals which explode violently when heated previous to melting. Tetraazido-*p*-benzoquinone, brownish-yellow crystals which are exceedingly explosive.

H. W.

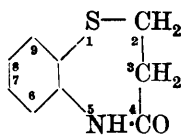
Seven-membered Rings containing Sulphur and Nitrogen.

FRITZ MAYER and CARL HORST (*Ber.*, 1923, 56, [B], 1415—1423).—

A series of compounds containing the heptathiazine ring, $\begin{array}{c} \text{C-S-C} \\ \text{C-N-C} \end{array} > \text{C}$, is described.

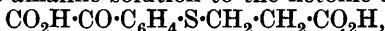
β -*o*-Nitrophenylthiolpropionic acid, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, m. p. 145°, is prepared in 71% yield by the action of *o*-nitrophenyl mercaptan on a solution of sodium β -chloropropionate; the methyl ester, pale yellow needles, m. p. 76°, and the ethyl ester, greenish-yellow leaflets, m. p. 69°, are described. The acid is reduced by ferrous sulphate and ammonia to β -*o*-aminophenylthiolpropionic acid, coarse, colourless needles, m. p. 84°; the hydrochloride, colourless needles, m. p. 189°, and the ethyl ester hydrochloride, colourless needles, m. p. 144°, are described. The ethyl ester is a liquid

which cannot be distilled. β -*o*-Hydroxyphenylthiolpropionic acid has m. p. 86—88°. The amino-acid is almost quantitatively converted at 150—190° into 4-ketotetrahydro-1 : 5-heptabenzthiazine (annexed formula), colourless leaflets or needles, m. p. 215—216°, which can also be obtained from the hydrochloride of the acid at 190—200° or by distillation of the ethyl



ester. The substance immediately dissolves in concentrated or dilute solutions of alkali, giving an odour of mercaptan; it is converted by concentrated hydrochloric acid at 110° into the hydrochloride of the amino-acid.

β -o-Cyanophenylthiolpropionic acid, m. p. $92-93^{\circ}$ after softening at 87° , is obtained from the corresponding amino-acid in the usual manner. It is converted by concentrated hydrochloric acid at 100° into β -o-carboxyphenylthiolpropionic acid, m. p. 140° after softening at 185° . The latter acid can also be obtained in the following manner: thionaphthenquinone is condensed with β -chloropropionic acid in alkaline solution to the ketonic acid,



yellow leaflets, m. p. 138° (oxime, colourless needles, m. p. 92°), which is then oxidised by hydrogen peroxide in the presence of sodium hydroxide to the desired compound.

The heptabenzthiazine is converted by sulphuryl chloride in the presence of benzene into 2(?)-chloroketotetrahydroheptabenzthiazine, pale yellow crystals, decomp. $138-143^{\circ}$, which is transformed by boiling ethyl alcohol into 2(?)-ethoxyketotetrahydroheptabenzthiazine, slender, colourless needles, m. p. $172-173^{\circ}$, and by methyl alcohol into 2(?)-methoxy-4-ketotetrahydroheptabenzthiazine, colourless needles, m. p. $175-176^{\circ}$. Ketoheptabenzthiazine-2(?)-thiolacetic acid has m. p. $209-210^{\circ}$. In the presence of chlorobenzene, the heptabenzthiazine is transformed by the requisite quantity of sulphuryl chloride into 2(?)-dichloroketotetrahydroheptabenzthiazine, colourless needles, m. p. $254-255^{\circ}$ (the sodium salt, $\text{C}_9\text{H}_6\text{ONCl}_2\text{SNa}$, colourless needles, decomp. 135° , is described). The action of acetic anhydride on the benzheptathiazine or on β -o-aminophenylthiohydraacrylic acid gives a substance, long colourless needles, m. p. 87° , the analyses of which do not appear to harmonise with those required by any simple derivative of the parent compound. β -o-Nitrophenylthiolpropionic acid is oxidised by potassium permanganate in alkaline solution to β -o-nitrophenylsulphonpropionic acid, $\text{C}_9\text{H}_9\text{O}_6\text{NS}$, colourless leaflets, m. p. 144° (ethyl ester, colourless needles, m. p. 45°). β -o-Aminophenylsulphonpropionic acid, colourless needles, m. p. 105° (hydrochloride, colourless, lustrous needles, m. p. $184-186^{\circ}$, after previous softening), is prepared by the reduction of the nitro-acid with ferrous sulphate and ammonia. It is converted when heated above its melting point into ketotetrahydroheptabenzsulphazone, $\text{C}_6\text{H}_4\langle\text{SO}_2\cdot\text{CH}_2\text{NH}\cdot\text{CO}\rangle\text{CH}_2$, colourless needles, m. p. $246-247^{\circ}$, which, however, is more conveniently prepared by oxidising the benzheptathiazine dissolved in glacial acetic acid with hydrogen peroxide. It is converted by concentrated hydrochloric acid at 125° into the hydrochloride of the amino-acid.

β -4-Chloro-2-nitrophenylthiolpropionic acid crystallises in pale yellow needles, m. p. $158-159^{\circ}$ (ethyl ester, pale yellow needles, m. p. 77°). It is reduced to β -4-chloro-2-aminophenylthiolpropionic acid, coarse, colourless needles, m. p. 90° after softening at 88° (hydrochloride, colourless needles, m. p. $162-163^{\circ}$). 7-Chloroketotetrahydroheptabenzthiazine, prepared by heating the amino-acid above its

melting point, crystallises in colourless needles, m. p. 217°, and is hydrolysed to the acid by concentrated hydrochloric acid. The action of acetic anhydride on the chloroheptathiazine and on the amino-acid gives the same product, colourless needles, m. p. 112—113° or 116°, which does not give readily interpreted results when analysed.

2(?) : 7-Dichloroketotetrahydroheptabenzthiazine, colourless needles, decomp. 207° after becoming yellow at 170°, is prepared in a not quite homogeneous condition by the action of sulphuryl chloride on the monochloro-compound dissolved in a mixture of benzene and chlorobenzene. It is converted by boiling ethyl alcohol into 7-chloro-2(?)-ethoxyketotetrahydroheptabenzthiazine, colourless needles, m. p. 180°. β -4-Chloro-2-nitrophenylsulphonpropionic acid, colourless leaflets, m. p. 183—184°, is prepared by the oxidation of the corresponding nitrothio-acid with permanganate. 7-Chloroketotetrahydroheptabenzsulphazone, obtained from the 7-chlorobenzthiazine and hydrogen peroxide, has m. p. 269° after softening at 260°.

H. W.

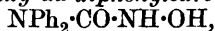
Reactions of β -Hydroxy- α -phenylcarbamide and of β -Hydroxy- $\alpha\alpha$ -diphenylcarbamide Interpreted from the Point of View of their Hydroxamic Acid Structures. CHARLES DEWITT HURD (*J. Amer. Chem. Soc.*, 1923, 45, 1472—1489).—Evidence is submitted which supports the hypothesis of Jones and Hurd (*A.*, 1922, i, 248), that if the radicle that wanders in a Beckmann conversion is potentially a free radicle, the change occurs with greater ease than otherwise. Thus derivatives of diphenylcarbamhydroxamic acid, the “free radicle” of which is NPh_2 , undergo rearrangement, but not derivatives of monophenylcarbamhydroxamic acid. The structure of carbanilido- β -hydroxy- α -phenylcarbamide, $\text{NPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{O}\cdot\text{CO}\cdot\text{NPh}$, is discussed, this formula being preferred to the alternative biuret structure,

$$\text{NPh}\cdot\text{CO}\cdot\text{N}(\text{OH})\cdot\text{CO}\cdot\text{NPh}.$$

It is shown that in the formation of this compound, by boiling a solution of β -hydroxy- α -phenylcarbamide, an intermediate decomposition into hydroxylamine and phenylcarbimide does not occur, since phenylurethane is not produced when alcohol is used as a solvent, and aniline similarly remains unattacked, although phenylcarbimide reacts much more rapidly with aniline than with β -hydroxy- α -phenylcarbamide. The addition of phenylcarbimide to monohydroxamic acids apparently occurs at the α - rather than at the β -hydroxylamino-position.

The benzoate of β -hydroxy- α -phenylcarbamide, $\text{NPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{OBz}$, heavy, crystalline clumps, m. p. 179° (decomp.), forms a *potassium* salt which is stable in cold aqueous solution, but gives *s*-diphenylcarbamide on boiling. The *acetate*, m. p. 121—123°, forms a *potassium* salt, m. p. 161°, and insoluble *copper* and *silver* salts. The *acid sodium* salt, $[\text{NPh}\cdot\text{CO}\cdot\text{N}(\text{OAc})]_2\text{HNa}$, produced in alcoholic solution, is converted by means of cold or boiling water, or dilute sodium hydroxide solution, into carbanilido- β -hydroxy- α -phenylcarbamide, and a *compound*, needles, m. p. 160—161°, which gives

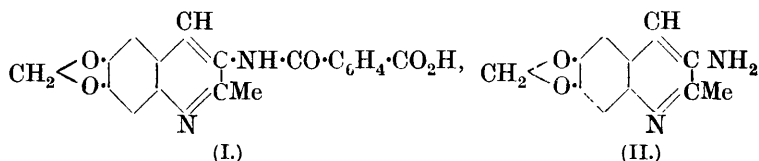
carbanilido- β -hydroxy- α -phenylcarbamide when dissolved in concentrated sulphuric acid and poured into water. *Diphenylcarbamhydroxamic acid* (β -hydroxy- $\alpha\alpha$ -diphenylcarbamide),



colourless needles, m. p. 134—134.5° (decomp.), is prepared by the action of hydroxylamine on diphenylcarbamide chloride in methyl alcoholic or benzene solution, and gives an *acetate*, white needles, m. p. 126.5—127°, the *sodium* salt of which is formed in alcoholic solution, together with tetraphenylcarbazine, $\text{CO}(\text{NH} \cdot \text{NPh}_2)_2$, a product of rearrangement. The sodium salt suffers rearrangement, when left over-night in aqueous solution, with formation of diphenylamine and *as*-diphenylhydrazine. The latter is converted into diphenylamine by the prolonged action of water. The *benzoate* of diphenylcarbamhydroxamic acid gives a *sodium* salt in alcoholic solution. Since diphenylcarbamhydroxamic acid is not formed during the preparation of β -hydroxy- $\alpha\alpha$ -diphenylcarbamide from phenylcarbimide and phenylhydroxylamine, the latter shows no tendency to undergo fission between the phenyl and hydroxylamino-groups. In the absence of solvents, phenylcarbimide and benzhydroxamic acid form an *additive* compound, m. p. 113—114°, which is converted into *s*-diphenylcarbamide by heating at 145°, or by the action of alcoholic sodium methoxide. W. S. N.

3-Amino- and 3-Hydroxy-quinolines. S. BERLINGOZZI (*Atti R. Accad. Lincei*, 1923, [v], **32**, i, 339—343).—With 6-aminopiperonaldehyde, acetylphthalimide and phenacylphthalimide react in the same way as with *o*-aminobenzaldehyde (cf. this vol., i, 482), the action of hydrochloric acid on the resulting products yielding 3-aminoquinoline derivatives, which are convertible into the corresponding 3-hydroxyquinoline derivatives by treatment with nitrous acid.

[With CLELIA NAPOLITANO.]—The compound (I), obtained by condensation of 6-aminopiperonaldehyde with acetylphthalimide in presence of sodium hydroxide, forms white needles, m. p. about 250° (decomp.).



3-Amino-6 : 7-methylenedioxy-2-methylquinoline, (II), obtained by boiling the preceding compound with 20% hydrochloric acid, forms pale yellow chips, m. p. 210°, and forms opalescent solutions in acids. The *acetyl* derivative, $\text{C}_{13}\text{H}_{12}\text{O}_3\text{N}_2$, forms tufts of white needles, m. p. 266—267°, and the *picrate*, lemon-yellow prisms, m. p. about 225° (decomp.).

3-Hydroxy-6 : 7-methylenedioxy-2-methylquinoline, $\text{C}_{12}\text{H}_9\text{O}_3\text{N}$, prepared from the preceding compound by diazotisation, forms straw-yellow scales, m. p. 284—285° (decomp.), gives opalescent solutions

in acids, and with ferric chloride in alcoholic solution yields a blood-red coloration, which is destroyed by addition of hydrochloric acid.

The compound obtained by condensation of 6-aminopiperonaldehyde with phenacylphthalimide in presence of sodium hydroxide, forms a white, microcrystalline powder, m. p. 265° (decomp.).

3-Amino-6 : 7-methylenedioxy-2-phenylquinoline crystallises in straw-yellow needles, m. p. 202° , and dissolves in acids, giving fluorescent solutions. The acetyl derivative, minute, lustrous, white needles, m. p. 234° , and the picrate, lemon-yellow needles, m. p. 217° (decomp.), were prepared.

3-Hydroxy-6 : 7-methylenedioxy-2-phenylquinoline, $C_{17}H_{11}O_3N$, forms lustrous, straw-yellow scales, m. p. 232° , yields opalescent solutions in acids, and in alcohol gives with ferric chloride an orange-red coloration, which is destroyed by hydrochloric acid.

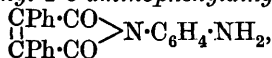
T. H. P.

Preparation of a Derivative of 5-Phenyl-5-ethylhydantoin.

CHEMISCHE FABRIK VON HEYDEN AKT.-GES. (D.R.-P. 360688; from *Chem. Zentr.*, 1923, ii, 481—482).—5-Phenyl-5-ethylhydantoin is acetylated, for example, by heating with acetic anhydride in the presence of a catalyst such as sulphuric acid. 1-Acetyl-5-phenyl-5-ethylhydantoin (annexed formula), thereby obtained, forms colourless crystals, m. p. 179° . The position of the acetyl group is inferred from the solubility of the compound in alkali.

G. W. R.

The Action of *o*-Phenylenediamine on Diphenylmaleic, Homophthalic, and Diphenic Anhydrides. A. BISTRZYCKI and KARL FÄSSLER (*Helv. Chim. Acta*, 1923, 6, 519—534).—The 1 : 2-*o*-benzoylene-1 : 3-benzodiazole obtained from phthalic anhydride and *o*-phenylenediamine (A., 1921, i, 456) has a yellow colour. To determine whether this colour is due to the type of fused ring system present in the compound, substances of similar character have been prepared by condensing *o*-phenylenediamine with other anhydrides of dibasic acids. Diphenylmaleic anhydride condenses with *o*-phenylenediamine in boiling alcohol to form 2 : 5-diketo-3 : 4-diphenyl-1-*o*-aminophenyldihydropyrrole,



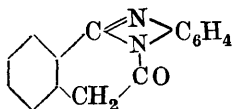
which forms orange, microscopic, prismatic needles, decomposing at $207\text{--}208^{\circ}$. It is a feebly basic substance and forms an acetyl derivative, yellow prisms or six-sided tables, m. p. 224° . When heated at 250° , the aminoanil loses 1 mol. of water, forming $\alpha\beta$ -diphenylacrylenebenziminazole, $\text{CPh} \begin{array}{c} \text{CO} \\ \diagup \\ \text{C} \end{array} \text{--} \text{N}\cdot\text{C}_6\text{H}_4, \text{CPh}\cdot\text{C} \begin{array}{c} \diagdown \\ \text{N} \end{array}$ brown, micro-

scopic groups of needles, m. p. 186° . The same compound is formed, but in poor yield, by heating together molecular proportions of *o*-phenylenediamine and diphenylmaleic anhydride. By alkalis it is readily converted into benziminazole-2- $\alpha\beta$ -diphenylacrylic acid, $\text{C}_6\text{H}_4 \begin{array}{c} \text{N} \\ \diagdown \\ \text{C} \end{array} \text{--} \text{CPh}\cdot\text{CPh}\cdot\text{CO}_2\text{H}$, crystallising with $1\text{H}_2\text{O}$

in colourless, microscopic crystals which when heated become orange, m. p. 186° (decomp.). From alcohol, the acid crystallises in long, colourless needles containing 1 mol. of the solvent. The *ethyl* ester forms colourless, microscopic needles which behave like the acid when heated, and the *anilide* forms microscopic needles decomposing at 278° .

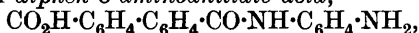
Homophthalic anhydride combines with *o*-phenylenediamine in alcoholic solution to form, probably, *o*-carboxymethylbenz-*o*-aminoanilide, $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$, although the possibility remains that combination takes place at the other carboxyl group.

The compound forms colourless leaflets, and when heated at 200° loses water, forming 1:2-*o*-phenyleneacetyl-1:3-benzdiazole (annexed formula), yellow, short, microscopic prisms, decomposing at 345° . In acetic anhydride

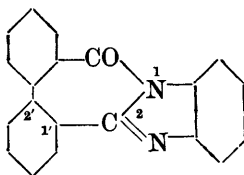


solution, it is blue and in concentrated sulphuric acid violet-brown. It can be regarded as a reduced *isoquinoline* derivative, and all attempts to open the new six-membered ring failed, the compound being remarkably stable.

Diphenic anhydride combines with *o*-phenylenediamine in boiling alcohol to form *diphen-o*-aminoanilidic acid,

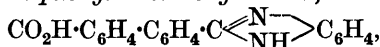


which forms colourless, rhombic tablets decomposing at 165° ; from alcohol, it crystallises with 1 mol. of solvent. The *silver*



salt forms a grey precipitate. When heated at 150° , the acid loses water, forming 2':1-*o*-benzoylene-2-phenyl-1:3-benzdiazole (annexed formula), which forms colourless, microscopic needles, m. p. 177 — 178° . The compound can be prepared in good yield by melting together diphenic anhydride and *o*-phenylenediamine and heating at 150° . It contains a new seven-membered ring, and, unlike the above compounds containing a six- or five-membered ring condensed with the benzdiazole ring, it is colourless. The new ring is readily ruptured by alkali, and in this respect resembles the 5-membered ring of the above diphenylmaleic derivative.

Benziminazole-2-diphenyl-2'-carboxylic acid,



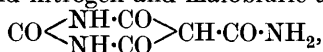
forms colourless, flat prisms which melt at 206 — 207° and lose water to form again the above seven-membered ring compound. The *silver* salt is white and but slightly sensitive to light. The *ethyl* ester forms short, flat, microscopic prisms, decomposing at 143° ; the *amide*, colourless, flat prisms, decomposing at 227° ; the *anilide*, rhombic tablets, decomposing at 248° ; the *phenylhydrazide*, microscopic rosettes of leaflets, decomposing at 157° . These amido-derivatives are all formed by the action of the base on the above benzoylene-phenylbenzdiazole. *N*-*o*-Acetamido-phenyl diphenimide, $\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$, forms colourless, microscopic

prisms, decomposing at 233° . It is formed when the primary product of combination of diphenic anhydride and *o*-phenylenediamine is acetylated.
E. H. R.

The Action of Carbamazide on Malonic Ester and on Barbituric Acid. TH. CURTIUS (*Ber.*, 1923, 56, [B], 1577—1583).—The action of carbamazide on ethyl malonate and barbituric acid occurs in two directions. On the one hand, the azide loses hydrazoic acid and leaves a residue of *isocyanic acid*, which is isolated as cyanuric acid or as urazole, whereas, on the other hand, it loses nitrogen and the residue, $\text{NH}_2\cdot\text{CO}\cdot\text{N}^{\cdot}$, unites with the partner in the reaction to yield substances containing the group $\text{NH}_2\cdot\text{CO}\cdot\text{NH}$.

Urazole, m. p. 245° , cyanuric acid, *ethyl dicarbamidomalonate*, $(\text{NH}_2\cdot\text{CO}\cdot\text{NH})_2\text{C}(\text{CO}_2\text{Et})_2$, small, pointed, anisotropic platelets, m. p. 170° , and *ethyl carbamidomalonate*, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}(\text{CO}_2\text{Et})_2$, colourless, anisotropic prisms, m. p. 145° , are obtained when carbamazide and ethyl malonate are warmed on the water-bath until evolution of nitrogen ceases. Urazole, cyanuric acid, and small amounts of a substance, m. p. 174° (decomp.), are the only products which could be isolated from the action of carbamazide and ethyl ethylmalonate.

Carbamazide and crystalline, hydrated barbituric acid when heated together yield nitrogen and malobiuric acid,



which is derived by the addition of nascent *isocyanic acid* to barbituric acid. The main product of the reaction, however, is a tile-red mass which is insoluble in all media and presumably contains bibarbituric acid. It is transformed by bromine water into a substance, $\text{C}_9\text{H}_7\text{O}_7\text{N}_7$, golden-yellow, anisotropic plates, dibromobibarbituric acid, and the hydrobromides of basic substances, which have not been investigated farther. The constitution of the compound $\text{C}_9\text{H}_7\text{O}_7\text{N}_7$ has not been elucidated; it yields highly characteristic additive compounds with bases such as aniline, ammonia, and hydrazine. It is extremely sensitive to reducing agents and is converted by stannous chloride into the compound, $\text{C}_8\text{H}_6\text{O}_5\text{N}_4$, small, red needles (the corresponding *monohydrate* is described). The substance can also be obtained by the use of sulphurous acid and, in this case, the mother-liquors contain a compound, $\text{C}_9\text{H}_5\text{O}_7\text{N}_9$, large, colourless leaflets, decomp. 268° , which has feeble acidic properties and yields a highly characteristic, gelatinous *silver salt*. It reacts violently with hydrazine in aqueous solution, giving an *acid*, $\text{C}_3\text{H}_6\text{O}_4\text{N}_4$, thin, anisotropic platelets.
H. W.

New Cases of Isomerism. II. Structural Association. GUSTAV HELLER and WILLI KÖHLER (*Ber.*, 1923, 56, [B], 1595—1600).—It has been shown previously in three instances that an unexpected isomerism is observed in the case of *p*-lactams, as a consequence of which substances with the group $\text{C}_6\text{H}_4 < \begin{array}{c} \text{CO} \\ \text{NH} \end{array}$ differ

from those containing the group $C_6H_4 \begin{smallmatrix} \text{C}\cdot\text{OH} \\ \text{N} \end{smallmatrix}$. A similar instance is presented by *o*-hydrazinobenzoic anhydride, $C_6H_4 \begin{smallmatrix} \text{CO} \\ \text{NH} \end{smallmatrix} \text{NH}$ (cf. Heller and Jacobsohn, A., 1921, i, 440), and 3-hydroxyindazole, $C_6H_4 \begin{smallmatrix} \text{C(OH)} \\ \text{N} \end{smallmatrix} \text{NH}$ (cf. Thode, A., 1904, i, 347). The latter substance resembles the structurally similar isatole and 4-hydroxyquinaldine in showing a more or less distinct tendency towards termolecular association in various solvents. To this tendency is attributed the ability of *p*-lactims to exist in two tautomeric forms, whereas in general only the lactam or the lactim is stable. It appears, therefore, that in these cases a new form of association is presented (structural association), as a consequence of which a form which is potentially tautomeric exists as a stable entity.

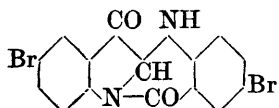
3-Hydroxyindazole (benzisopyrazolone), m. p. 206° , is conveniently obtained by heating *o*-aminobenzhydrazide at 200 — 210° in the presence of quinoline. It is converted by cautious treatment with acetic anhydride into 2-acetyl-3-hydroxyindazole, $C_6H_4 \begin{smallmatrix} \text{C(OH)} \\ \text{N} \end{smallmatrix} \text{NAc}$, m. p. 188° (decomp.), which is transformed when heated with glacial acetic acid into *bis*-N-acetylidazyl 3-ether, $O \left(C \begin{smallmatrix} \text{NAc} \\ \text{C}_6H_4 \end{smallmatrix} N \right)_2$, m. p. 190° ; the latter compound is hydrolysed by concentrated hydrochloric acid to *monoacetylidazyl ether*, $C_{16}H_{12}O_2N_4$, rhombic plates, m. p. 206° . 3-Hydroxyindazole is transformed by phosphoryl chloride and phosphorus pentachloride into *bisbenzisopyrazolyl*, $C_6H_4 \begin{smallmatrix} \text{CO} \\ \text{NH} \end{smallmatrix} \text{N} \cdot C \begin{smallmatrix} \text{C}_6H_4 \\ \text{NH} \end{smallmatrix} \text{N}$, leaflets, m. p. 228° , which is converted by acetic anhydride into a compound, needles, m. p. 250° . 3-Hydroxyindazole and nitrous acid yield 1:2-dinitroso-3-ketodihydroindazole, $\left(C_6H_4 \begin{smallmatrix} \text{CO} \\ \text{N(NO)} \end{smallmatrix} \right)_2$, pale yellow rhombohedra, m. p. 249° (decomp.). H. W.

The Nature of Isatoids. II. GUSTAV HELLER and HELLMUTH LAUTH (*Ber.*, 1923, 56, [B], 1591—1594).—Further examples of isatoids have been investigated.

5-Bromoisatin is treated with a solution of sodium in absolute alcohol. The precipitated sodium salt is removed and converted into the corresponding silver salt, which is treated with methyl iodide in the presence of ether and subsequently dissolved in acetic anhydride and exposed to light. 5-Bromo- β -methylisatoid (5-bromoisatoid *O*-methyl ether), $C_6H_3Br \begin{smallmatrix} \text{CO} \\ \text{NH} \end{smallmatrix} C(OMe) \cdot N \begin{smallmatrix} \text{C}_6H_3Br \\ \text{CO} \end{smallmatrix}$, is thereby precipitated in orange-red needles, m. p. 262° (decomp.) after darkening at 225° and softening at 240° . When dissolved in hot benzene, it appears to become isomerised to the α -form, m. p. 259 — 260° (decomp.) after incipient darkening at 238° . It is converted by *N*-sodium hydroxide solution into *bromo- γ -methylisatoid*, m. p. 306 — 307° (decomp.) after becoming discoloured at about 190° , and more strongly so at 240 — 250° . 5-Bromoethyl-

isatoid crystallises in orange-red needles, m. p. 247° (decomp.) after darkening at 224° and softening at 240°; it does not appear to become isomerised in benzene solution. 5-Bromo-n-propylisatoid forms slender, orange-red needles, m. p. 232° (decomp.) after incipient decomposition at 227°.

5-Bromomethylisatoid is converted by glacial acetic acid and hydrobromic acid (*d* 1.48) into *anhydro-5-bromoindoxyl-α-4'-bromo-*

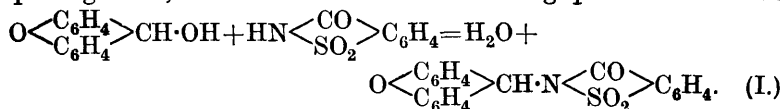


anthranilide (annexed formula), small granules, m. p. 309—310° (decomp.); the compound is also obtained from 5-bromoethylisatoid. It is converted by chromic and glacial acetic acids into *anhydro-5-bromoisatin-α-4'-bromoanthranilide*, slender, yellow needles, m. p. 318°.

H. W.

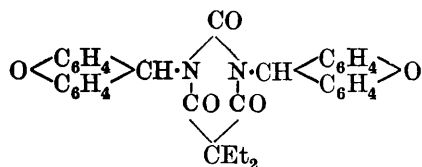
Indine and isoIndigotin. O. DORNIER and JH. MARTINET (*Bull. Soc. chim.*, 1923, **33**, 779—786).—A summary of the evidence on the subject of the composition of α- and β-indines and of isoindigotin. The present authors conclude from spectrographic evidence that all three are identical. From the product of action of glycerol on dioxindole, they have isolated a violet powder which appears to be a mixture of indirubin and isoindigotin. H. H.

Xanthyl Derivatives. RENÉ FABRE (*Bull. Soc. chim.*, 1923, [iv], **33**, 791—804).—Crystalline condensation products of xanthidrol with substances containing a reactive hydrogen atom are described, and it is suggested that they may be of use for the characterisation of the parent substances. "Saccharin," antipyrine, and derivatives of veronal were studied in this connexion, the reaction being quite general, and with "saccharin" taking place as follows:



As a preliminary investigation, the p_H of some of the solutions employed was determined. Antipyrine, M/10 per litre, $p_H=6.3$; pyrimidone (dimethylaminoantipyrine), M/10 per litre, $p_H=8.2$; veronal [5:5-diethylbarbituric acid], M/100 per litre, $p_H=5.6$; "saccharin," M/1000 per litre, $p_H=3.1$.

The condensation is effected by means of acetic acid, which must be free from mineral acid. It is sufficient merely to warm a mixture of the acetic acid solutions of the components; on cooling, the condensed compound crystallises out and may be recrystallised



from the usual solvents. The following compounds are described: "xanthylsaccharin" (I), m. p. 199—200°; 1:3-dixanthyl-5:5-diethylbarbituric acid (annexed formula), m. p. 245—246°; 1:3-dixanthyl-5-phenyl-5-ethylbarbituric acid, m. p. 218—219°; 1:3-dixanthyl-5:5-diallylbarbituric acid,

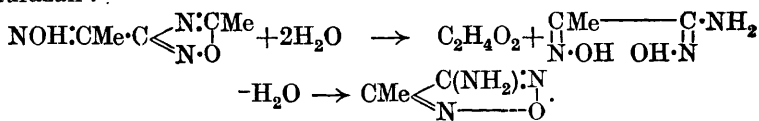
acid, m. p. 218—219°; 1:3-dixanthyl-5:5-diallylbarbituric acid,

m. p. 242—243°; 1 : 3-dixanthyl-5-ethyl-5-butylbarbituric acid, m. p. 242—243°; 1 : 3-dixanthyl-5-ethyl-5-isobutylbarbituric acid, m. p. 259—260°; 1-phenyl-4-xanthyl-2 : 3-dimethylpyrimidone, m. p. 178—179°. Pyramidone, which contains no replaceable hydrogen atom, does not give a xanthyl derivative. H. H.

Dioximes. VII. G. PONZIO and G. RUGGERI (*Gazzetta*, 1923, **53**, i, 297—305).—The relationship of aminomethylglyoxime (A., 1922, i, 627) to certain acyl derivatives of the azoximes and to aminomethylfurazan has now been studied. The furazan derivative is not obtained directly from aminomethylglyoxime by elimination of a molecule of water from the two oximino-groups according to the usual method of preparing furazans from α -dioximes. When, however, aminomethylglyoxime is boiled with excess of acetic anhydride, the following series of four reactions occurs : (1) $\text{NOH}:\text{CMe}\cdot\text{C}(\text{NH}_2):\text{NOH} + \text{Ac}_2\text{O} \rightarrow \text{NOAc}:\text{CMe}\cdot\text{C}(\text{NH}_2):\text{NOAc}$, (2) $-\text{H}_2\text{O} \rightarrow \text{NOAc}:\text{CMe}\cdot\text{C} \begin{smallmatrix} \text{N}:\text{CMe} \\ \text{N}:\text{O} \end{smallmatrix}$, (3) $+\text{H}_2\text{O} \rightarrow \text{CH}_3\cdot\text{CO}_2\text{H} + \text{NOH}:\text{CMe}\cdot\text{C} \begin{smallmatrix} \text{N}:\text{CMe} \\ \text{N}:\text{O} \end{smallmatrix}$; the latter, on hydrolysis with dilute hydro-

chloric acid, (4) $+\text{H}_2\text{O} \rightarrow \text{CH}_3\cdot\text{CO}_2\text{H} + \text{CMe} \begin{smallmatrix} \text{C}(\text{NH}_2):\text{N} \\ \text{N} \text{---} \text{O} \end{smallmatrix}$. The second of these reactions is analogous to the synthesis of the azoximes from acyl derivatives of the amidoximes, $\text{NH}_2\cdot\text{CR}:\text{N}\cdot\text{CO}\cdot\text{OR}^1 - \text{H}_2\text{O} \rightarrow \text{CR} \begin{smallmatrix} \text{N}:\text{CR}^1 \\ \text{N}:\text{O} \end{smallmatrix}$. The fourth reaction, representing the trans-

formation, not previously observed, of an azoxime into a furazan derivative, probably results first in the formation of an intermediate labile form of aminomethylglyoxime, which, unlike the stable form (*loc. cit.*), undergoes spontaneous anhydridation to aminomethylfurazan :



This view is in agreement with the facts (1) that elimination of a molecule of water from the amino-group and the neighbouring benzoyl group of the dibenzoyl derivative of aminomethylglyoxime by treatment with boiling acetic anhydride yields the benzoyl derivative of the oxime of 3-acetyl-5-phenyl-1 : 2 : 4-oxadiazole,

$\text{OBz}\cdot\text{N}:\text{CMe}\cdot\text{C}(\text{NH}_2):\text{NOBz} - \text{H}_2\text{O} = \text{OBz}\cdot\text{N}:\text{CMe}\cdot\text{C} \begin{smallmatrix} \text{N}\cdot\text{CPh} \\ \text{N}:\text{O} \end{smallmatrix}$; (2) that,

from the same dibenzoyl derivative, by elimination of a molecule of water as above and replacement of a benzoyl group by a hydrogen atom by treatment with hot dilute sodium hydroxide solution, the oxime of 3-acetyl-5-phenyl-1 : 2 : 4-oxadiazole is obtained, and (3) that the last compound is convertible into aminomethylfurazan by the action of dilute hydrochloric acid.

As regards aminomethylfurazan, the presence of the amino-

group modifies profoundly the properties of the ring, $O \begin{smallmatrix} \text{N}:\text{C}- \\ \text{N}:\text{C}- \end{smallmatrix}$,

which is not so stable as in the furazans, $O \begin{smallmatrix} \text{N}:\text{CR} \\ \text{N}:\text{CR}^1 \end{smallmatrix}$, where R and

R¹ are alkyl or aryl groups. Aminomethylfurazan may be diazotised by means of nitrous acid and then yields azoiminomethylfurazan, $\begin{smallmatrix} \text{N}:\text{CMe} \\ \text{O}-\text{N} \end{smallmatrix} \begin{smallmatrix} \text{C}:\text{N} \\ \text{N} \end{smallmatrix} \cdot \text{NH} \cdot \text{C} \begin{smallmatrix} \text{CMe}:\text{N} \\ \text{N}-\text{O} \end{smallmatrix}$, so readily that the diazo-

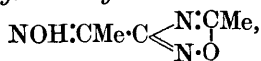
compound cannot be made to react with other bases. Moreover, although the methyl group of the methylfurazans is oxidisable to carboxyl, that of aminomethylfurazan exhibits marked resistance towards energetic oxidising agents such as permanganate and concentrated nitric acid, which, however, dehydrogenate the amino-group, two residues then uniting to form azomethylfurazan, $\begin{smallmatrix} \text{N}:\text{CMe} \\ \text{O}-\text{N} \end{smallmatrix} \begin{smallmatrix} \text{C}:\text{N} \\ \text{N} \end{smallmatrix} \cdot \text{C} \begin{smallmatrix} \text{CMe}:\text{N} \\ \text{N}-\text{O} \end{smallmatrix}$; the latter may be readily reduced to hydrazomethylfurazan.

The *diacetyl* derivative of aminomethylglyoxime,



crystallises in lustrous prisms or flattened needles, m. p. 123° (anhydrous).

The *oxime* of 3-acetyl-5-methyl-1:2:4-oxadiazole,



forms elongated prisms, m. p. 145°, and its *benzoyl* derivative, $\text{NOBz}:\text{CMe} \cdot \text{C}_3\text{H}_3\text{ON}_2$, long needles, m. p. 198—199°.

The *oxime* of 3-acetyl-5-phenyl-1:2:4-oxadiazole, $\text{C}_{10}\text{H}_9\text{O}_2\text{N}_3$, crystallises in stout prisms, m. p. 205—209°, and its *benzoyl* derivative in long needles, m. p. 174—175°.

Aminomethylfurazan, $\text{C}_3\text{H}_5\text{ON}_3$, crystallises in large, white, odourless prisms, m. p. 72—73°, does not volatilise in a current of steam, and remains unchanged when heated with sodium hydroxide solution or hydrochloric acid. Its *acetyl* derivative, $\text{C}_3\text{H}_3\text{ON}_2 \cdot \text{NHAc}$, crystallises in lustrous laminæ, m. p. 115—116°; its *benzylidene*

derivative, $\text{CHPh}(\text{NH} \cdot \text{C} \begin{smallmatrix} \text{N}-\text{O} \\ \text{CMe}:\text{N} \end{smallmatrix})_2$, in flattened needles, m. p. 155—156°, and its *cinnamylidene* derivative,



forms straw-coloured laminæ, m. p. 126°.

Azomethylfurazan, $\text{C}_6\text{H}_6\text{O}_2\text{N}_6$, forms orange laminæ, m. p. 107°, and *hydrazomethylfurazan*, $\text{C}_6\text{H}_8\text{O}_2\text{N}_6$, which is readily oxidised to the azo-compound, white prisms (+H₂O), m. p. 118—119° (slight decomp.).

Azoiminomethylfurazan, $\text{C}_6\text{H}_7\text{O}_2\text{N}_7$, crystallises in straw-coloured laminæ (+aq.), m. p. 114°; its *silver* salt, $\text{C}_6\text{H}_6\text{O}_2\text{N}_7\text{Ag}$, forms a white powder stable towards light and explodes violently when heated; its *acetyl* derivative, $\text{C}_8\text{H}_9\text{O}_3\text{N}_7$, crystallises in white laminæ, m. p. 72°.

T. H. P.

Dioximes. VIII. G. PONZIO and L. AVOGADRO (*Gazzetta*, 1923, **53**, i, 305—311).—By the action of aniline on the peroxide of α -phenylglyoxime (phenylfuroxan) in benzene solution, Wieland and Semper (A., 1908, i, 108) obtained a compound, m. p. about 180° (decomp.), which, from its method of formation and from the intense colour it gives with ferric chloride, they regarded as the substituted amidoxime, $\text{NOH}\cdot\text{CPh}\cdot\text{C}(\text{:NOH})\cdot\text{NHPh}$. The authors find that this anilinophenylglyoxime exists in two modifications interrelated in the same way as the two aminophenylglyoximes (this vol., i, 472). α -Anilinophenylglyoxime, m. p. 188° , when prepared as described by Wieland and Semper, is accompanied by another compound, m. p. 202° , which is being investigated. This α -compound does not form complex salts, but the β -isomeride, obtained either by the action of dilute acetic acid on the α -form or by the interaction of aniline and chlorophenylglyoxime (this vol., i, 473), acts in aqueous solution on certain metals of the eighth group with formation of the corresponding complex salts. Both α - and β -forms exhibit distinct basicity and yield moderately stable hydrochlorides, but are also soluble in strong bases.

The action of aniline on chloromethylglyoxime or that of hydroxylamine on acetylphenylisuretin yields β -anilinomethylglyoxime, which is a strong base but unstable, and gives a complex nickel compound.

α -Anilinophenylglyoxime forms : a *hydrochloride*, $\text{C}_{14}\text{H}_{13}\text{O}_2\text{N}\cdot\text{HCl}$, long, white needles, m. p. 208 — 209° (decomp.), which is moderately stable in the air but is rapidly hydrolysed by water; a *diacetyl* compound, $\text{C}_{18}\text{H}_{17}\text{O}_4\text{N}_3$, white needles, m. p. 179° , which yields α -anilinophenylglyoxime, together with a little phenylaminophenylfuran (see below), when suspended in 20% sodium hydroxide solution; a *dibenzoyl* compound, $\text{C}_{28}\text{H}_{21}\text{O}_4\text{N}_3$, which forms small crystals, m. p. 201° , and is not appreciably changed when heated with 20% sodium hydroxide solution.

Anilinophenylfuran, $\text{O} < \begin{smallmatrix} \text{N:CPh} \\ \text{N:C}\cdot\text{NHPh} \end{smallmatrix}$, obtained by boiling α -anilinophenylglyoxime with 20% sodium hydroxide solution (see above), forms lustrous, white needles, m. p. 158° .

β -Anilinophenylglyoxime, $\text{C}_{14}\text{H}_{13}\text{O}_2\text{N}_3$, crystallises in small, white needles, m. p. 124° (slight decomp.) with previous softening, gives an intense blue coloration with ferric chloride, and, in aqueous solution, attacks compact nickel even in the cold and copper and cobalt when heated. The *hydrochloride*, $\text{C}_{14}\text{H}_{13}\text{O}_2\text{N}_3\cdot\text{HCl}$, forms rhombic plates, m. p. 210 — 211° (decomp.); the *nickel* salt, $(\text{C}_{14}\text{H}_{12}\text{O}_2\text{N}_3)_2\text{Ni}$, dark red prisms or thin, pale coffee-coloured, silky laminæ ($+2\text{H}_2\text{O}$), m. p. 268° (decomp.), not reacting with ammonia solution; and the *diacetyl* derivative, $\text{C}_{18}\text{H}_{17}\text{O}_4\text{N}_3$, groups of white needles, m. p. 150° , with previous softening.

Anilinomethylglyoxime, $\text{NOH}\cdot\text{CMe}\cdot\text{C}(\text{:NOH})\cdot\text{NHPh}$, is unstable; its *nickel* salt, $(\text{C}_9\text{H}_{10}\text{O}_2\text{N}_3)_2\text{Ni}$, crystallises in lustrous, wine-red laminæ, m. p. 242° (decomp.), and dissolves in 20% sodium hydroxide solution giving a brownish-red coloration, but is insoluble in ammonia solution.

T. H. P.

Dioximes. IX. G. PONZIO and L. AVOGADRO (*Gazzetta*, 1923, 53, i, 311—318).—Further experimental data are described which show the marked difference in behaviour between the two forms of phenylglyoxime and thus confirm the view that the isomerism of the α -dioximes cannot be explained by the theory of Hantzsch and Werner.

When treated with concentrated sulphuric acid, α -phenylglyoxime loses a molecule of water, giving phenylfurazan, whereas two molecules of the β -isomeride lose a molecule of hydroxylamine with formation of the compound, $C_{16}H_{13}O_3N_3$, already obtained by Müller and Pechmann (A., 1890, 51) by treating phenylglyoxal with hydroxylamine hydrochloride, by Scholl (A., 1891, 287) by heating oximinoacetophenone with excess of hydroxylamine hydrochloride, by Korten and Scholl (A., 1901, i, 549) by the action of hydroxylamine on ω -dibromoacetophenone, and by Diels and Sasse (A., 1907, i, 1086) by preparing the oxime of the product resulting from the anhydridation of oximinoacetophenone. The method used by the authors to obtain this compound is in agreement with Scholl and Baumann's view that it consists of 1-phenyl-3-oximinobenzyl-2-isooxazolono-xime (A., 1907, i, 492).

Both dioximes of phenylglyoxal are readily coupled with phenyldiazonium chloride yielding unstable compounds which readily lose nitrogen and then give α - and β -benzildioximes, respectively; the latter only forms a complex nickel compound. Just as with the phenylglyoximes, these two benzildioximes cannot be regarded as geometrical isomerides.

The authors confirm Russanov's statement (A., 1892, 321) that both forms of phenylglyoxime yield the same diacetyl derivative, and find that the α - but not the β -compound yields at the same time phenylfurazan, and that the α -compound cannot be benzoylated. The conclusion is drawn that α -phenylglyoxime yields a diacetyl derivative, not directly, but only after isomerisation to the β -form. This view is confirmed by the fact that the action on the two phenylglyoximes of propionic anhydride, which exhibits comparatively slight dehydrating properties, yields two different dipropionyl derivatives.

Dipropionyl- α -phenylglyoxime, $COEt \cdot ON : CPh \cdot CH : NO \cdot COEt$, crystallises in prisms, m. p. 75° , and is slowly dissolved by 20% sodium hydroxide solution, with formation of phenylfurazan, which then undergoes partial isomerisation into benzoyl cyanide oxime (oximino-benzyl cyanide) under the influence of the strong base.

Dipropionyl- β -phenylglyoxime crystallises in laminæ, m. p. $89-90^\circ$, and is converted into β -phenylglyoxime by treatment with 20% sodium hydroxide solution.

Dibenzoyl- β -phenylglyoxime, $C_{22}H_{16}O_4N_2$, forms flattened needles, m. p. 150° .

Attempts to benzoylate α -phenylglyoxime in pyridine solution results in the formation of the benzoyl-derivative of benzoyl cyanide oxime (Zimmermann, A., 1903, i, 91).

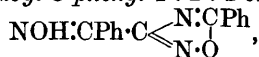
Phenylfurazan crystallises in white prisms, m. p. $35-36^\circ$ (cf. Russanov, *loc. cit.*).
T. H. P.

Dioximes. X. G. PONZIO and L. AVOGADRO (*Gazzetta*, 1923, 53, i, 318—327; cf. this vol., i, 472).—Treatment of α -aminophenylglyoxime with acetic anhydride in the cold yields the diacetyl derivative, $\text{NOAc}:\text{CPh}\cdot\text{C}(\text{NHAc}):\text{NOH}$, which is converted by sodium hydroxide into acetamidophenylfuran. Under similar conditions, β -aminophenylglyoxime gives the diacetyl compound, $\text{NOAc}:\text{CPh}\cdot\text{C}(\text{NH}_2):\text{NOAc}$, which, with sodium hydroxide, yields first 3-acetoximinobenzyl-5-methyl-1:2:4-oxadiazole and then 3-oximinobenzyl-5-methyl-1:2:4-oxadiazole. When either the latter or acetamidophenylfuran is heated with dilute hydrochloric acid, aminophenylfuran is obtained. From these results it is evident that the two oximino-groups of β -aminophenylglyoxime are equivalent, whereas those of the α -isomeride are not equivalent.

The action of sodium hydroxide on the dibenzoyl derivative of α -aminophenylglyoxime yields aminophenylfuran and 3-oximinobenzyl-5-phenyl-1:2:4-oxadiazole, whereas the dibenzoyl compound of the β -glyoxime gives the latter itself and also 3-oximinobenzyl-5-phenyl-1:2:4-oxadiazole, which is converted into aminomethylfuran by means of dilute hydrochloric acid. The action of water on the oximes of 3-acyl-5-alkyl(or aryl)-1:2:4-oxadiazoles serves as a general method for the preparation of aminofurazans. The behaviour of such oximes is, indeed, entirely different from that of the isomeric 3-acyl-5-aminoaryl-1:2:4-oxadiazoles, investigated by Holleman (A., 1893, i, 205), Böseken (A., 1898, i, 696; 1910, i, 643) and Wieland and Gmelin (A., 1910, i, 784). Thus, the oxime of 3-benzoyl-5-phenyl-1:2:4-oxadiazole yields benzoic acid and aminophenylfuran when heated with dilute hydrochloric acid, whereas 3-benzoyl-5-anilino-1:2:4-oxadiazole gives benzoic acid and phenylecyanocarbamide when heated with sodium hydroxide.

Diacetyl- α -aminophenylglyoxime, $\text{NOAc}:\text{CPh}\cdot\text{C}(\text{NHAc}):\text{NOH}$, crystallises in flattened needles, m. p. 150—151°, and the dibenzoyl compound in slender needles, m. p. 189—190° (Wieland and Semper, A., 1908, i, 108, gave m. p. 176°).

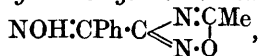
The oxime of 3-benzoyl-5-phenyl-1:2:4-oxadiazole,



forms slender needles, m. p. 148°.

Diacetyl- β -aminophenylglyoxime, $\text{NOAc}:\text{CPh}\cdot\text{C}(\text{NH}_2):\text{NOAc}$, crystallises in large prisms, m. p. 133—134°.

The oxime of 3-benzoyl-5-methyl-1:2:4-oxadiazole,



forms lustrous, white needles, m. p. 202—203° (slight decomp.), its *acetyl* derivative, $\text{NOAc}:\text{CPh}\cdot\text{C}_2\text{ON}_2\text{Me}$, needles, m. p. 101—102°, and its *benzoyl* derivative, $\text{C}_{17}\text{H}_{13}\text{O}_3\text{N}_3$, long, slender needles, m. p. 152—153°.

Dibenzoyl- β -aminophenylglyoxime, $\text{NOBz}:\text{CPh}\cdot\text{C}(\text{NH}_2):\text{NOBz}$, crystallises in flattened prisms, m. p. 185—186°.

Aminophenylfuran, $\text{O} \begin{array}{l} \nearrow \text{N}:\text{CPh} \\ \searrow \text{N}:\text{C}\cdot\text{NH}_2 \end{array}$, crystallises in white prisms

or long needles, m. p. 98—99°, and is stable towards alkali hydroxide, concentrated hydrochloric or sulphuric acid or 4*N*-nitric acid, even when heated, but decomposes violently with formation of *p*-nitrobenzoic acid when heated with concentrated nitric acid (*d* 1.4). Its *acetyl* derivative, $C_2ON_2Ph \cdot NHAc$, crystallises in lustrous needles, m. p. 181—182°, and its *diacetyl* derivative, $C_2ON_2Ph \cdot NAc_2$, in long, broad laminæ, m. p. 71°.

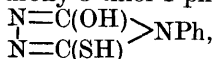
Azophenylfuran, $C_2ON_2Ph \cdot N \cdot N \cdot C_2ON_2Ph$, forms long, orange needles, m. p. 134—135°, and *hydrazophenylfuran*, $C_{16}H_{12}O_2N_6$, almost white laminæ, m. p. 169°. T. H. P.

Preparation of Carbamic Acid Derivatives of the Pyrazolone Series. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 360424; from *Chem. Zentr.*, 1923, ii, 407—408).—4-Aminopyrazolones or their derivatives are treated with alkali hydrogen carbonates. Basic pyrazolones of the accompanying general formula (where R_1 and R_2 =hydrogen or alkyl), and in which the phenyl group may or may not be substituted, are thereby changed into soluble alkali salts with neutral reaction. An alkali carbonate, or hydroxide in the presence of carbon dioxide, may be used in place of a hydrogen carbonate. 4-Amino-1-phenyl-2 : 3-dimethyl-5-pyrazolone gives a corresponding *carbamate*; it is a white powder. 1-*p*-Arsenodiphenyl-di(4-amino-5-pyrazolone) (A., 1921, i, 752) gives a *carbamate* as a clear, stable solution.

G. W. R.

Preparation of 4-Dimethylamino-1-aryl-2 : 3-dialkyl-5-pyrazolones. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 360423; from *Chem. Zentr.*, 1923, ii, 407).—4-Amino-1-aryl-2 : 3-dialkyl-5-pyrazolones are treated with formaldehyde or its polymerisation products in the presence of aqueous formic acid. Methylation takes place without formation of quaternary ammonium bases. 4-Dimethylamino-1-phenyl-2 : 3-dimethyl-5-pyrazolone, 4-dimethylamino-1-phenyl-3-methyl-2-ethyl-5-pyrazolone, m. p. 107°, and 4-dimethylamino-1-*p*-tolyl-2 : 3-dimethyl-5-pyrazolone, m. p. 105°, are mentioned. G. W. R.

Syntheses of 3-Hydroxy-5-thioltriazoles. E. FROMM and E. NEHRING (*Ber.*, 1923, 56, [B], 1370—1375).—Ethyl δ -phenylthiosemicarbazide- α -carboxylate, $NHPh \cdot CS \cdot NH \cdot NH \cdot CO_2Et$, slender crystals, m. p. 141°, is prepared by the gradual addition of ethyl chloroformate to a boiling alcoholic suspension of δ -phenylthiosemicarbazide; it is converted by boiling, aqueous sodium hydroxide solution into 3-hydroxy-5-thiol-4-phenyltriazole,



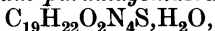
coarse prisms (+ H_2O), m. p. 193° after softening at 130—140°. The *lead* salt, $C_{16}H_{12}O_2N_6S_2Pb$, is described. 3-Hydroxy-5-benzylthiol-4-phenyltriazole crystallises in colourless needles, m. p. 158°; it is converted by benzoyl chloride into 3-hydroxy-2-benzoyl-5-benzylthiol-4-phenyltriazole, colourless needles, m. p. 122°. 3-Hydroxy-

5-benzylthiol-4-phenylmethyltriazole has m. p. 126° . 3-Hydroxy-5-thiol-4-phenyltriazole combines with phenylhydrazine to form the salt, $C_{14}H_{15}ON_5S$, colourless crystals, m. p. 169° ; it is oxidised by bromine water to the corresponding disulphide, $C_{16}H_{12}O_2N_6S_2$, m. p. 286° .

The action of ethyl chloroformate on thiosemicarbazide in the presence of benzene leads to the formation of mixtures which are almost non-separable into their components; on one occasion, *ethyl semicarbazidedicarboxylate* (?), m. p. 130° , was isolated. In alcoholic solution, on the other hand, the substances yield *ethyl thiosemicarbazide- α -carboxylate*, $NH_2 \cdot CS \cdot NH \cdot NH \cdot CO_2Et$, colourless crystals, m. p. 184° , in which the position of the carbethoxyl group is proved by the failure of the compound to react with benzaldehyde. It is converted by benzyl chloride and sodium hydroxide in the presence of alcohol into ethyl δ -benzylisothiosemicarbazide-carboxylate, $CH_2Ph \cdot S \cdot C(=NH) \cdot NH \cdot NH \cdot CO_2Et$, m. p. 145° . It is transformed by two equivalent proportions of sodium hydroxide in aqueous solution into 3-hydroxy-5-thioltriazole, m. p. 202° (Arndt, A., 1922, i, 277 gives m. p. 206°), which is most readily prepared by the action of hydrogen sulphide on the corresponding *lead salt*. 3-Hydroxy-5-benzylthioltriazole crystallises in colourless leaflets, m. p. 182° ; the corresponding *diacetyl* compound forms colourless needles, m. p. 89° . 3-Hydroxy-5-thioltriazole gives a salt with phenylhydrazine, m. p. 155° ; it is converted by bromine water into the disulphide, $C_4H_4O_2N_6S_2$, m. p. 245° . H. W.

The leuco-Sulphinic Acids of the Triphenylmethane Dyes.

G. SCHEUING and R. BERLINER (*Ber.*, 1923, 56, [B], 1583—1568; cf. Wieland, A., 1919, i, 355; Wieland and Scheuing, A., 1922, i, 58).—Under suitable conditions, paramagenta can be dissolved in alkaline sodium hyposulphite solution to yield a concentrated vat from which *ammonium paramagentaleucosulphinate*,



is precipitated by addition of solid ammonium chloride and *paramagentaleucosulphinic acid*, $C_{19}H_{19}O_2N_3S_2H_2O$, is obtained by cautious addition of acetic acid. They are soluble in cold, dilute alkali hydroxide, but decompose rapidly in warm solution into *paraleucoaniline* and sulphite. The neutral solution of the sodium salt is oxidised by air with production of the paramagenta salt of paramagentaleucosulphonic acid; in the presence of an excess of alkali hydroxide the products are leucoaniline, and a mixture of rosaniline and the salt of the leucosulphonic acid. In acid solution, the leucosulphinic acid undergoes autoxidation to paramagenta and sulphurous acid.

The direct conversion of paramagentaleucosulphinic acid into the corresponding sulphinic acid does not appear to be capable of accomplishment.

In a similar manner, aurin is converted into *sodium aurinleucosulphinate*, $C_{19}H_{15}O_5SNa$, which is less stable than the similar compounds which have been described previously. In other respects it resembles these substances very closely. Autoxidation

of the sulphinic acid in alkaline solution leads to the production of sulphite and aurin; the latter is mixed with 4:4'-dihydroxy-benzophenone, so that a benzene nucleus is removed from the dye by the action of atmospheric oxygen. H. W.

The Bromine Reaction of Magenta-sulphurous Acid. G. SCHEUING and O. SCHAAFF (*Ber.*, 1923, 56, [B], 1588—1591).—Guareschi (A., 1913, ii, 333) has shown that magenta-sulphurous acid can be used for the detection of bromine, with which it gives a reddish-violet coloration, whereas chlorine gives a pale yellow coloration and iodine is without action; confusion with the aldehyde reaction is avoided by the use of solutions which do not contain free sulphurous acid.

The action of an excess of cold bromine water on a solution of paramagentaleucosulphonic acid in dilute hydrochloric acid leads to the production of hexabromopararosaniline, which, in part, undergoes further oxidation to tetrabromo-4:4'-diaminobenzophenone. Paramagenta itself behaves in a similar manner. In both cases, bromination appears to proceed directly to the formation of the hexabromo-derivative. In the case of the sulphonic acid, the loss of sulphur dioxide occurs spontaneously from the hexabrominated derivative: $\text{HCl}(\text{H}_2\text{N}\cdot\text{C}_6\text{H}_2\text{Br}_2)_3\cdot\text{C}\cdot\text{SO}_3\text{H} = (\text{H}_2\text{N}\cdot\text{C}_6\text{H}_2\text{Br}_2)_2\text{C}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{NH}\cdot\text{HCl} + \text{H}\cdot\text{SO}_3\text{H}$.

The bromine reaction of Schiff's reagent thus resembles closely the reaction with aldehydes. In both cases, a leucosulphonic acid is formed which decomposes spontaneously into dye and sulphurous acid. A difference is found in the ability of bromine to produce the unstable sulphonic acid immediately, whereas with aldehydes a more stable, partly substituted sulphonic acid is formed as intermediate product. H. W.

Xanthyl Derivatives of Allophanic Acid, Thiosinamine, and Allantoin. R. FOSSE and A. HIEULLE (*Compt. rend.*, 1923, 176, 1719—1721).—The allophanic esters in diluted acetic acid solution condense with xanthidrol to give a xanthyl derivative, m. p.

230°, having the constitution $\text{CO}_2\text{Et}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}\langle\text{C}_6\text{H}_4\rangle\text{O}$.

Like the mono-substituted thiocarbamides, thiosinamine also condenses with xanthidrol, giving a monoxanthyl derivative, which decomposes on heating at 159—165°. Similarly, allantoin gives

xanthylallantoin, $\text{O}\langle\text{C}_6\text{H}_4\rangle\text{CH}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}\langle\text{NH}\cdot\text{CO}\rangle\text{CO}\cdot\text{NH}$, which

crystallises in characteristic tabular crystals, m. p. 214—215°. The above xanthyl derivatives are valuable for the detection and characterisation of the parent substances in biochemical work, and allantoin, for example, was easily identified by means of its xanthyl derivative in the urine of the dog and rabbit, and in the young leaves of the plane tree. G. F. M.

The Influence of Hydrogen-ion Concentration on the Solubility of Uric Acid. II. A. JUNG (*Helv. Chim. Acta*, 1923, 6, 562—593).—In a previous paper (A., 1922, i, 1070) it

was shown that the solubility of uric acid is influenced by the hydrogen-ion concentration, and it is now shown that the results obtained fit in with Michaelis's formula, $\Lambda = \lambda + k\lambda/[H^+]$, where Λ is the total solubility, λ is the partial solubility (the solubility when dissociation is suppressed), and k is the dissociation constant. Although the ammonium salt is the least soluble salt of uric acid, ammonium compounds in the buffer solution do not influence the solubility of uric acid provided p_H is less than 6.8. The solubility of other urates in water corresponds with the hydrogen-ion concentration brought about by the hydrolysis of the salt. A large number of solubility measurements were made at 18° and at 37°, using uric acid and sodium urate in different buffer salt solutions, and it is concluded that the results obtained can generally be interpreted by the mass action law. Uric acid and a urate can exist in solution side by side, but the solubility product of the least soluble urate is never exceeded. The variable results obtained sometimes in urate and uric acid solubility determinations may be accounted for by the slow rate at which equilibrium may be attained between the dissociated and undissociated acid and its salts. Dissociated uric acid and its salts change gradually in salt solutions into the sparingly soluble undissociated acid, and the slowness of this change may lead to apparently irreconcilable results. Sodium urate readily undergoes bacterial decomposition, which is specially rapid in pure water and in sodium phosphate solutions.

E. H. R.

Diazotisation of *p*-Nitroaniline. CHARLES SUNDER and HENRI SUNDER (*Bull. Soc. Ind. Mulhouse*, 1923, 89, 237—240).—The diazotisation of *p*-nitroaniline is most conveniently carried out by quickly adding dilute hydrochloric acid (an excess not greater than one-tenth molecule is used) to a solution containing the theoretical amounts of sodium nitrite and *p*-nitroaniline at 10—14°. An unsatisfactory result is obtained when the addition is made in the reverse order. If the diazotisation of *p*-nitroaniline is effected in the presence of an excess of hydrochloric acid not exceeding one-tenth molecule, the solution thereby obtained may be used for the production of good shades of Para-red without adding sufficient sodium acetate to convert the whole of the diazonium chloride into the corresponding acetate. [Cf. *J.S.C.I.*, 1923, 713A.]

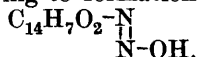
A. J. H.

The Diazonium Hydroxides of Anthraquinone. M. BATTÉ-GAY and J. BÉHA (*Bull. Soc. Ind. Mulhouse*, 1923, 89, 241—246).—By diazotisation of α - and β -aminoanthraquinones and preparation of the corresponding chloroplatinates, chloraurates, and cobaltinitrites, it is shown that anthraquinonediazonium hydroxide exists in the form $C_{14}H_7O_2-N-OH$.

$$\begin{array}{c} ||| \\ N \end{array}$$

A solution of anthraquinonediazonium hydroxide was obtained by the careful addition of barium hydroxide to a solution containing anthraquinonediazonium hydrogen sulphate and subsequently removing, by filtration, the barium sulphate

thereby precipitated. This solution, when freshly prepared at 0°, was alkaline to methyl-orange, Thiazole Yellow, and Dobbin's reagent, but it became acidic within a few minutes (the α -diazonium compound was more stable than the β -compound) owing to formation of the corresponding *antidiaz*-compounds,

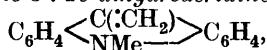


Crystalline compounds were obtained by addition of chloroplatinic acid, chlorauric acid, and sodium cobaltinitrite to solutions containing anthraquinonediazonium hydroxide, a good yield of the chloroplatinate of diazo- α -anthraquinone being thereby quite readily obtained, since it is only slightly soluble in water or dilute alcohol. When sodium chloroplatinate is used instead of chloroplatinic acid, formation of the chloroplatinate of diazoanthraquinone is not complete, since the sodium hydroxide formed in the reaction, converts a portion of the diazonium hydroxide into the *antidiazot*ate which does not form a chloroplatinate.

A. J. H.

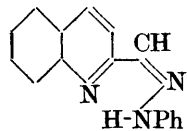
The Mechanism of Coupling Reactions. III. The Production of Azo-dyes from 1-Alkyl-2-methylenedihydroquinolines. W. KÖNIG (*Ber.*, 1923, 56, [B], 1543—1550).—1-Alkyl-2-methylenedihydroquinolines couple readily with diazo-compounds; the alkyl groups are thereby replaced by hydrogen and a class of iminoazo-dyes is produced. Such dyes which contain the nitro-group in the para-position in the diazonium component yield normal yellow hydrochlorides, whereas the corresponding free bases appear to belong to a class of inner hydrogen complex salts which in their colour resemble the alkali conjunction-salts of the *p*-nitrophenylhydrazone of quinoline-2-aldehyde. The azo-dyes and the hydrazones of this class are geometrical isomerides, the former having the *syn*- and the latter the *anti*-configuration.

10-Methyl-5-methylene-5 : 10-dihydroacridine,



pale yellow needles, m. p. 93°, is prepared by the action of sodium hydroxide in the presence of ether on an aqueous solution of 5 : 10-dimethylacridinium perchlorate. In the acridine series, the isolation of the methylene base in substances is thus shown to be possible, whereas this does not appear to be the case in the quinoline series.

2-Benzeneazomethylene-1 : 2-dihydroquinoline (annexed formula)

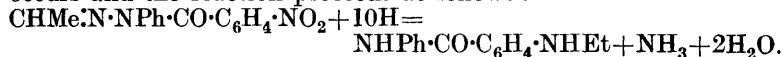


is obtained in the form of its *hydrochloride*, reddish-yellow needles, m. p. 211—212°, by the simultaneous addition of solutions of sodium hydroxide and phenyldiazonium chloride to 2-methylquinoline methiodide dissolved in water; the free base could not be caused to crystallise. 2-*p'*-Nitrobenzene-azomethylene-1 : 2-dihydroquinoline *hydrochloride*, dark red needles, m. p. 241°, is prepared in a similar manner from 2-methylquinoline methiodide, ethiodide, or *isoamyl*iodide; the corresponding free base crystallises in small, almost black needles with a bronze reflex, m. p.

171°. The anti-*p*-nitrophenylhydrazone of quinoline-2-aldehyde, yellowish-brown needles, m. p. 245°, is prepared from its components in boiling alcoholic solution; the corresponding sodium salt, the hydrochloride, tile-red needles, m. p. 258°, and the sulphate are described. H. W.

The Action of Halogens on Phenylhydrazones. I. The Action of Bromine. JAMES ERNEST HUMPHRIES, EDWARD BLOOM, and ROY EVANS (T., 1923, 123, 1766—1772).

Migration of Alkyl and Alpharyl Residues in the Reduction of Nitrobenzoylphenylhydrazones. GEORG LOCKEMANN (Z. angew. Chem., 1923, 36, 349—351).—The action of *p*-nitrobenzoyl chloride on phenyl- α -ethylidenehydrazine [acetaldehydephenylhydrazone] in the presence of pyridine and complete absence of moisture yields a *p*-nitrobenzoylphenylethylidenehydrazine melting at 116—116.5° (cf. Lockemann and Liesche, A., 1906, i, 111). This, when reduced with zinc dust and sulphuric acid, does not give rise to *p*-aminobenzanilide and ethylamine, but migration occurs and the reaction proceeds as follows:



This migration may be intramolecular, or intermolecular with the intermediate formation of a Schiff's base. α -*p*-Nitrobenzoyl-*p*-tolyl- β -ethylidenehydrazine (m. p. 149—150°) and the *p*-nitrobenzoyl derivative of phenylpropylidenehydrazine behave just like the above when reduced with zinc and sulphuric acid. In the case of the *p*-nitrobenzoylphenylbenzylidenehydrazines the acid used largely determines the course of the reaction. With zinc and sulphuric acid the *p*-compound yields mainly, and the *o*- and *m*-compounds only, aminobenzanilide and benzylamine, whilst, if acetic acid is used instead of sulphuric, a considerable proportion of benzylaminobenzanilide is formed, the reaction proceeding in the latter sense to the extent of 42% with the ortho-compound, 35% with the meta-compound, and 60% with the para-compound. W. T. K. B.

Enantiotropic Transformation of Phthalylphenylhydrazide. FUSAO ISHIKAWA (Bull. Inst. Phys. Chem. Res. [Rikwagaku Kenkyujo Iho], 1923, 2, 264—267).—Chattaway and Lambert (T., 1915, 107, 1773) determined the solubility of phthalylphenylhydrazide in chloroform, ethyl acetate, and acetone and found its transition point to be 9.5°. From the solubility data, the author has calculated the heat of transition, the transition point, and the transition affinity of the compound. The heat of transition of 1 g. of the light yellow modification into the deep yellow one at 9.5° in chloroform is 2.72 cal. and in ethyl acetate 2.89 cal. From the solubility in chloroform at 5° and 15°, the transition point was calculated to be 9.4°. From the solubility in chloroform, the transition affinity per 1 g. molecule was calculated as follows: For the change $\beta \rightarrow \alpha$, 5.75 cal. at 5°, 2.38 cal. at 8°, and 1.26 cal. at 9°. For the change $\alpha \rightarrow \beta$, 1.78 cal. at 10°, 2.28 cal. at 11°, 7.41 cal. at 15°, and 21.49 cal. at 25°.

From the solubilities at 25°, the transition affinities in chloroform,

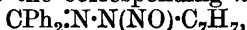
ethyl acetate, and acetone per 1 g. molecule are 21.49, 21.35, and 21.98 cal. respectively.

K. K.

Nitrosohydrazones. II. M. BUSCH and S. SCHÄFFNER (*Ber.*, 1923, **56**, [B], 1612—1616).—It has been shown previously that the nitroso-derivatives of aldehydrazones are nitrosoamines, and that their conversion into nitroaldehydrazones is due to the migration of the nitroso-group from nitrogen to carbon. In nitrosoketo-hydrazones, the nitroso-group shows a similar tendency to change its place in the molecule, so that, by union with another atom of oxygen, nuclear nitration ensues. In this manner, nitrosobenzophenonephenylhydrazone, $\text{CPh}_2\text{:N}\cdot\text{NPh}\cdot\text{NO}$, yields benzophenone-*p*-nitrophenylhydrazone, $\text{CPh}_2\text{:N}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$. The properties of the latter substance are very similar to those of the compound obtained by Bamberger, Schmidt, and Levinstein (*A.*, 1900, **i**, 566) from diazotised aniline and nitromethane in alkaline solution, and considered by them to be benzeneazonitrodiphenylmethane, $\text{NO}_2\cdot\text{CPh}_2\text{:N}\cdot\text{NPh}$. Re-examination of the reaction has shown that the ultimate product is benzophenone-*p*-nitrophenylhydrazone, which results from the isomerisation of primarily formed benzeneazonitrodiphenylmethane by boiling alcohol used in its purification.

A series of further examples of the conversion of nitrosoketo-hydrazones into nuclear nitrated hydrazones is given.

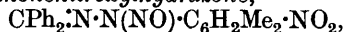
Benzophenone-p-tolylhydrazone, pale yellow leaflets or large plates, m. p. 88° , is converted by sodium nitrite in the presence of glacial acetic acid into the corresponding *nitrosoamine*,



lemon-yellow needles, m. p. 108° after darkening at 98° and softening with evolution of nitrous fumes above 100° . When dissolved in ether containing a little acetic acid, the nitrosoamine gradually passes at the atmospheric temperature into *benzophenone-o-nitro-p-tolylhydrazone*, $\text{CPh}_2\text{:N}\cdot\text{NH}\cdot\text{C}_7\text{H}_6\cdot\text{NO}_2$, pale red, transparent leaflets, m. p. 164° . The nitro-compound is reduced by zinc dust and acetic acid to *benzophenone-o-amino-p-tolylhydrazone*, yellow leaflets, m. p. 202° .

Benzophenone-o-tolylhydrazone, pale yellow, cubic crystals, m. p. 102° , is converted by sodium nitrite and glacial acetic acid into *benzophenone-p-nitro-o-tolylhydrazone*, straw-yellow, prismatic rods, m. p. 176° .

Benzophenone-as-m-xyllylhydrazone, pale yellow, lustrous needles, m. p. 84° , is transformed by nitrous acid into the *nitrosoamine*, $\text{CPh}_2\text{:N}\cdot\text{N}(\text{NO})\cdot\text{C}_8\text{H}_9$, lustrous, orange-yellow prisms, m. p. 104° (a diazonium salt is simultaneously produced by fission of the hydrazone). When dissolved in benzene and treated with alcoholic hydrogen chloride, the nitrosoamine is converted into the *nitrosoamine* of *benzophenonenitroxylhydrazone*,



lustrous, blood-red needles, m. p. 119 — 120° (decomp.). H. W.

Tetrazones from Hydrazones and Azo-compounds. M. BUSCH, HELMAT MÜLLER, and EUGEN SCHWARZ (*Ber.*, 1923, **56**, [B], 1600—1612).—It has been shown previously that benzalde-

hydephenylhydrazone unites readily with benzeneazobenzoyl to give an unstable tetrazen derivative which readily passes into the stable hydrazinohydrazone or becomes converted into the formazyl derivative (cf. Busch and Kunder, A., 1917, i, 56). Similar observations are now recorded with a series of similar azo-compounds.

The action of azodibenzoyl on benzaldehydephenylhydrazone in ethereal solution leads to the production of $\gamma\delta$ -dibenzoyl- β -phenyl- α -benzylidenetetrazen, $\text{CHPh}\cdot\text{N}\cdot\text{NPh}\cdot\text{NBz}\cdot\text{NHBz}$, yellow needles, m. p. 139°. It is readily reduced to benzaldehydephenylhydrazone and dibenzoylhydrazine. When heated slightly above its melting point or when treated with boiling alcohol containing a little hydrochloric acid, it becomes isomerised to *dibenzoylhydrazinobenzaldehydephenylhydrazone*, $\text{NHPh}\cdot\text{N}\cdot\text{CPh}\cdot\text{NBz}\cdot\text{NHBz}$, colourless needles, m. p. 192°; the constitution of the substance is deduced from its hydrolysis to tribenzoylhydrazine and phenylhydrazine. The tetrazen is not affected by ammonia or pyridine.

The interaction of azodibenzoyl with benzaldehyde-*p*-bromophenylhydrazone in cold ethereal solution gives rise to *dibenzoylhydrazinobenzaldehyde-p-bromophenylhydrazone*, colourless, crystalline needles, m. p. 200°, as isolatable product; it is hydrolysed to tribenzoylhydrazine and *p*-bromophenylhydrazine.

Azodibenzoyl reacts with the β - and α -forms of acetaldehydephenylhydrazone to give β -dibenzoylphenylethylidenetetrazen, $\text{CHMe}\cdot\text{N}\cdot\text{NPh}\cdot\text{NBz}\cdot\text{NHBz}$, lustrous yellow needles, m. p. 158°, and α -dibenzoylphenylethylidenetetrazen, yellow needles, m. p. 144–145°. The β -variety readily passes into the α -isomeride under the influence of ammonia in alcoholic solution. Either form is converted by hydrochloric acid in the presence of alcohol into *dibenzoylhydrazinoacetaldehydephenylhydrazone*, $\text{NHPh}\cdot\text{N}\cdot\text{CMe}\cdot\text{NBz}\cdot\text{NHBz}$, needles, m. p. 178–179°.

Acetophenone- and benzophenone-phenylhydrazones do not appear to react with azodibenzoyl.

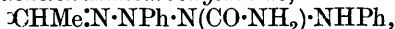
The catalytic aid of hydrogen is necessary for the combination of hydrazones with ethyl phenylazocarboxylate. The latter substance unites with benzaldehydephenylhydrazone to give *ethyl $\beta\delta$ -diphenyl- α -benzylidenetetrazen- γ -carboxylate*,

$\text{CHPh}\cdot\text{N}\cdot\text{NPh}\cdot\text{N}(\text{CO}_2\text{Et})\cdot\text{NHPh}$,
yellow needles, m. p. 124–125° (slight decomp.). It is readily reduced by zinc dust and acetic acid to ethyl phenylhydrazinecarboxylate and benzaldehydephenylhydrazone. It is relatively very stable towards acids. When treated with a little potassium hydroxide in the presence of alcohol it is converted into 4-anilino-1 : 3-diphenyltriazolone, $\text{NPh}\cdot\text{CO} > \text{N}\cdot\text{NHPh}$, lustrous needles, m. p. 175°.

Ethyl diphenylethylidenetetrazen-carboxylate,
 $\text{CHMe}\cdot\text{N}\cdot\text{NPh}\cdot\text{N}(\text{CO}_2\text{Et})\cdot\text{NHPh}$,
crystallises in yellow needles, m. p. 105–106°; it is obtained from either form of the acetaldehydephenylhydrazone. It is moderately stable towards mineral acids, but appears to be converted by alkali hydroxide into a formazyl derivative which could not be caused to crystallise.

Phenylazoacetaldehydeoxime shows the least tendency among acylazo-compounds to yield tetrazans. It unites, however, with β -acetaldehydephenylhydrazone in ethereal solution in the presence of a little acetic acid to give *diphenylethylidenetetrazanacetaldehydeoxime*, $\text{CHMe}\cdot\text{N}\cdot\text{NPh}\cdot\text{N}(\text{CMe}\cdot\text{N}\cdot\text{OH})\cdot\text{NHPh}$, orange-yellow needles, m. p. 83° ; under the influence of glacial acetic acid, this compound is also produced from α -acetaldehydephenylhydrazone.

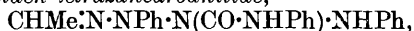
Diphenylethylidenetetrazancarboxylamide,



yellow leaflets, m. p. 164° , is produced from phenylazocarboxylamide and β -acetaldehydephenylhydrazone in neutral, alcoholic solution or from the corresponding α -compound in the presence of a trace of hydrochloric acid. It is converted in boiling alcoholic solution to which a little potassium hydroxide or hydrochloric acid has been added into 4-anilino-1-phenyl-3-methyltriazolone, $\begin{matrix} \text{NPh}\cdot\text{CO} \\ \text{N}=\text{CMe} \end{matrix} > \text{N}\cdot\text{NHPh}$,

small, colourless needles, m. p. 148° ; the corresponding nitroso-derivative crystallises in pale yellow needles, m. p. 68° .

Diphenylethylidenetetrazancarbanilide,

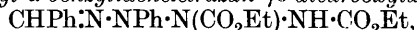


lustrous, yellow needles, m. p. 158° , is most conveniently prepared by heating acetaldehydephenylhydrazone and phenylazocarbanilide on the steam-bath until a clear, molten product is obtained. It is converted by boiling alcoholic hydrogen chloride into 2-acetyl-1:4-diphenylsemicarbazide, $\text{NHPh}\cdot\text{NAc}\cdot\text{CO}\cdot\text{NHPh}$, colourless needles, m. p. 179 — 180° . *Diphenylbenzylidenetetrazancarbanilide*, $\text{CHPh}\cdot\text{N}\cdot\text{NPh}\cdot\text{N}(\text{CO}\cdot\text{NHPh})\cdot\text{NHPh}$, crystallises in small, yellow needles, m. p. 133° (decomp.). It is transformed by alcoholic potassium hydroxide solution into diphenylanilino-triazolone, m. p. 175 — 176° , and a formazyl derivative which was not isolated in a homogeneous condition. Acetonephenylhydrazone and phenylazocarbanilide yield *diphenylisopropylidenetetrazancarbanilide*,



small, yellow needles, m. p. 150° (decomp.) in small yield.

Ethyl β -phenyl- α -benzylidenetetrazan- $\gamma\delta$ -dicarboxylate,



pale lemon-yellow needles, m. p. 106° , is readily prepared from benzaldehydephenylhydrazone and ethyl azodicarboxylate. It is readily converted by alkali hydroxides or mineral acids into *ethyl ketodiphenyltetrahydrotetrazinecarboxylate*, $\text{CO}_2\text{Et}\cdot\text{N} < \begin{matrix} \text{CPh}=\text{N} \\ \text{NH}-\text{CO} \end{matrix} > \text{NPh}$,

colourless, lustrous leaflets, m. p. 149 — 150° , which is indifferent towards nitrous acid and highly resistant towards hydrolysis. *Ethyl β -phenyl- α -m-nitrobenzylidenetetrazan- $\gamma\delta$ -dicarboxylate*, yellow prisms, m. p. 159 — 160° (decomp.), is converted in a similar manner into *ethyl ketophenyl-m-nitrophenyltetrahydrotetrazinecarboxylate*, colourless needles, or hexagonal leaflets, m. p. 179 — 180° . *Ethyl β -phenyl- α -o-hydroxybenzylidenetetrazan- $\gamma\delta$ -dicarboxylate* forms pale yellow crystals, m. p. 147 — 148° , depending on the rate of heating, whereas *ethyl ketophenyl-o-hydroxyphenyltetrahydrotetrazinecarboxylate* crystallises in aggregates of needles, m. p. 184 — 185° . *Ethyl*

β -phenyl- α -ethylidenetetraza- $\gamma\delta$ -dicarboxylate is obtained from α - or β -acetaldehydephenylhydrazone as a viscous, red liquid, which is converted by hydrochloric acid into *ethyl ketophenylmethyltetrahydrotetrazinecarboxylate*, small, colourless needles, m. p. 112°.

Ethyl azodicarboxylate does not show any tendency to unite with ketonehydrazones.

Ethyl β -o-tolyl- α -benzylidenetetraza- $\gamma\delta$ -dicarboxylate, yellow prisms or plates, m. p. 145° (or +C₆H₆, m. p. 112—113°), is converted by potassium hydroxide or hydrochloric acid in alcoholic solution into *ethyl ketophenyl-o-tolyltetrahydrotetrazinecarboxylate*, colourless, lustrous needles, m. p. 93—94° after softening at 90°. *Ethyl β -o-tolyl- α -hydroxybenzylidenetetraza- $\gamma\delta$ -dicarboxylate* crystallises in small, yellow prisms, m. p. 104—106°, whereas *ethyl keto-o-hydroxyphenyl-o-tolyltetrahydrotetrazinecarboxylate* forms colourless needles, m. p. 178°.

H. W.

The Behaviour of the Most Important Proteins, Ferments, and Toxins towards Aluminium Hydroxide. M. A. RAKUZIN (*Ber.*, 1923, 56, [B], 1385—1388).—Amphoteric aluminium hydroxide does not behave exclusively as an adsorbent towards the most important proteins. Normal adsorption occurs only with the casein molecule; in other cases, fission of the protein molecule is usually observed. Very characteristic decomposition is observed with technical pepsin, chondrin, and antidiabetic serum, which leads to the isolation of pure substances and to their quantitative estimation (cf. A., 1917, i, 181, 427). In general, the processes occur quantitatively within twenty-four hours if anhydrous aluminium hydroxide is employed; otherwise adsorption is not complete even in aqueous solution. The action of aluminium hydroxide is due to its amphoteric nature, since ferric hydroxide or oxide has no action on similar solutions under identical conditions. Towards alcoholic extracts aluminium hydroxides exert a peculiar selective action, causing the successive elimination of complex after complex from the protein derivatives down to the associated crystalline carbohydrates.

H. W.

The Hydrolysis of Proteins by Dilute Acids. N. ZELINSKI and W. SADIKOV (*Biochem. Z.*, 1923, 138, 156—160).—Catalytic hydrolysis of proteins is effected by the use of dilute hydrochloric acid (1—2%) at 180° in an autoclave. Hydrolysis is as complete in two to six hours as when excess of strong acids is used at lower temperatures and for longer periods, and little or no coloured decomposition products are formed. Whole organs and small entire animals (mice, guinea-pigs, small dogs, and cats) treated in this way are completely broken down, and in addition to the usual amino-acids and peptides, anhydrides (diketopiperazines) have been obtained. The hydrolytic product thus prepared from whole organs is a convenient nutrient medium for bacteria. J. P.

Amount of Tryptophan in Various Proteins. YOSHIHIKO MATSUYAMA and TAKEJIRO MORI (*J. Chem. Soc. Japan*, 1923, 44, 377—381).—The authors have improved May and Rose's method of estimating tryptophan (this vol., i, 160). 0.1 G. of the sample

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is placed in an Erlenmeyer flask, 2 c.c. of 0.2% sodium hydroxide solution are added; the flask is warmed at 40—50°, cooled; 100 c.c. of hydrochloric acid (1 : 1) and 1 c.c. of Ehrlich's reagent are added, heated at 25° for twenty-four hours, and set aside for twenty-four to forty hours. The blue colour thus produced is compared with that of casein, treated in the same manner, assuming the content of tryptophan in casein to be 1.5%. Estimations of tryptophan in various proteins by the old and new methods respectively gave the following results: beef protein, 1.20, 1.28; tunny protein, 1.18, 1.01; salmon protein, 1.03, 0.92; scallop protein, 1.18, 1.09; syntonin, 0.63, 0.82; serum-albumin, 1.62, 1.45; fibrin, 1.71, —; hæmoglobin, 1.80, —; egg albumin, 1.18, 1.11; fibroin, trace, trace; mucin, 0, 0; gelatin, 0, 0; globulin, 1.62, 1.52; soja bean protein, 0.82, —; rice protein, 1.33, —; edestin, 1.46, 1.40; legumin, 0.94, 0.67; conglutin, 1.45, 1.28; wheat gluten, 1.00, 0.95; zein, 0, 0; protein of *Fagopyrum esculentum*, 0.68, 0.83%; and protein of pine nut, 0, trace.

K. K.

Preparation of Tryptophan from the Products of Hydrolysis of Lactalbumin with Baryta. HENRY C. WATERMAN (*J. Biol. Chem.*, 1923, **56**, 75—77).—The lactalbumin (200 g.) is hydrolysed by heating at about 85° for forty hours with a solution of baryta (700 g.) in water (4 litres). The tryptophan is then isolated from the product by means of Hopkins and Cole's mercuric sulphate reagent. Baryta hydrolysis possesses certain advantages over trypsin digestion; it is quicker and it renders the isolation process simpler since cystine is destroyed.

E. S.

Effect of Ultra-violet Rays on Protein Solutions. RUDOLF MOND (*Pflüger's Archiv*, 1922, **196**, 540—559; from *Chem. Zentr.*, 1923, i, 559).—Ultra-violet radiation increases the stability of globulin and fibrinogen solutions, whilst the stability of albumin solutions is diminished. The reaction of serum-globulin and albumin solutions is rendered more acid, whilst the surface tension shows a decrease which is least in the case of albumin. Viscosity increases owing, probably, to the formation of aggregates.

G. W. R.

A Spontaneous Crystallisation of a Bence-Jones Protein. D. WRIGHT WILSON (*J. Biol. Chem.*, 1923, **56**, 203—214).—A case is recorded in which a Bence-Jones protein crystallised spontaneously from the urine. Of the total nitrogen of the protein, 4.86% was present as free amino-nitrogen; this small percentage is additional evidence in favour of classing the compound as a protein and not as an albumose.

E. S.

Physical Chemistry of the Proteins. II. The Relation between the Solubility of Casein and its Capacity to Combine with Base. The Solubility of Casein in Systems containing the Protein and Sodium Hydroxide. EDWIN J. COHN and JESSIE L. HENDRY (*J. Gen. Physiol.*, 1923, **5**, 521—553; cf. *A.*, 1922, i, 882).—Measurements have been made of the solubility

of highly purified casein in solutions of sodium hydroxide. It appears that the solubility represents the sum of the solubility of the protein molecule itself along with that of the caseinate-ion, which would seem to be doubly charged. On these assumptions, it is found that the solubility of casein is approximately 0.09 g. per litre at 25°, and that the product of the two dissociation constants of casein, K_a and K_b , is 24×10^{-12} . Each gram-molecule of sodium hydroxide combines with 2100 g. of casein. W. O. K.

A New Sulphur-containing Amino-acid Isolated from the Hydrolytic Products of Protein. J. HOWARD MUELLER (*J. Biol. Chem.*, 1923, **56**, 157—169).—The sulphur-containing product isolated from the hydrolytic products of casein, which appeared to be required for growth by hæmolytic streptococci (*J. Bact.*, 1922, **7**, 309, 325), has been found to lose its growth-promoting properties on purification. The pure substance is an *amino-acid*, $C_5H_{11}O_2NS$, hexagonal plates, m. p. (decomp.) 283° (uncorr.) after darkening at 278°, $[\alpha]_D^{20} -7.2^\circ$ in aqueous solution (partial racemisation may have occurred during the extraction process), and is isomeric with ethylcysteine. It forms a *naphthylcarbamide-derivative*, short needles, m. p. 186° (uncorr.), a *copper salt*, $(C_5H_{10}O_2NS)_2Cu$, hexagonal plates, and a precipitate with mercuric chloride which has approximately the composition



The isolation of the new amino-acid is troublesome owing to the difficulty of separating it from phenylalanine and glutamic acid. An isolation process has, however, been elaborated whereby yields of 0.2 to 0.4% have been obtained from casein, egg-albumin, edestin, and wool; gelatin gives much smaller yields. The isolation process is described in detail in the original; it consists essentially of hydrolysis of the protein by sulphuric acid or sodium hydroxide, precipitation of the amino-acid by mercuric sulphate, and, after recovery, precipitation by mercuric chloride. When recovered from the latter it is in a moderately pure condition; further purification, with considerable loss, may be effected by repeating the precipitation with mercuric chloride. The structure of the compound has not, so far, been determined. The sulphur is more firmly bound than in cysteine; it does not give the nitroprusside reaction, neither does it blacken lead. The amino-group is probably in the α -position, since the nitrogen is given off quantitatively in three minutes in Van Slyke's apparatus. The evidence at present available points to the compound being a primary cleavage product of proteins. E. S.

Adsorption and Hæmoglobin. A. V. HILL (*Nature*, 1923, **111**, 843—844).—The specific colour changes which occur when reduced blood or hæmoglobin is shaken with oxygen or carbon monoxide support the theory of chemical change as against that of adsorption. The deduction from the phase rule that oxygen and reduced hæmoglobin are not separate chemical compounds is valid only if the hæmoglobin unit itself is a separate phase; this is purely hypothetical. Facts are briefly stated to show that the

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union of hæmoglobin with carbon dioxide is, in fact, of a different nature from that with oxygen (cf. Bayliss, this vol., i, 618).

A. A. E.

Adsorption and Hæmoglobin. N. K. ADAM (*Nature*, 1923, **111**, 844—845).—A reply to Bayliss (this vol., i, 618). A. A. E.

Valency Rule and Alleged Hofmeister Series in the Colloidal Behaviour of Proteins. I. The Action of Acids. II. The Influence of Salts. JACQUES LOEB and M. KUNITZ (*J. Gen. Physiol.*, 1923, **5**, 665—691, 693—707).—The previous work of Loeb is confirmed and extended. The influence of acids on the four properties of gelatin (membrane potentials, osmotic pressure, swelling, and viscosity) depends on the valency and strength of the acid and not on the particular anion. If the p_H is taken into account, the Hofmeister series is not valid. In the same way, on the acid side of the isoelectric point, the effect of salts depends on the valency of the anion and not on its chemical nature, and not at all on the kation.

W. O. K.

The Theory of Negative Adsorption. III. The Adsorption of Sodium Chloride and other Compounds by Gelatin. M. A. RAKUZIN and (MLLE) TATIANA ALFR. HENKE (*J. Russ. Phys. Chem. Soc.*, 1922, **54**, 248—256).—In order to test the well-established view that dry gelatin absorbs water when brought into contact with aqueous solutions of different substances and thus causes an increase in the concentration of the solution, 3% by weight of dry gelatin was introduced into a variety of aqueous solutions of both crystalloids and colloids. It was found in all cases that although the concentration of the solution rose after twenty-four hours' contact with gelatin, the increase was due to the passage of gelatin into the solution; this was confirmed by careful experiments on the action of gelatin on solutions of sodium chloride at different concentrations; in no case could the crystallisation of a saturated salt solution be induced by contact with gelatin. Attempts to induce the crystallisation of saturated solutions of ammonium chloride and barium chloride by the repeated addition of gelatin (up to 9%) were equally unsuccessful. G. A. R. K.

The Theory of Negative Adsorption. IV. The Action of Gelatin on some Acids. M. A. RAKUZIN and (MLLE) TATIANA ALFR. HENKE (*J. Russ. Phys. Chem. Soc.*, 1922, **54**, 256—258).—Using an experimental method similar to that previously described (preceding abstract), the authors have studied the action of gelatin on solutions of four inorganic and five organic acids. The results clearly suggest an interaction, probably with the formation of salt-like complexes, in all the cases examined.

G. A. R. K.

An Albumose from Wool. LEON MARCHLEWSKI and (MLLE) A. NOWOTNÓWNA (*Istny Zjazd Chemików Polskich*, 1923, 26).—A small amount of albumose, giving all the ordinary reactions for albumoses, is obtained by the hydrolysis of wool with solutions of calcium or barium hydroxide.

R. T.

The Active Principle of Pepsin. M. A. RAKUZIN and S. L. IVANOV (*J. Russ. Phys. Chem. Soc.*, 1922, **54**, 234—242).—The extraction of dry preparations of pepsin with 95% alcohol for three days leads to a loss in weight of 87.46%. The insoluble residue is nitrogenous and has proteolytic properties, its activity being about one-half that of the original pepsin, in spite of the prolonged heating with alcohol. The portion soluble in alcohol is non-nitrogenous, has no action on proteins, and is shown to consist of inositol; it has m. p. 176—177°, $[\alpha]_D +45.35^\circ$ after purification.

The nitrogenous constituent of pepsin can, apparently, also be separated from pepsin solutions by adsorption by means of alumina, a constant fraction of the original solid (12.4%) being removed from the solution, and the carbohydrate constituent being left.

The nitrogen in the active principle of pepsin appears to be combined in the form of lecithin or nucleoprotein. G. A. R. K.

The Products of the Digestion of Blood Pigment by Pepsin. A. DMOCHOWSKI (*Istov Zjazd Chemików Polskich*, 1923, 58—59).—Quantitative determinations are made of the products of digestion with pepsin of blood and of oxyhæmoglobin derived from horse blood. The production of digestive hæmatin from the latter is found to be 4.3%, thus confirming the results of Schultz and Zawrow. It was not found possible to determine quantitatively the percentage of hæmatin produced from blood, owing to the difficulty of separating fatty and cellular materials from the latter.

R. T.

The Effect of Radioactive Radiations and X-Rays on Enzymes. I. The Effect of Radiations from Radium Emanation on Solutions of Trypsin. RAYMOND G. HUSSEY and WILLIAM R. THOMSON (*J. Gen. Physiol.*, 1923, **5**, 647—659).—The decomposition of trypsin by radium emanation is a unimolecular reaction, and the rate of destruction is proportional to the concentration of trypsin and to the quantity of emanation.

W. O. K.

Hydrolysis of Collagen by Trypsin. ARTHUR W. THOMAS and F. L. SEYMOUR-JONES (*J. Amer. Chem. Soc.*, 1923, **45**, 1515—1522).—A study has been made of the hydrolysis of collagen by means of trypsin, by controlling the acidity during digestion and pre-treatment, and examining the effects of varying the time of digestion, concentration of enzyme, and size of the collagen particles. The optimum hydrion concentration for the hydrolysis is found to be at P_H 5.9. Pre-treatment of the collagen in solutions of various degrees of acidity does not influence the subsequent tryptic digestion. The speed of hydrolysis increases as the size of the collagen particles decreases, the reaction probably occurring at the surface. Hydrolysis increases with increasing concentration of trypsin, but is never complete under the limits of experimental conditions. The hydrolysis-time curve shows slight reversibility. It is pointed out that the hydrolysis of soluble proteins by means of trypsin is probably a surface reaction, the proteins being merely colloiddally dispersed, rather than in true solution.

W. S. N.

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The Composition and Properties of Papain. M. A. RAKUZIN and S. L. IVANOV (*J. Russ. Phys. Chem. Soc.*, 1922, **54**, 243—247).—Papain differs from pepsin in giving the Adamkiewicz reaction for tryptophan; the Ostromisslenski reaction, which pepsin gives to a small extent, is well marked, whilst Molisch's reaction is common to both ferments; the Liebermann reaction is negative. The rotation of papain is $+32.9^\circ$. Its behaviour towards organic "tanning" agents is characteristic: formaldehyde, phenol, and α -naphthol react with the whole of the nitrogen, and the solution after treatment with these reagents still gives a coloration with Molisch's reagent for carbohydrates, but the Adamkiewicz and Ostromisslenski tests are negative. Picric acid reacts only with tryptophan, affecting the Adamkiewicz test alone; β -naphthol has no action on papain.

Papain contains no iron; chlorine, phosphorus, and sulphur (as cystine) are present. Unlike pepsin, papain is not adsorbed by alumina. Extraction of the dry substance with 95% alcohol removes 69%; the residue does not give the Ostromisslenski reaction; the extract contains a crystalline substance melting at 179° .
G. A. R. K.

Enzyme Action. XXIII. The Spontaneous Increase in Saccharase Activity of Banana Extracts. GRACE MCGUIRE and K. GEORGE FALK (*J. Amer. Chem. Soc.*, 1923, **45**, 1539—1551).—The saccharase extracts are prepared by grinding banana pulp with solutions of different salts, the ratio of g. of pulp to c.c. of solution being 2:1. During the slow filtration of the mixture, toluene is generally added as a preservative; the extracts are subsequently dialysed to remove most of the salts. The saccharase action, as measured by incubating the enzyme preparation, suitably diluted, with sucrose solutions for one to four hours at $37.5 \pm 0.05^\circ$, and determining the reducing substances with Fehling's solution, increases on keeping, even at low temperatures (5 — 10°) from 40—100%, and then decreases. This behaviour is independent of the composition of the extracting solution, or of the preservative used. Banana cells and bacteria are absent during the period of change. An alteration in the hydrogen-ion concentration is insufficient to account for the phenomenon, because an extract made using 0.6*M*-magnesium sulphate, filtered during less than one hour, and dialysed for two to three hours against tap water, had P_H 5.0, and no change in this value, as measured by means of indicators, could be detected on keeping. That the change in hydrogen-ion concentration, necessary to account for the increase in activity, could be detected by means of the indicators used is shown by a series of experiments, using the extract mentioned, in which the effect, on the ageing of the extract, of added hydrochloric acid, sodium hydroxide solution, or citrate buffer solution is studied. A previous observation (*J. Gen. Physiol.*, 1921, **3**, 595; *J. Biol. Chem.*, 1922, **54**, 655), that for the maximum saccharase activity of banana extracts there is an optimum P_H zone between 3.5 and 5.0, is confirmed.

The explanation favoured is that banana extracts contain material which "spontaneously" forms new enzyme, but that, once formed, banana saccharase loses its activity steadily. This accounts both for the initial increase and for the occurrence of a maximum of activity. W. S. N.

Lipase. II. A Comparison of the Hydrolysis of the Esters of the Dicarboxylic Acids by the Lipase of the Liver.

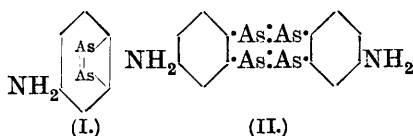
ELIZABETH C. HYDE and HOWARD B. LEWIS (*J. Biol. Chem.*, 1923, 56, 7—15).—Ethyl glutarate and ethyl adipate are completely hydrolysed by lipase from pig's liver, thus differing from ethyl malonate and ethyl succinate, which are only hydrolysed as far as the half ester (cf. Christman and Lewis, A., 1921, i, 755). If, in the case of the two former esters, the acid liberated in the early stages of the hydrolysis is neutralised with sodium hydroxide, the action stops when 50% of the ester has been hydrolysed. Adipic acid was isolated from the product in such a case. The rates of hydrolysis by lipase of the above four esters increase with the molecular weight of the ester. E. S.

Existence of Arsino-magnesium Compounds. ANDRÉ JOB and RENÉ REICH (*Compt. rend.*, 1923, 177, 56—58).—Phenylarsine (1 mol.) and magnesium ethyl bromide (2 mols.) interact in ethereal solution to give ethane (2 mols.) and the oily *arsino-magnesium* compound, $\text{AsPh}(\text{MgBr})_2$. This substance, which is readily oxidised, and is decomposed by water to give phenylarsine, is apparently converted by carbon dioxide into the compound, $\text{AsPh}(\text{CO}_2\text{MgBr})_2$, which is decomposed even by water, regenerating the arsine. Ethyl chloroformate converts the *arsino-magnesium* compound into the *ester*, $\text{AsPh}(\text{CO}_2\text{Et})_2$, a colourless oil, b. p. 180—183°/20 mm., and apparently stable in air. Hydrolysis with alkali regenerates phenylarsine. E. E. T.

Aromatic Diarsinic Acids and their Reduction Products.

III. H. LIEB and O. WINTERSTEINER (*Ber.*, 1923, 56, [B], 1283—1291).—A continuation of previous work (cf. Lieb, A., 1921, i, 696; Lieb and Wintersteiner, this vol., i, 408).

4-Nitrophenylene-1 : 2-diarsinic acid, $\text{NO}_2\cdot\text{C}_6\text{H}_3(\text{AsO}_3\text{H}_2)_2\cdot\text{H}_2\text{O}$, long, prismatic needles, is prepared by diazotising 5-nitro-2-amino-phenylarsinic acid and treatment of the product with alkaline sodium arsenite solution in the presence of a little copper powder; it is conveniently purified by means of the zinc salt. When heated above 100° it passes into the corresponding *anhydride*. The nitro-acid is reduced by ferrous chloride to **4-aminophenylene-1 : 2-diarsinic acid**, $\text{C}_6\text{H}_9\text{O}_6\text{NAs}_2\cdot\text{H}_2\text{O}$, the zinc salt and the *anhydride* of which have been prepared. Complete reduction of the amino-acid



by hypophosphorous acid leads to the production of **4-amino-1 : 2-arsenobenzene** or **4 : 4'-diamino-1 : 2 : 1' : 2'-diarsenodibenzene** (annexed formulæ I or II), a yellow, amorphous

substance, the *hydrochloride* of which is described. The decision

between the alternative formulæ could not be effected by determinations of the molecular weight, since it yields a colloidal solution in pyridine, which is the only available solvent.

2-Hydroxyphenylene-p-diarsinic acid, colourless or pale pink rhombic leaflets, which becomes discoloured at 220° , but does not melt or decompose below 315° , is obtained by diazotising 2-aminophenylene-*p*-diarsinic acid and heating the product with water. When reduced with hypophosphorous acid, it gives 2-hydroxy-1:4-arsenobenzene or 2:2'-dihydroxy-1:4:1':4'-diarsenodibenzene, a reddish-brown, amorphous substance which is fairly stable towards air when dry, but is exceptionally readily oxidised in solution.

2-Chlorophenylene-p-diarsinic acid, $C_6H_5O_6ClAs_2 \cdot 0.5H_2O$, colourless, rhombic leaflets which soften and become discoloured at 210° but do not melt below 315° , is prepared by the action of copper bronze on a diazotised solution of 2-aminophenylene-*p*-diarsinic acid in the presence of hydrochloric acid, and is purified conveniently by means of its zinc salt. It may be also obtained by diazotising 3-chloro-4-aminophenylarsinic acid and coupling the product with sodium arsenite, but the yields are very poor. It is reduced by hypophosphorous acid to an amorphous, yellow product which appears to be 2-chloro-1:4-arsenobenzene or 2:2'-dichloro-1:4:1':4'-diarsenodibenzene.

2-Bromophenylene-p-diarsinic acid, $C_6H_5O_6BrAs_2 \cdot 0.5H_2O$, is prepared in the same manner as the corresponding chloro-derivative.

H. W.

Preparation of Hydroxides and Oxides of Triarylstibine.

LUDWIG KAUFMANN (D.R.-P. 360973; from *Chem. Zentr.*, 1923, ii, 336).—Triarylstibines, in solution or in suspension, are treated with peroxides in the presence or absence of catalysts such as metals, salts, or metallic oxides. For example, triphenylstibine gives with 3% hydrogen peroxide in the presence of dilute potassium hydroxide solution, or with sodium peroxide, *triphenylstibine hydroxide*; it forms crystals, m. p. 212° . *p-Tritolylstibine hydroxide* has m. p. 225° ; the *acetate* has m. p. about 165° .

G. W. R.

Physiological Chemistry.

Physiological Action of Proteinogenic Amines. VII. The Influence of Di-iodotyrosine, Di-iodotyramine, and Hordenine on the Gaseous Exchange. J. ABELIN (*Biochem. Z.*, 1923, **138**, 161—168).—Tables are given showing the effect of oral and subcutaneous administration of di-iodotyrosine, di-iodotyramine, and hordenine (ω -dimethyltyramine) on the gaseous exchange of the white rat. In contrast to tyramine (cf. A., 1920, i, 264; A., 1922, i, 610), di-iodotyrosine and di-iodotyramine have little or no influence on the gaseous metabolism. The oral adminis-

tration of hordenine produces a diminution in the exchange, thus acting in the same way as tyramine, phenylethylamine, and adrenaline.
J. P.

The Reduction of Nitro-groups by Living Tissues. WERNER LIPSCHITZ (*Biochem. Z.*, 1923, **138**, 274—278).—A reply to the criticisms by Waterman and Kalf (this vol., i, 415), of the author's results on the reduction of *m*-dinitrobenzene by excised tissues and tumours (A., 1921, i, 203).
J. P.

The Phosphorus Compounds in Normal Blood. MARY V. BUELL (*J. Biol. Chem.*, 1923, **56**, 97—107).—Analyses have been made of the phosphorus content of human blood and of blood from normal dogs, precautions being taken to prevent changes in the distribution between the corpuscles and plasma after collection. The results indicate that, in the living organism, the inorganic phosphate of the blood is present only in the plasma, and the organic phosphate only in the corpuscles.
E. S.

Chemical Factors in Fatigue. II. Further Changes in some of the Blood Constituents following Strenuous Muscular Exercise. NORRIS W. RAKESTRAW [with CHARLES V. BARLEY and YOUNG D. HAHN] (*J. Biol. Chem.*, 1923, **56**, 121—124; cf. *ibid.*, 1921, **47**, 565).—Short periods of strenuous exercise are followed by increases in the uric acid and sugar content of the blood. The increase in the former substance continues for more than one and a half hours after exercise; the sugar, however, falls to a value below normal in this time. Slight increases have also been observed in the chloride content; that of amino-acids and free and conjugated phenols remains unchanged.
E. S.

Variations in the Distribution of the Non-protein Nitrogenous Constituents of Whole Blood and Plasma during Acute Retention and Elimination. E. D. PLASS (*J. Biol. Chem.*, 1923, **56**, 17—29).—Analyses have been made of the non-protein nitrogenous constituents of whole-blood and plasma during pregnancy and eclampsia. The results indicate that these constituents diffuse into the corpuscles during periods of retention and again return to the plasma when their concentration in the latter has been reduced by improved elimination.
E. S.

Is Pyruvic Acid a Stage in the Decomposition of Dextrose during Glycolysis? J. SIMON and E. AÜBEL (*Compt. rend.*, 1923, **176**, 1925—1927).—Pyruvic acid is not a normal constituent of the blood of animals, whether fasting or on full diet, neither is sodium pyruvate decomposed by blood in vitro more rapidly than by water. Pyruvic acid is not produced during glycolysis, and therefore cannot be an intermediary between dextrose and lactic acid.
E. E. T.

Relation between Hæmoglobin-content and Surface of Red Blood-cells. E. GORTER (*Nature*, 1923, **111**, 845).—A consideration of the mode of distribution of hæmoglobin molecules in red blood-cells.
A. A. E.

Origin and Nature of Thrombin. P. NOLF (*Arch. Néerland physiol.*, 1922, 7, 348—351; from *Chem. Zentr.*, 1923, i, 619).—Blood plasma is a mixture of proteins of various origin, including thrombozymes from the white blood corpuscles and endothelial cells outside the liver, and other proteins (fibrinogen, thrombogen, antithrombosin, and antithrombolysin) secreted by the liver. Both groups include albumins and globulins. Coagulation, which consists of the combination of thrombozyme with liver proteins, does not take place when the least soluble thrombozyme (thrombozyme globulin) and the least soluble liver protein (fibrinogen) are brought together, but is facilitated by the presence of the more soluble thrombogen. There is an excess of slightly soluble liver proteins in plasma. Of the complexes formed by coagulation, one part contains fibrinogen and fibrin and the other part (thrombin) little or no fibrinogen. The thrombin of normal serum is a soluble fibrin which forms an insoluble fibrin with fibrinogen or, more slowly, with the more easily soluble liver colloids with formation of meta-thrombin (β -proferment of Morawitz). G. W. R.

Chemical Constituents of Saliva as Indices of Glandular Activity. J. LUCIEN MORRIS and VERNON JERSEY (*J. Biol. Chem.*, 1923, 56, 31—42).—Estimations have been made of the urea, ammonia, amino-nitrogen, creatinine, and uric acid content of human saliva collected in successive half-hour periods from resting glands and from glands stimulated into activity by chewing. Similar estimations have been made following the ingestion of acetic acid, pilocarpine, and atropine. The different effects of the various stimuli on the volume and composition of the saliva indicate that several factors are involved in the elaboration of the secretion.

E. S.

The Rôle of Oxyproteic Acids in the Acidity of the Human System. STANISŁAW BĄDZYŃSKI and WACŁAW KARCZEWSKI (*I^{ny} Zjazd Chemików Polskich*, 1923, 52—53).—The view that the action on proteins is the same in the intestines as in the body-cells is shown to be incorrect; in the former case, the only action is hydrolysis to amino-acids, whilst in the latter case, this is preceded by oxidation. That the oxyproteic acids produced by the latter process are highly oxidised is shown by the very high silver or barium content of their salts; the oxygen content is from 1.4 to 2 times as high as that of the proteins from which they are derived. The excretion of oxyproteic acids is increased by the addition of larger quantities of proteins to the diet, by bacterial poisoning, or by poisoning with carbon monoxide, chloroform, ether, atophan, etc. The average daily excretion of these acids is calculated to be 4.85 g., and the quantity of alkali removed from the body, combined with the acids, is equivalent to 241—376 c.c. of *N*/10-sodium hydroxide solution. R. T.

Influence of the Condition of Acidosis on the Metabolism of the Alkaline-earth Metals of the Organism. MICHELE FLORIS (*Arch. Farm. speriment. Sci. aff.*, 1923, 35, 88—96, 97—103, 113—121, 129—138, 145—153, 161—166).—The author gives a

summary of previous work on the biological and pharmacological action of calcium and magnesium compounds, and on the interchanges of these compounds both after administration of acids and during a condition of pathological acidosis. The results of his own experiments on dogs show that ingestion per day of 5 c.c. of lactic acid or 0.89 c.c. per kg. of body-weight, extending over a period of five days, produces a marked diminution in the proportions of calcium and magnesium in the faeces and a slight increase in those in the urine. Both calcium and magnesium are retained to an appreciable extent by the organism. A daily dose of 1.37 c.c. of the acid per kg. of body-weight for four days caused increases in the faecal and urinary elimination of the lime and impoverishment of the organism; the elimination of magnesia by the faeces diminished and that by the urine increased, the balance being in favour of the organism. Ingestion of lactic acid reproduces especially those conditions in which, owing to abnormal fermentation, organic acids are produced in considerable proportions in the digestive tract, and causes an analogous loss of calcium by the organism.

T. H. P.

Creatine and Creatinine Metabolism. V. The Metabolism of Creatine. STANLEY R. BENEDICT and EMIL OSTERBERG (*J. Biol. Chem.*, 1923, 56, 229—252).—Although the view, originally expressed by Folin, that urinary creatinine is not derived from creatine has from time to time been questioned (cf. for example, Rose and Dimmitt, A., 1916, i, 774; Behre and Benedict, A., 1922, ii, 789), decisive evidence against it has not hitherto been forthcoming. A survey of the literature has shown that, in experiments which apparently support this view, the creatine administered to the animals employed has not been accounted for in any way. Experiments have accordingly been carried out in which small amounts of creatine were fed daily for long periods to dogs, initially in approximate nitrogen equilibrium, estimations being made of the creatine and creatinine eliminated. During roughly the first week, no effect on the elimination of these substances was observed; thereafter, however, increased amounts of both were excreted, until finally approximately 50% of the creatine administered in a given period was eliminated unchanged. At the same time, there was a large retention of nitrogen and two out of the three animals increased considerably in weight. When the administration of creatine was stopped, there was an immediate cessation in the elimination of this substance; creatinine, on the other hand, continued to be excreted in amounts considerably larger than normal. When the urinary creatinine again reached a normal figure, it was found that, in each case, the amount of additional creatinine excreted during the whole experimental period corresponded with approximately one-third of the creatine otherwise unaccounted for. These results appear to indicate that creatine is metabolised extremely slowly and in two distinct ways, one of which yields, apparently indirectly, creatinine. On this basis, two distinct types of creatinuria should exist: one due to an excess of creatine

in the organism, and the other due to a failure to utilise that portion of the creatine which normally does not yield creatinine. E. S.

Pyrimidine Metabolism. D. WRIGHT WILSON (*J. Biol. Chem.*, 1923, **56**, 215—227).—Experiments on rabbits and man show that, although free uracil is not attacked in the body, when administered in the form of a nucleoside or a nucleotide it is to a large extent destroyed, only a small portion being excreted unchanged; when administered as yeast-nucleic acid, it is completely destroyed. Hence the first step in the metabolism of nucleic acid is some change in the pyrimidine group, which evidently precedes hydrolysis into the nucleotides. E. S.

Aqueous Extracts of Pancreas. I. Influence on the Carbohydrate Metabolism of Depancreatized Animals. JOHN R. MURLIN, HARRY D. CLOUGH, C. B. F. GIBBS, and ARTHUR M. STOKES (*J. Biol. Chem.*, 1923, **56**, 253—296; cf. Banting, Best, Collip, Macleod, and Noble, this vol., i, 420).—Preparations of insulin made by extracting the pancreas with 0.2*N*-hydrochloric acid and subsequently neutralising with sodium hydroxide have as great an effect on the blood sugar and the dextrose : nitrogen ratio of depancreatized animals as those prepared by extraction with alcoholic hydrochloric acid according to the method of Banting and Best. Extremely toxic effects result from the administration of such preparations unless the acid is previously neutralised and the trypsin completely destroyed.

A rise in the respiratory quotient and a considerable utilisation of sugar have been observed in depancreatized animals (dogs) following the administration by the stomach of extracts of ox pancreas; the minimal dose which produced this effect was equivalent to about 125 g. of the pancreas.

Acid extracts of pancreas may be boiled for at least five minutes without destroying the insulin. This substance is, however, largely removed by filtration of the extracts through charcoal or Lloyd's reagent.

It is stated that the above aqueous extracts of pancreas contain, in addition to insulin, a substance which produces a rise in the blood-sugar of both normal and diabetic animals, but details are reserved for a future publication. E. S.

Boron in Animal Organs. GIUSEPPE MOSCATI (*Arch. Sci. biol.*, 1922, **3**, 279—288; from *Chem. Zentr.*, 1923, i, 362).—Boron occurs in human organs, the minimum amount being present in the liver and the maximum amount in the kidneys. It occurs also in foetal liver and spleen. Urine also contains boron. In the case of a dog, administration of borax resulted in the presence of boron in the blood and all organs. G. W. R.

Chemistry of the Oils of Marine Animals. ÉMILE ANDRÉ (*Bull. Soc. chim.*, 1923, **33**, [iv], 469—506).—Lectures given at the Collège de France. G. F. M.

The Endothermic Reaction which Accompanies the Appearance of a Visible Curd in Milks Coagulated by Heat : A Contribution to the Theory of the Heat Coagulation of Milk. ALAN LEIGHTON and COURTLAND S. MUDGE (*J. Biol. Chem.*, 1923, 56, 53—73).—The coagulation of casein produced by heating skimmed milk or evaporated skimmed milk is accompanied by an endothermic reaction which results, apparently, in the precipitation of calcium and magnesium as phosphates and citrates. The metals combined, as well as those uncombined, with the casein enter into this reaction.

The thickening of condensed milk is due to a chemical reaction and does not result from bacterial action. The effect of the degree of forewarming on the stability of both condensed and evaporated milk has been investigated in some detail. [Cf. *J.S.C.I.*, 1923, 737A.] E. S.

Comparative Elimination of Total Nitrogen, Urea, Amino-acids, and of Ammonia during Waking Hours and during Sleep. I. Physiological Conditions. II. Total Starvation. GEORGES FONTÈS and ALEXANDRE YOVANOVITCH (*Bull. Soc. Chim. biol.*, 1923, 5, 348—362, 363—371).—Analyses have been made of urine secreted during sleep and during waking hours under comparable conditions as regards food, activity, temperature of surroundings, etc. The excretion of water, total nitrogen, urea, and to a very slight degree of amino-acid nitrogen are decreased whilst that of ammonia and acidity to phenolphthalein is increased during sleep. Very similar results are obtained if food is not administered during the experiment. W. O. K.

The Salicylates. XIV. Liberation of Salicyl from and Excretion of Acetylsalicylic [*o*-Acetoxybenzoic] Acid. P. J. HANZLIK and ELIZABETH PRESHO (*J. Pharm. Expt. Ther.*, 1923, 21, 247—261).—The rate of hydrolysis of *o*-acetoxybenzoic acid is minimum in neutral solution, but markedly increases if the reaction is slightly acid or alkaline. At $p_H 5.5$, 34% is hydrolysed in eighteen hours, and at $p_H 8$, 45%. Thus *o*-acetoxybenzoic acid ought to be fairly stable in buffer mixtures such as are encountered in the alimentary canal. This is verified by the fact that after administration of *o*-acetoxybenzoic acid, varying quantities, 5.3 to 41.1%, may be recovered from the urine. W. O. K.

The Examination of the Blood of Pigeons suffering from Avitaminosis. LEON MARCHLEWSKI and (Mlle) A. NOWOTNÓWNA (*Istov Zjazd Chemików Polskich*, 1923, 26).—The amount of non-albuminous nitrogen in the blood of pigeons suffering from avitaminosis is greater than the normal, pointing to an inability to synthesise proteins from amino-acids. R. T.

Importance of Calcium and Potassium in the Pathological Physiology of Cancer. MAURICE WOLF (*Compt. rend.*, 1923, 176, 1932—1934).—A study of the effect of calcium and potassium on the growth of an epithelioma of the mammary gland of the mouse. For normal (mouse) tissue, the ratio K/Ca varies from

5.41 (liver) to 0.053 (connective-tissue). For tissue infected with pneumococci, these values are respectively 4.21 and 1.51. For a rapidly and slowly developing epithelioma, respectively, the ratio is 20:15 and 5:10 (with occasional deviations within the limits of 57 and 0.049). Calcium retards and potassium stimulates, growth. The former causes concentration, the latter dilution, of cytoplasm. Calcium is absorbed diffusely, potassium mainly in the neighbourhood of the nucleus. E. E. T.

Diphtheria Toxin. I. The Influence of Hydrogen-ion Concentration on Diphtheria Toxin. FR. VON GRÖER (*Biochem. Z.*, 1923, 138, 13—33).—The addition of dilute hydrochloric acid, in appropriate amount, to diphtheria toxin produces a precipitate, soluble in excess of acid, which contains practically all the toxic principle. The zone of precipitation is broad and indefinite and lies on both sides of p_H 5; precipitation is practically complete at p_H 3— p_H 4. The toxin itself is regarded as analogous to an amphoteric electrolyte and shows a maximum toxicity at p_H 8.5— p_H 9.2. At p_H 5 and p_H 12 it is inactive. In an addendum the author points out that his results accord qualitatively but not quantitatively with those of Walbum (*A.*, 1922, i, 902). J. P.

Diphtheria Toxin. II. Investigations on the Formation of Toxin. FR. VON GRÖER (*Biochem. Z.*, 1923, 138, 34—42).—Daily determinations were made of the alterations in hydrogen-ion concentration, optical rotation, refractive index, amino-nitrogen, and toxicity of actively growing diphtheria cultures. It is concluded that "actual" toxicity is dependent on the formation of new toxin, activation of the toxin by increasing alkalinity, and by autolysis of the toxin. The "absolute" toxicity of a culture is attained at p_H 8.6—8.8. J. P.

Toxicity of a Polymeride of Hydrocyanic Acid. CH. BEDEL (*Compt. rend.*, 1923, 176, 1927—1929).—The tetrameride of hydrocyanic acid was purified as described previously (this vol., i, 190). Hypodermic injections of 0.028 g. per kg. body-weight (guinea-pig) produced no apparent distress (cf. Desgrez, *A.*, 1911, ii, 756). Buccal administration allowed of the use of greater concentrations, the toxic dose being found to be 0.75 g. per kg. body-weight. The symptoms produced resemble those obtained with hydrocyanic acid, post-mortem examination (six hours after administration of the toxic dose) revealing hypertrophy of the stomach, the volume of which is trebled, owing to the presence of fluid full of granules, but devoid of the tetrameride. Free hydrocyanic acid is present in the kidneys and, to a less extent, in the stomach.

Sodium thiosulphate, antidotal to hydrocyanic acid, does not react with the tetrameride, either in vitro or in vivo. If it is injected simultaneously with the tetrameride, the effects are modified. Death follows a single crisis, instead of several, and post-mortem examination shows a complete absence of hydrocyanic acid. E. E. T.

Chemistry of Vegetable Physiology and Agriculture.

The Use of Calcium Carbonate in Nitrogen Fixation Experiments. P. L. GAINNEY (*J. Agric. Res.*, 1923, 24, 185—190).—An inquiry is made as to the advisability of adding calcium carbonate to nutrient media for nitrogen fixation tests. A number of soils were examined and the organisms grown in media with and without calcium carbonate. The number of soils capable of initiating the growth of *Azotobacter* under experimental conditions was 20% greater when calcium carbonate was added to the media. The amount of nitrogen fixed in the presence of calcium carbonate was never less and was usually greater than in its absence. The beneficial effect of calcium carbonate was greater on other nitrogen-fixing organisms than on *Azotobacter* itself. A. G. P.

Pyruvic Acid considered as an Anaërobiotic Factor. ALBERT BERTHELOT (*Compt. rend.*, 1923, 176, 1929—1932; cf. A., 1921, i, 909).—*Bacillus aminophilus*, grown in peptonised dextrose solution, or in a synthetic mixture, causes the formation (among other reducing substances such as acetylmethylcarbinol) of pyruvic acid. When acetone-producing or acidaminolytic organisms are cultivated in a synthetic medium, where nitrogen is furnished by ammonium sulphate and potassium nitrate and carbon by an acyclic acid, pyruvic is the most readily utilised acid of the latter type (cf. Aubel, A., 1922, i, 201).

It is shown that the action of *B. aminophilus* and other favourable organisms is connected to a certain extent with the formation of pyruvic acid. Several strictly anaërobic bacilli were successfully cultivated in open tubes in presence of pyruvic acid, growth being more rapid after the formation of other reducing substances such as acetaldehyde or acetylmethylcarbinol. Under such conditions, pathogenic or saprophytic aerobic bacilli probably develop in addition. E. E. T.

Production of Oxidising Ferments. O. FERNÁNDEZ and T. GARMÉNDIA (*Anal. Fis. Quím.*, 1923, 21, 166—180).—A study of the effect of the commoner carbohydrates and amino-acids on the production of peroxydase and catalase by *Bacillus coli* under aerobic and anaerobic conditions. G. W. R.

Production of β -Hydroxybutyric Acid by certain Bacteria of the Group *Bacillus subtilis*. M. LEMOIGNE (*Compt. rend.*, 1923, 176, 1761—1763).—Macerations in sterile distilled water of certain microbes of the group *B. subtilis* rapidly become strongly acid. This acidity is due to the formation of β -hydroxybutyric acid, which was detected in the non-volatile residue by conversion into α -crotonic acid, m. p. 70—71°, by distillation with sulphuric acid, and by the formation of acetone on oxidation with dichromate. G. F. M.

Antiseptic Action of Pyromucic Acid. H. P. KAUFMANN (*Ber. Deut. pharm. Ges.*, 1923, **33**, 132—139).—Pyromucic acid serves for inhibiting the growth of bacteria in pure cultures, but is useless for the preservation of fruit or meat. [*Cf. J.S.C.I.*, 1923.]
T. H. P.

The Problem of Aldehydes in Wines. J. ESTALELLA (*Anal. Fis. Quím.*, 1923, **21**, 33—44; cf. this vol., ii, 98; i, 181).—The author discusses the estimation of volatile acids and aldehydes in wines. The origin of aldehydes in wines is also discussed. These may be formed either as defensive secretions against added sulphites or else as intermediate stages in the formation of ethyl alcohol.
G. W. R.

Comparative Studies in Respiration. XXV. Action of Chloroform on the Oxidation of some Organic Acids. GEORGE B. RAY (*J. Gen. Physiol.*, 1923, **5**, 611—622).—When organic acids are treated with hydrogen and ferrous sulphate, carbon dioxide is evolved. Addition of an anæsthetic, e.g., chloroform, causes variation in the rate of production of the carbon dioxide. The curves showing the rate of production of carbon dioxide after addition of the anæsthetics resemble those obtained in a similar way using the alga *Ulva* instead of the acid (cf. this vol., i, 520). For example with tannic acid in presence of hydrogen peroxide and ferrous sulphate, the rate is initially decreased, then increased, and finally decreased again. Fumaric, maleic, oleic, and cinnamic acids—compounds containing a double bond—are all influenced by chloroform with regard to the rate at which carbon dioxide is produced.
W. O. K.

Comparative Studies on Respiration. XXVI. The Production of Carbon Dioxide from Organic Acids in Relation to their Iodine Absorption. GEORGE B. RAY (*J. Gen. Physiol.*, 1923, **5**, 623—627).—The effect of chloroform on the rate of adsorption of iodine by unsaturated acids runs very closely parallel to its effect on the rate of production of carbon dioxide under the influence of hydrogen peroxide and ferrous sulphate (cf. preceding abstract).
W. O. K.

The Composition of the Cell Sap of the Plant in Relation to the Adsorption of Ions. D. R. HOAGLAND and A. R. DAVIS (*J. Gen. Physiol.*, 1923, **5**, 629—646).—Measurements made of the composition and p_H of the cell sap of the fresh-water alga *Nitella* show that in the sap there is a much higher concentration of the inorganic ions than in the water in which the plants grow.
W. O. K.

The Glycerophosphatase of Plant Seeds. II. ANTONÍN NĚMEC (*Biochem. Z.*, 1923, **138**, 198—204).—A continuation of the author's previous work on the distribution and activity of glycerophosphatase in plant seeds (*A.*, 1920, i, 268, 354). The influence of acidity of seed extracts and reaction media is further

investigated. Five g. of each of a large number of fresh, finely powdered seeds are incubated for forty-eight hours with (1) 100 c.c. of water, (2) 100 c.c. of 1% sodium glycerophosphate, each in the presence of 2 c.c. of toluene, at p_H ranging from 4.65 to 7.3. The rate of hydrolysis of the glycerophosphate is measured by the difference of free P_2O_5 in (2) and (1), and the activity of the enzyme is plotted against the p_H of the series of substrates. The optimum p_H is found to be 5.65. It is concluded that for a wide range of seeds the activity of glycerophosphatase is entirely a function of the p_H of the substrate, and not of varying amounts of enzyme.

J. P.

Proteins of the Cantaloupe Seed, *Cucumis melo*. Isolation of a Crystalline Globulin [identical with] the Crystalline Globulin of the Squash Seed. D. BREESE JONES and C. E. F. GERSDORFF (*J. Biol. Chem.*, 1923, 56, 79—96).—By extraction with hot 2% sodium chloride solution, a crystalline globulin has been isolated from cantaloupe seeds. It crystallises in octahedra which have n_D^{20} 1.545 approximately, has the elementary composition C=52.65, H=6.67, N=18.41, S=1.13%, and contains the following percentages of diamino-acids: arginine 16.26, histidine 4.22, lysine 3.29, cystine 1.27, tryptophan 2.63. It appears to be identical with the globulin isolated by Osborne (A., 1893, i, 380) from squash seed (*Cucurbita maxima*). A careful comparison of the globulins from the two sources has shown that they are identical in composition and in crystallographic and optical properties. Anaphylaxis experiments revealed no distinction immunologically.

When extracted with 0.5% sodium hydroxide, the residues from the extraction of the globulin yielded a glutelin with the elementary composition C=55.20, H=7.02, N=16.28, S=0.90%, and containing the following percentages of diamino-acids: arginine 12.42, histidine 2.72, lysine 4.59, cystine 1.09, tryptophan 3.03. The maximum yields of the proteins obtained were: globulin 12.07%, glutelin 5.78%. No albumin was detected in the seeds. E. S.

Safflower Seed and its Germination. V. A. TAMHANE (*Mem. Dept. Agric. India*, 1923, 6, 223—244).—The reserve materials in the safflower seed are chiefly oil and protein matter, no starch, glucosides, or tannin, and only a small proportion of a non-reducing sugar occurring in the resting seed. During germination, very little change occurs until the radicle protrudes from the seed, after which the oil rapidly disappears, a corresponding increase in the nitrogen-free extract occurs, due mainly to the formation of sugars. The lipase and oxydase rapidly increase as the radicle develops and reach a maximum when the lateral roots begin to appear, and at this stage the protein matter is largely solubilised. As the regular feeding roots are formed the proportion of enzymes gradually declines. It was observed that during germination the rise in the amount of oxydase follows somewhat the decomposition of the oil, but it is shown that the acidification of the oil during germination is not due to enzyme action.

G. F. M.

Incrustive Substances of Plants. IV. ERICH SCHMIDT and ALBERT MIERMEISTER (*Ber.*, 1923, 56, [B], 1438—1440).—The application of chlorine dioxide and sodium sulphite for the removal of incrustations from plants (cf. A., 1921, i, 912; 1922, i, 206; this vol., i, 274) is unsuitable for the *Algæ*, the skeleton substance of which is dissolved by the alkali sulphite solution. In these cases, therefore, the latter reagent is replaced by alcohol.

The finely divided plant is washed, dried, powdered, and extracted with a mixture of alcohol and benzene (1:1) until the extract is colourless. Inorganic salts are removed by treatment with sulphuric acid (2%), after which the product is thoroughly washed with water. It is then subjected to the action of dilute chlorine dioxide solution (0.7%) in a closed vessel exposed to diffuse daylight during seventy-two hours. The residue is filtered, thoroughly agitated with water to remove excess of chlorine dioxide, repeatedly washed to eliminate hydrochloric acid, and extracted with boiling alcohol until the solvent is no longer coloured. The processes are repeated (about three times) until the removal of the incrustation is complete. The polysaccharides are obtained from the aqueous solutions derived from the first three treatments; the membrane components which are attacked by chlorine dioxide are isolated from the alcoholic extracts.

Laminaria hyperborea yields 19.5% of skeleton substance (ash 0.3%), 10.2% of polysaccharides (ash 20—22%) and 5% of attackable membrane, whereas *Fucus serratus* gives 26.8% of skeleton substances (ash 2.7%), 21.5% of polysaccharides (ash 20—25%), and 8.5% of attackable membrane. H. W.

Nitrogen Reserve in Apple Trees. R. H. ROBERTS (*Proc. Amer. Soc. Hort. Sci.*, 1921, 143—145; from *Physiol. Abstr.*, 1923, 8, 107).—Chemical analysis of branches of apple trees indicate that the carbohydrates decrease with an increase in nitrogen content, and increase with a decrease in nitrogen. Abundant blossom-bud formation occurred only on the trees which had an intermediate percentage of nitrogen and the reciprocal condition of an intermediate percentage of carbohydrate reserves.

W. O. K.

The Behaviour of Bast Fibres under the Influence of Alkali Hydroxides. C. R. NODDER and R. W. KINKEAD (*J. Text. Inst.*, 1923, 14, T133—156).—The percentage contraction produced by sodium hydroxide solutions of various concentrations in single fibres of flax and ramie and in yarns spun from these materials has been measured and the contraction-concentration curves are discussed, comparisons being made with the curves obtained by Willows and his colleagues for cotton (*ibid.*, 1922, 13, 229). The twisting phenomena exhibited by flax and ramie fibres during mercerisation have also been studied and the bearing of the results obtained on the production of lustre on materials composed of bast fibres is indicated. The existence of certain relationships between the molecular composition of sodium hydroxide solutions and their action on vegetable fibres is discussed,

Coward and Spencer's data for cotton (this vol., i, 404) also being quoted. It is pointed out that the maximum contraction for bast fibres is with sodium hydroxide of d 1.111, *i. e.*, a solution containing $H_2O : NaOH$ in the ratio 20 : 1. This corresponds with one of the maxima for cotton. Another maximum for cotton is at d 1.172, which corresponds with the maximum specific conductivity of sodium hydroxide solutions.

J. C. W.

The Alleged Dextrin Reserves of Monocotyledons. H. COLIN and H. BELVAL (*Compt. rend.*, 1923, **176**, 1493—1495).—The water-soluble carbohydrate of *Hyacinthus orientalis* was examined and found to be a lævulosan, insoluble in alcohol, and yielding lævulose but not dextrose on hydrolysis. This appears to be characteristic of a number of monocotyledons, although starch is present in many cases, so that the views which have been put forward as to a carbohydrate reserve in the form of dextrins, and also as to the synthesis of starch from the latter, must be modified to some extent.

H. J. E.

The Simultaneous Existence of both Optical Antipodes of Asparagine in the Germinating Lupin (*Lupinus albus*). A. PIUTTI (*Bull. Soc. chim.*, 1923, [iv], **33**, 804—806).—By prolonged boiling of an aqueous solution of 34 g. of *l*-asparagine, 0.545 g. of the *d*-isomeride was obtained, but it is possible to avoid this inversion by working at temperatures not exceeding 55°. The juice of the germinating lupin was expressed and the asparagine isolated as the copper salt. On removal of the copper by means of hydrogen sulphide (which has no inverting action on asparagine), a solution was obtained, which, on concentration in a vacuum at 40°, deposited crystals of both *d*- and *l*-asparagine. In a second experiment, the protein matter in the juice was precipitated by means of alcohol, and the asparagine obtained by crystallisation in a vacuum at 40°. Both isomerides were obtained as before. The small quantity of the *d*-form obtained points to the fact that this form is utilised by the plant in preference to the *l*-isomeride.

H. H.

Composition of Maize Pollen. II. Concerning certain Lipoids, a Hydrocarbon, and Phytosterol Occurring in the Pollen of "White Flint" Maize. R. J. ANDERSON (*J. Biol. Chem.*, 1923, **55**, 611—628; cf. A., 1922, i, 508).—From alcoholic and ethereal extracts of the pollen the author has isolated a saturated hydrocarbon, m. p. 63.5—64°, which is apparently *n*-nonacosane; a saturated alcohol, $C_{30}H_{62}O$, m. p. 136°, isomeric with myricyl alcohol; and a phosphatide containing 4.09% of phosphorus. The substance, m. p. 88—89°, previously regarded as myricyl alcohol has now been identified as phytosterol palmitate. On hydrolysis, it yields palmitic acid and a mixture of phytosterols. The latter have been separated by fractional crystallisation into two fractions melting at 122° and 136.5°, respectively; the higher melting fraction gave an acetyl derivative, m. p. 101°. Other phytosterol preparations isolated from the pollen had melting points ranging from 121—154°. The preparation, m. p. 154°, gave an acetyl derivative,

m. p. 134°. All the phytosterol preparations differed from ordinary phytosterol in being optically inactive and in crystallising without water of crystallisation.

E. S.

Composition of *Nectandra coto*. HARVEY A. SEIL (*J. Amer. Pharm. Assoc.*, 1922, **11**, 904—906).—The light petroleum extract (12·69%) of the bark of *Nectandra coto* contains most of the cotoin, whilst the ethyl-alcoholic extract (8·02%, after removal of 10·25% with ethyl ether) contains most of the tannin and alkaloids; the latter are present to the extent of 1·38%, of which 0·60% has phenolic properties. The non-phenolic alkaloid, *parostemine*, gives a crystalline precipitate with potassium mercuri-iodide reagent, and with a solution of iodine in aqueous potassium iodide. The phenolic alkaloid, *parosteminine*, gives a purplish-red colour with alcoholic ferric chloride.

CHEMICAL ABSTRACTS.

Hydrocyanic Acid in the Burma Bean (*Phaseolus lunatus*, sp.) F. J. WARTH (*Mem. Dept. Agric. India*, 1923, **7**, 1—29).—For the estimation of hydrocyanic acid, auto-enzyme hydrolysis gives the best results, as when the organs, particularly the fresh leaves, are plunged into boiling water the glucoside is hydrolysed to a considerable extent, and part of the hydrocyanic acid is converted into a form which is not recoverable by acid hydrolysis. During sun-drying, hydrolysis occurs with evolution of hydrocyanic acid. Hydrolysis also occurs during slow drying, but auto-digestion of the hydrocyanic acid takes the place of evolution. Hydrocyanic acid has a powerful effect on cell permeability in the fresh leaf, and acts therefore as a regulator or hormone. Its presence brings glucoside hydrolysis to a premature end, and this paralysis of the enzyme plays an important part in regulating hydrocyanic acid liberation within the plant. In the green plant, the hydrolytic enzyme is active in the stalk, but the green pod and young ripe seed have no hydrolytic power. As the seed grows older, however, the enzyme develops.

G. F. M.

The Formation of Essential Oils in Conifers. I. The Process of Formation of the Essential Oil of *Pinus cembra*. G. V. PIGULEVSKI (*J. Russ. Phys. Chem. Soc.*, 1922, **54**, 259—276).—The yield and nature of the essential oil from the needles and from the branches of several specimens of the Siberian cedar (*Pinus cembra*, L.), grown near Petrograd, were investigated. It was found that the yield of oil varied from 0·42 to 1·49 c.c. per 100 g. of raw material. Old trees appear to give a smaller yield of oil; trees growing in the sun give more oil than those grown in the shade. The rotation of the different samples also presents very considerable differences, thus $[\alpha]_D$ varies from $-0·88^\circ$ to $+22·96^\circ$; their dispersion from $-19·8$ to $1·83$.

Fractionation of the oil shows that it is mainly composed of two constituents; the low-boiling portion consists of *d*-pinene (b. p. 155·5—156·5°, $[\alpha]_D +36·84$,* $[\alpha]_D/[\alpha]_D$ 1·94), the amount present varying from 65 to 78%; the high boiling portion consists of *l*-cadinene (b. p. 135—145°/12—15 mm., $[\alpha]_D -67·52$,*

* These are the maximum rotations observed.

$[\alpha]_t/[\alpha]_c$ 2.50). From these rotations and the rotations of the individual oils it is possible to calculate the percentage of the two constituents in them; the calculated values agree quite well with those arrived at by fractionating the samples; strongly dextrorotatory samples contain more *d*-pinene, and *vice versa*.

The oil obtained from the branches of *P. cembra* is lævorotatory, $[\alpha]_D$ -29.86° to -47.76° , $[\alpha]_t/[\alpha]_c$ 1.77 to 2.15. The yield varies from 0.68 to 1.30% and is highest in trees which also give a high yield of needle-oil.

G. A. R. K.

The Formation of Essential Oils in Conifers. II. The Nature of the Essential Oil in Different Plant Organs. G. V. FIGULEVSKI (*J. Russ. Phys. Chem., Soc.* 1922, **54**, 277—295).—A comparison is made between the oils obtained from the needles and the branches of the following conifers: *Pinus silvestris* from the Crimea, *P. cembra* (Petrograd), *Abies sibirica* (Petrograd) and *Cupressus sempervirens* (Crimea).

For the first-named, it was found that the oil from the needles was feebly dextrorotatory $[\alpha]_D +3.32^\circ$, $d_4^{16.3}$ 0.8692, whilst the oil from the twigs, etc., is lævorotatory, $[\alpha]_D -10.12^\circ$ to -14.00° , $n_D^{16.3}$ 0.8659 to 0.8643; the oil derived from a whole tree shows intermediate properties. On fractionation, the needle oil gives about 40%, b. p. $157-160^\circ$, $[\alpha]_D +7.24^\circ$, and 21%, b. p. $160-161.5^\circ$, $[\alpha]_D +5.88^\circ$; these fractions contain pinene which appears to be largely racemised; the high fraction is lævorotatory. When similarly treated the oil from the twigs gives about 61% of a fraction b. p. $162.5-168^\circ$, $[\alpha]_D -7.28^\circ$, also containing pinene together with a lævorotatory high fraction; the boiling point of the main portion of this oil is thus higher than that of the needle oil and the rotation of opposite sign.

The oil derived from the whole plant gives both these fractions, the lowest possessing a positive, the second a negative rotation. It may be mentioned that in all these experiments, the oxygen-containing constituents of the oils were destroyed by boiling with sodium.

The oil from the twigs of *P. cembra* (cf. preceding abstract) gives 80—84% of low fraction, b. p. $159-171^\circ$, $[\alpha]_D -21.68-41.92^\circ$, the residue showing a feeble lævorotation (-4.04° to -6.52°) although it may contain a dextrorotatory constituent.

As in the case of *P. silvestris*, the oil prepared from twigs shows a higher boiling point and negative rotation.

The oil from the Siberian fir (*A. sibirica*) is characterised by its high content of esters (bornyl acetate). The oil derived from the needles has a rotation of about -46° and a dispersion of 2.02 to 2.04. On fractionation, the hydrocarbon fraction obtained boils between 157° and 163° and has $[\alpha]_D -54^\circ$ to -56° , $[\alpha]_t/[\alpha]_c$ 2.11; the ester content is about 48%. The oil derived from the twigs has a lower rotation ($[\alpha]_D -30^\circ$ to -32° , $[\alpha]_t/[\alpha]_c$ 1.88 to 1.92). The hydrocarbon fraction has b. p. $163-170^\circ$, $[\alpha]_D -39.20^\circ$, $[\alpha]_t/[\alpha]_c$ 1.98; the ester content is much lower, being only about 20%.

The properties of cypress oil have already been described (cf. this vol., i, 817); in this case again, the needle oil is dextrorotatory,

has a low coefficient of dispersion and a high ester content; the oil from the branches and stem is lævorotatory, has a lower ester content and the hydrocarbon fraction has a higher boiling point.

The reasons leading to the differences in the character of the oils are discussed. It is suggested that in those parts of the plant in which the oxidative processes are most marked (*e.g.*, the needles) the production of oxygen-containing compounds will be highest, and *vice versa*. It is well known that the presence of chlorophyll is connected with the same factor and it is suggested that the high ester content of Siberian fir-needle oil is due to the fact that the resinous ducts in this plant are situated in a region rich in chlorophyll, and, moreover, are not surrounded by a ring of bast fibres, as in *P. silvestris* and *P. cembra*. G. A. R. K.

Availability of Potassium in Orthoclase for Plant Nutrition.

DENNIS EDWARD HALEY (*Soil. Sci.*, 1923, **15**, 167—190).—The solubility of the potassium in orthoclase under varying conditions was determined by using the orthoclase as sole source of potassium in a series of sand cultures of buckwheat. A considerable amount of potassium could be extracted from a 200-mesh sample of orthoclase by water. The availability of potassium from orthoclase was sufficient for the growth of crops even larger than those obtained by the use of a complete nutrient solution. Calcium carbonate and sulphate tended to increase the amount of available potassium in orthoclase. Sodium sulphate made no appreciable difference to the availability of the potassium, and sodium chloride in most cases decreased it. When, however, the potassium supply became the limiting factor in the growth of the plant the addition of sodium chloride to orthoclase produced crop increases. The use of dextrose in the orthoclase mixture tended to lower the dry weight of plants produced. Similar results were obtained with starch, but in this case the addition of calcium carbonate brought about an increase in the dry weight of, and potassium absorbed by, the plants. A. G. P.

Adsorption and Replacement of Plant Food in Colloidal Oxides of Iron and Aluminium.

D. C. LICHTENWALNER, A. L. FLENNER, and NEIL E. GORDON (*Soil Sci.*, 1923, **15**, 157—165).—The adsorption of salts of calcium, potassium, and magnesium was studied by shaking standard solutions of the salts with iron and aluminium hydroxide gels and determining the quantities remaining in solution in the supernatant liquid. The order of adsorption of the kations was found to be calcium, magnesium, potassium, and of the anions phosphate, sulphate, nitrate. In the case of nitrates, adsorption was very slight. The time taken to reach equilibrium was considerably greater for phosphates than with other salts. The amount of adsorption of a particular salt increased with increased concentration. The adsorption of a kation depended to some extent on the particular anion with which it was associated. Phosphates replaced adsorbed sulphates, but the reverse change did not occur. Sulphates and nitrates adsorbed by hydrogels could be removed by washing, but about two-thirds of the adsorbed phosphate could not be leached out. A. G. P.

Organic Chemistry.

Preparation of Petroleum from Vegetable Oils. A. MAILHE (*Compt. rend.*, 1923, 177, 202—204).—The yellow, strongly-smelling olefinic hydrocarbons (b. p. 240—280°) resulting from the pyrogenetic decomposition of vegetable oils (this vol., i, 88), on heating with anhydrous zinc chloride, are partly converted into viscous polymerisation products boiling above 330°, the portion (b. p. 240—280°) not polymerised now being colourless and odourless, but fluorescent.

Colza oil, on heating with a tenth of its weight of zinc chloride at 350—400°, is converted into water, acraldehyde, a gas, and a slightly acid liquid. The latter (the main product), after being washed with alkali, etc., has d^{18} 0.8358, and on distillation affords the following fractions: (1) b. p. below 150°, d^{18} 0.7202, analogous to American oil, (2) b. p. 150—240°, d^{18} 0.7796, analogous to kerosene, (3) b. p. 240—280°, heavy oil, d^{18} 0.8115, (4) b. p. 280—300°, heavy oil, d^{18} 0.8358, (5) b. p. 300—320°, heavy oil, d^{18} 0.8436, and (6) b. p. up to 400°. The entire product consists of paraffin and olefine hydrocarbons. Redistillation of the lower fraction shows the presence of hexane, hexylene, and two seven-carbon hydrocarbons.

The heavy oils boiling above 300° are partly polymerised when heated with zinc chloride, giving a yellow, fluorescent, viscous oil, b. p. 250—280°/37 mm., d^{18} 0.9004. Further polymerisation produces a solid, m. p. 40—42°. E. E. T.

Preparation of Petroleum from Vegetable and Animal Oils. ALPHONSE MAILHE (*Compt. rend.*, 1923, 177, 329—331).—Most of these oils, when heated with anhydrous zinc chloride, give products similar to those previously obtained from colza oil (preceding abstract). Rape-seed oil gives, after a single heating with 10% of its weight of zinc chloride, a mixture of paraffins and olefines, b. p. 60—310°, together with higher boiling substances (containing oxygen), which, on reheating with zinc chloride, afford a product resembling vaselin. Zinc chloride may be replaced, in these conversions, by anhydrous calcium, magnesium, barium, or sodium chlorides.

Karité butter, on heating with calcium chloride, affords an oil of d^{20} 0.7158, b. p. mainly from 150—400°. When magnesium chloride is used, hydrogen chloride is evolved, but the product is similar. Whale oil and magnesium chloride give a liquid of approximately the same properties. E. E. T.

The Relation between Low-temperature Tar, Coke-oven Tar, and Petroleum. FRANZ FISCHER (*Ber.*, 1923, 56, [B], 1791—1794).—Low-temperature tar has been regarded by Fischer
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as closely allied to natural petroleum, whereas Schütz has considered it to be closely related to coke-oven tar. Resemblances to petroleum are found in the optical activity of the hydrocarbons of low-temperature tar, the high hydrogen content of low-temperature tar, light oils, and the presence of solid paraffins (in place of anthracene). Benzene is only present in very small proportion (cf. Broche, this vol., i, 907); its presence in natural petroleum has been frequently observed. The occurrence of considerable proportions of carboic acid and of acetone in low-temperature tar has been observed solely by Schütz; it has not been confirmed in manufacturing practice by other workers. H. W.

Hydration of Hydrocarbons. PAUL WOOG (*Compt. rend.*, 1923, 177, 60—62, 207—208).—By measuring the voltage required to produce a flow of current through an apparatus containing various saturated and unsaturated oily hydrocarbons (which are dry or moist in different experiments), the author concludes that unsaturated hydrocarbons have a greater affinity for water than saturated ones. The latter give up contained water more readily to the glass walls of the containing vessel.

If a saturated and an unsaturated oil are exposed, under the same conditions, to a moist atmosphere, the former soon becomes cloudy, whereas the latter remains transparent for a considerable time. If oils of the two types, and containing sufficient moisture to render them both cloudy, are warmed under similar conditions, the saturated oils clear first. This and the experiments above show that the hydration of saturated hydrocarbons is less stable than that of unsaturated ones.

When a drop of water on a glass rod is brought near to a bubble blown with the oils, a series of colour changes on the part of the oil film follows every movement of the water, the sensitiveness of this phenomenon being greater with unsaturated than with saturated hydrocarbons, owing to the action of the ethylenic linkings. The saturated molecules also, however, must possess points especially sensitive to the presence of water vapour. E. E. T.

A Saturated Hydrocarbon from Shark Liver Oils. YOSHIYUKI TOYAMA (*Chem. Umschau*, 1923, 30, 181—187).—The hydrocarbon isooctadecane ($C_{18}H_{38}$) previously isolated by Tsujimoto from one sample of the liver oil of the giant shark was isolated from the liver oils of a number of species of shark and appears to be a general constituent of various liver oils containing squalene. The pure hydrocarbon, which is named *pristane*, has the following characters: n_D^{15} 1.4410, n_D^{20} 1.4390; d_4^{15} 0.7871, d_4^{20} 0.7835; b. p. $158^\circ/10$ mm., $169^\circ/15$ mm., $187^\circ/30$ mm., $220^\circ/100$ mm., $296^\circ/760$ mm., without decomposition. Absolute viscosity at 30° , 0.443. It is optically inactive. H. C. R.

Action of Selenium Oxychloride on Ethylene, Propylene, Butylene, and Amylene. CARL E. FRICK (*J. Amer. Chem. Soc.*, 1923, 45, 1795—1800).—When selenium oxychloride reacts with the olefines, the dichlorides of the corresponding alkyl selenides are formed, regardless of whether the olefine or the selenium oxy-

chloride is in excess. Thus the product from ethylene and selenium oxychloride is di- β -chloroethylselenium dichloride, whilst di- β -chloropropylselenium dichloride is formed when propylene is used; di- β -chlorobutylselenium dichloride, from β -butylene, and di- β -chloroamylselenium dichloride, from amylene, although probably formed when the reaction is conducted at temperatures below 10° , were not isolated in a pure condition. This reaction, which is formulated: $2C_nH_{2n} + 2Cl_2SeO = (ClC_nH_{2n})_2SeCl_2 + SeO_2$, leads, therefore, to the same products as the action of excess of selenium monochloride on olefines (Boord and Cope, A., 1922, i, 421), $2C_nH_{2n} + 2Cl_2Se : Se = (ClC_nH_{2n})_2SeCl_2 + 3Se$; it is held that these results confirm the unsymmetrical formula, $Se:SeCl_2$, for selenium monochloride. W. S. N.

Catalytic Hydrogenation and Steric Hindrance. G. VAVON and S. KLEINER (*Compt. rend.*, 1923, 177, 401—403; cf. this vol., i, 464).—A study of the relative extents of hydrogenation of (a) Δ^7 -heptene, (b) $\beta\delta$ -dimethyl- Δ^8 -pentene, (c) γ -ethyl- Δ^8 -pentene, and (d) β -methyl- Δ^8 -pentene. The olefine (1 mol.) to be examined was mixed with either α -pinene or undecenoic acid (1 mol.) in presence of an inert solvent (*cyclohexane* or *pinane*), and the mixture allowed to combine with 1 mol. of hydrogen, in presence of platinum black. The amount of hydrogen appropriated by the olefine was determined polarimetrically in the case of pinene mixtures, and by extraction with alkali, followed by bromine titrations of each layer in the case of mixtures with the acid. Olefines *b* and *c* reduce to about the same extent, which is greater than that for *d* and less than that for *a*.

Similar experiments on the addition of bromine (in presence of undecenoic acid) to the olefines indicated that the four substances in question combine with bromine in the (decreasing) order: *d*, *b*, *c*, *a*. These results, unlike those with hydrogen, do not fall into line with the theory of steric hindrance. E. E. T.

A Method for the Bromination of Organic Substances. ERICH KRAUSE (*Ber.*, 1923, 56, [B], 1801).—The method described recently by Rosenmund and Kuhnheim (this vol., i, 782) has been used previously by the author (A., 1918, i, 415). H. W.

Specific Gravity of Absolute Ethyl Alcohol at 20° . C. N. RÜBER (*Z. Elektrochem.*, 1923, 29, 334—338).—Absolute ethyl alcohol, purified by boiling with calcium ethoxide and repeated fractionation in a current of hydrogen, has been used for the determination of its specific gravity. As the mean of three values which differ only in the seventh place of decimals, the value $d_{4}^{20^{\circ}}$ 0.789334 ± 0.000003 is obtained, using the value $d_{4}^{20^{\circ}}$ 0.998232 for water. The figure given refers to ethyl alcohol saturated with dry air at 20° . J. F. S.

New Method of Passing from Mesityl Oxide to Tetramethylglycerol [$\beta\delta$ -Dimethylpentane- $\beta\gamma\delta$ -triol]. PASTUREAU and H. BERNARD (*Compt. rend.*, 1923, 177, 327—329; cf. A., 1922, i, 717; this vol., i, 646).—Magnesium methyl iodide converts

mesityl oxide into $\beta\delta$ -dimethyl- Δ^3 -pentene- δ -ol (cf. von Fellenberg, A., 1904, i, 961), which, with hypiodous acid, affords the iodohydrin of tetramethylglycerol. This substance, when heated with powdered potassium hydroxide, gives the corresponding glycide, whilst silver acetate affords the acetin (m. p. 87°). The glycide is converted into tetramethylglycerol by evaporating its aqueous solution.

The pentenol (above) cannot be oxidised, using permanganate, to give the glycerol, both this substance and the pentenol being oxidised to give acetone, formaldehyde, and formic acid. In the case of the glycerol, this oxidation is even effected by oxygen in presence of ferrous sulphate solution.

Hypochlorous acid converts the pentenol, not into the expected chlorohydrin, but into a crystalline *substance* of unknown constitution. E. E. T.

Oxonium Compounds in the Vapour State. Methyl Ether-Hydrogen Chloride. O. MAASS and D. M. MORRISON (*J. Amer. Chem. Soc.*, 1923, **45**, 1675—1682).—Equal volumes of methyl ether and hydrogen chloride were mixed in the gaseous state at atmospheric pressure and the resultant pressures of the mixture were recorded over the temperature range 30° to -10° . From these data the amount associated to form the oxonium compound, OHMe_2Cl , has been calculated, and the resultant pressures on mixing these gases at pressures other than atmospheric and in unequal proportions were deduced. These latter have been checked experimentally, thus proving the original assumption to be correct, namely, that an equimolecular compound between methyl ether and hydrogen chloride exists in the vapour state, the dissociation of which increases with rising temperature. The similarity between methyl ether-hydrogen chloride and ammonium chloride has been pointed out, and the formation of the first-named compound is attributed to induced polarity in the methyl ether molecule caused by the polar hydrogen chloride molecule. J. F. S.

Dipropargyl Methylene Ether. HERBERT H. GUEST (*J. Amer. Chem. Soc.*, 1923, **45**, 1804—1807).—Dibromohydrin and paraformaldehyde react in the cold in the presence of dry hydrogen chloride, or at 125 — 150° in the presence of anhydrous ferric chloride, giving *di-(β - γ -dibromopropyl)methylene ether*,
 $(\text{CH}_2\text{Br}\cdot\text{CHBr}\cdot\text{CH}_2\cdot\text{O})_2\text{CH}_2$,

b. p. $220^\circ/7$ mm., which is converted, by the action of a slight excess of finely powdered potassium hydroxide on its cold ethereal solution, into *di-(β -bromoallyl)methylene ether*, $(\text{CH}_2\cdot\text{CHBr}\cdot\text{CH}_2\cdot\text{O})_2\text{CH}_2$, b. p. 135 — $140^\circ/10$ mm. If, however, boiling aqueous alcoholic potassium hydroxide is used, the product is *dipropargylmethylene ether*, $(\text{CH}\cdot\text{C}\cdot\text{CH}_2\cdot\text{O})_2\text{CH}_2$, b. p. 75 — $80^\circ/10$ mm., or $162^\circ/760$ mm. This forms an explosive *silver* salt, but the silver atom is non-reactive towards alkyl halides. Dipropargylmethylene ether reacts with magnesium ethyl bromide in cold ethereal solution with evolution of ethane, but a pure product has not been isolated.

W. S. N.

Preparation of Esters and Ethers of Ethylidene Glycol and Vinyl Alcohol. CONSORTIUM FÜR ELEKTROCHEMISCHE INDUSTRIE (Brit. Pat. 182112).—A mixture of acetylene and the vapours of a substance containing a hydroxyl or carboxyl group is passed over a heated catalyst, metals, and their oxides and salts, being especially effective [cf. *J.S.C.I.*, 1923, 42, 861A]. W. T. K. B.

Esters of Chromic Acid. II. Esters of Chromic Acid with Alcohols of the Aliphatic and Aromatic Series. HEINRICH WIENHAUS and WILHELM TREIBS (*Ber.*, 1923, 56, [B], 1648—1653).—The esters indicated in the title cannot be prepared as in the case of terpene and sesquiterpene alcohols by agitating the alcohols with aqueous chromic acid solution. It is generally necessary to treat the solution of the alcohol in light petroleum, carbon tetrachloride, carbon disulphide, or benzene with solid chromium trioxide. The action of organic halides on silver chromate is fairly generally applicable.

Unstable chromates are produced by the action of chromium trioxide on methyl, ethyl, or *isopropyl* alcohol dissolved in much light petroleum or carbon tetrachloride; cetyl and melissyl chromates appear to be rather more stable. The results point to the possibility of isolating the esters at a sufficiently low temperature. *Trimethylcarbinyl chromate*, $(C_4H_9)_2CrO_4$, is obtained as an unstable, viscous, red liquid by the action of chromium trioxide on trimethylcarbinol in the presence of light petroleum or from chlorotrimethylmethane and silver chromate in the presence of ether or light petroleum. *Dimethylethylcarbinyl chromate* is prepared in a similar manner. Dimethylpentadecylcarbinol, m. p. 34—35°, dissolved in light petroleum, is converted by chromium trioxide into *dimethylpentadecyl chromate*, a yellowish-red, wax-like mass; it is very stable, although decomposing readily on exposure to light. *Linalyl*, *dihydrolinalyl*, and *tetrahydrolinalyl chromates* are red liquids.

The presence of a phenyl group generally renders the chromates unstable. If, however, the solubility of the product in dissociating media is depressed by the presence of a relatively large, aliphatic radicle, chromates containing the phenyl group can be readily prepared in a state of purity; they are stable. *Phenylmethylethylcarbinyl chromate* is highly unstable; *diphenylmethylcarbinyl chromate*, a red oil which does not solidify, is considerably more stable. *Diphenylpentadecylcarbinyl chromate* is a viscous, red liquid which is stable except towards light. Triphenylcarbinyl chromate, prepared from triphenylcarbinol and chromium trioxide in the presence of benzene or carbon tetrachloride, forms red crystals.

H. W.

Mixed Organic Sulphides and Cyanogen Bromide. JULIUS VON BRAUN and PAUL ENGELBERTZ (*Ber.*, 1923, 56, [B], 1573—1577).—The action of cyanogen bromide on mixed organic sulphides containing purely aliphatic radicles results in the exclusive elimination of the smaller group as alkyl bromide. The benzyl radicle is more readily lost than the smallest aliphatic group. With benzyl allyl sulphide, both groups are removed from the sulphur

atom, but the extent is much greater with the benzyl complex. An almost complete parallelism exists between sulphur and nitrogen with regard to the relative firmness with which the separate organic radicles are attacked. With arsenic, the parallelism is not quite so close, doubtless owing to the more metallic nature of the element.

Ammonium dithiocarbamate is gradually transformed by *n*-butyl bromide in the presence of alcohol into *n*-butyldithiourethane, $C_5H_{11}NS_2$, m. p. 46—47°, which is converted by dilute potassium hydroxide solution into *n*-butyl mercaptan, b. p. 99—100°, the yield being 70% of that theoretically possible.

n-Propyl *n*-butyl sulphide, a colourless, mobile liquid, b. p. 153—155°, is converted by cyanogen bromide at 60—70° into *n*-propyl bromide and *n*-butyl thiocyanate, b. p. 173—175°. Ethyl propyl sulphide gives ethyl bromide and propyl thiocyanate, b. p. 161—163°, whereas methyl ethyl sulphide yields methyl bromide and ethyl thiocyanate, b. p. 140—141°. Benzyl methyl sulphide is transformed into benzyl bromide and methyl thiocyanate, b. p. 130—132°, whereas *benzyl allyl sulphide*, b. p. 121—122°/12 mm., is converted to a small extent into allyl bromide and benzyl thiocyanate, but mainly into benzyl bromide and allyl thiocyanate.

H. W.

A New Preparation of Monochloroacetic Acid. L. J. SIMON and G. CHAVANNE (*Bull. Soc. chim. Belg.*, 1923, **32**, 285—287).—A republication of work previously described (this vol., i, 177). As sulphuric acid of definite concentration must be used, the following reaction mechanism is suggested: (1) addition of sulphuric acid as with ethylene, $CH_2Cl \cdot CCl_2 + H_2SO_4 \rightarrow CH_2Cl \cdot CCl_2 \cdot O \cdot SO_3H$, (2) hydrolysis of the resulting sulphonic acid, $CH_2Cl \cdot CCl_2 \cdot O \cdot SO_3H + H_2O \rightarrow CH_2Cl \cdot CCl_2 \cdot OH + H_2SO_4$, and $CH_2Cl \cdot CCl_2 \cdot OH \rightarrow CH_2Cl \cdot COCl + HCl$, (3) reaction with water of the acid chloride so formed, $CH_2Cl \cdot COCl + H_2O \rightarrow CH_2Cl \cdot CO_2H + HCl$.

The use of fuming sulphuric acid (cf. Böeseken, A., 1913, i, 330) with subsequent dilution results in a much reduced yield.

H. J. E.

Heptadecoic Acid. A. HEIDUSCHKA and J. RIPPER (*Ber.*, 1923, **56**, [B], 1736—1739).—An intimate mixture of silver stearate, iodine, and fragments of porcelain is heated at 130—140°, whereby *heptadecyl stearate*, $C_{17}H_{35} \cdot CO_2C_{17}H_{35}$, small leaflets, m. p. 64·6°, is obtained; this is hydrolysed by boiling alcoholic potassium hydroxide solution to heptadecyl alcohol, leaflets, m. p. 54°, the yield being 55%. The alcohol is converted into heptadecoic acid, $C_{16}H_{33} \cdot CO_2H$, microscopic rhombs, m. p. 59·9°, by treatment with molten potassium hydroxide in an open vessel at 240—250°. *Lead*, *silver*, and *copper heptadecoates* are described.

H. W.

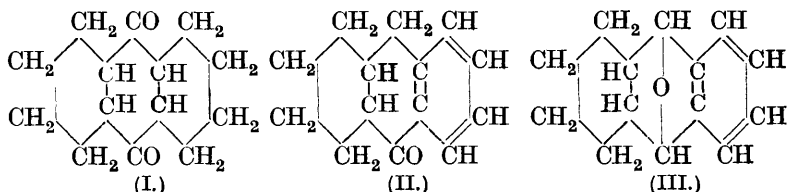
The X-Ray Investigation of Fatty Acids. ALEX. MÜLLER (*T.*, 1923, **123**, 2043—2047).

The Spectrochemical Behaviour and the Constitution of Methyl β -Mesityloxydioxalate [Methyl 2 : 2-Dimethyl-2 : 3-dihydro-4-pyrone-6-carboxylate]. K. VON AUWERS and W. DIECKMANN (*Ber.*, 1923, 56, [B], 1527—1530).—Previous refractometric measurements with this compound have afforded

evidence in favour of the closed ring formula, $\text{CO}\cdot\text{CH}=\text{C}\cdot\text{CO}_2\text{Me}$, $\text{CH}_2\cdot\text{CMe}_2\cdot\text{O}$, rather than the open-chain formula, $\text{CMe}_2\cdot\text{CH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CO}_2\text{Me}$. These measurements, however, were made in chloroform solution, on account of the high melting point of the compound. New measurements have been made with the ester in the fused state at 85.9° and have confirmed the older view that the ester contains the group $-\text{CO}\cdot\text{C}\cdot\text{C}\cdot\text{CO}-$, and must therefore possess the cyclic structure. This view is supported by measurements made with the ethyl ether of ethyl acetoneoxalate, $\text{COMe}\cdot\text{CH}\cdot\text{C}(\text{OEt})\cdot\text{CO}_2\text{Et}$. The following figures are quoted. Methyl β -mesityloxydioxalate, d_4^{25} 1.0933, $d_4^{25.9}$ 1.0920, n_D 1.46398, n_D 1.45814 [? 1.46814], n_B 1.47959 at 85.9° ; ethyl ether of ethyl acetoneoxalate, b. p. $131^\circ/14$ mm., $128-129^\circ/10$ mm., $d_4^{14.05}$ 1.0661, $d_4^{15.3}$ 1.0644, d_D^{20} 1.061, 1.060, n_D 1.46773, n_D 1.47212, n_B 1.48437 at 14.05° , n_D 1.46655, n_D 1.47103, n_B 1.48316, n_D 1.49452 at 15.3° , n_D^{20} 1.4694, 1.4689. H. H.

Thermal Decomposition of some Dicarboxylic Acids.

A. WINDAUS and M. EHRENSTEIN (*Nachr. K. Ges. Wiss. Göttingen*, 1922, 1—7; from *Chem. Zentr.*, 1923, i, 831; cf. Windaus and Hückel, A., 1922, i, 658).—Barium $\beta\beta$ -dimethylglutarate by dry distillation gives, in addition to unidentified products, acetone, mesityl oxide, and isophorone. Dimethylcyclobutanone, although not found, was probably formed as an intermediate stage, giving mesityl oxide by rearrangement. Acetone was probably formed by hydrolytic decomposition of mesityl oxide, and isophorone by condensation of acetone, or of acetone with mesityl oxide. *cis*-Hexahydrophthalic anhydride gives off carbon dioxide at about 380° , a dodecahydroanthraquinone (I) being probably first formed, which loses hydrogen by which the keto-groups are reduced. A certain amount of anthraquinone was found as well as a compound, $\text{C}_{14}\text{H}_{16}\text{O}$, which was probably an anthracene derivative (II or III). It is a yellowish-brown, slightly fluorescent oil, forming



white platelets, m. p. $97-98^\circ$. A mixture of hydrogenated anthracenes was also obtained in which the hydrocarbons $\text{C}_{14}\text{H}_{20}$ and $\text{C}_{14}\text{H}_{22}$ predominated. Hexahydro-*o*-phthalic acid is obtained by catalytic hydrogenation of tetrahydro-*o*-phthalic acid.

G. W. R.

Resolution of the $\alpha\delta$ -Dihydroxy- α -methyl- δ -isopropyladipic Acids. THOMAS ANDERSON HENRY and HUMPHREY PAGET (T., 1923, 123, 1878—1887).

Dihydroxymaleic Acid (Dihydroxyfumaric Acid). J. BÖESEKEN and J. I. DE VOOGD (*Rec. trav. chim.*, 1923, 42, 745—749).—The authors have prepared dihydroxymaleic and dihydroxyfumaric acids by a method which is a slight modification of that of Fenton (T., 1894, 65, 899) and have investigated these two substances by means of electrical conductivity and refractive index measurements, and conclude that these two acids are both dihydroxymaleic acids. J. F. S.

Citrates of Calcium and Strontium. K. P. CHATTERJEE (*J. Proc. Asiatic Soc. Bengal*; *Proc. Eighth Indian Sci. Cong.*, 1921, 17, cxxix—cxxx).—The gelatinous, hygroscopic compound $\text{Ca}_3(\text{C}_6\text{H}_5\text{O}_7)_2 \cdot 16\text{H}_2\text{O}$ is precipitated when strong solutions of sodium citrate and calcium chloride are mixed. It passes rapidly into the hexahydrate, which separates in the cold with increasing rapidity up to 70° ; above this temperature, the tetrahydrate separates, its solubility decreasing with temperature. On being warmed, the hexahydrate yields the tetrahydrate, the compound $\text{Ca}_3(\text{C}_6\text{H}_5\text{O}_7)_2 \cdot 1.5\text{H}_2\text{O}$ being obtained at 110° . Gelatinous strontium citrate, and a penta- and a mono-hydrate, having analogous properties, have been obtained. CHEMICAL ABSTRACTS.

Preparation of Glyoxal and Glyoxal Sulphate. CHEMISCHE FABRIKEN VORM. WEILER-TER MEER (KARL OTT) (D.R.-P. 362743; from *Chem. Zentr.*, 1923, ii, 743).—Tetrahalogenoethanes are treated with fuming sulphuric acid with or without addition of heavy metals, and glyoxal is obtained from the sulphate thus formed. For example, tetrachloroethane with mercuric sulphate or copper sulphate in suspension is added to fuming sulphuric acid containing 65% of sulphur trioxide. *Glyoxal sulphate*, which separates on cooling, forms colourless needles, m. p. 176 — 177° . The reaction whereby it is formed is probably $\text{C}_2\text{H}_2\text{Cl}_4 + 4\text{SO}_3 + 2\text{H}_2\text{SO}_4 = 4\text{SO}_3\text{HCl} + \text{SO}_2 \cdot \text{CH} \cdot \text{CH} \cdot \text{SO}_2$. Glyoxal is obtained by heating the sulphate with water. G. W. R.

Condensing Action of Mixed Magnesium Alkylloxides, $\text{RO} \cdot \text{Mg} \cdot \text{X}$. V. GRIGNARD and M. DUBIEN (*Compt. rend.*, 1923, 177, 299—302).—The condensation of ketones, which sometimes occurs during their interaction with Grignard reagents (cf., this vol., i, 739), has been traced to the condensing action of compounds of the type $\text{RO} \cdot \text{Mg} \cdot \text{X}$, produced during such reactions. Thus *n*-butaldehyde is rapidly converted, in presence of an ethereal suspension of magnesium ethoxyiodide, into β -hydroxy- α -ethyl-*n*-hexanal, $\text{CH}_2\text{Me} \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CHEt} \cdot \text{CHO}$ (colourless liquid, b. p. 103 — $105^\circ/14$ mm., polymerising readily and giving a semicarbazone, m. p. 147°), small quantities of *n*-butyl and ethyl butyrates being formed in addition.

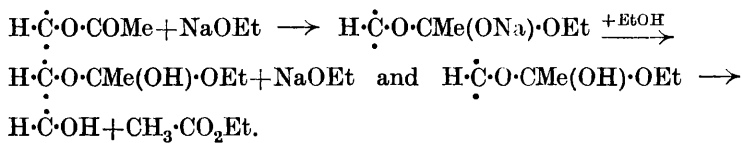
Magnesium ethoxyiodide causes the partial conversion of acetone into diacetone alcohol (cf. Locquin, this vol., i, 440).

The magnesium derivative formed by the addition of magnesium methyl iodide to *n*-butylideneacetone causes the condensation of the latter substance to give a carbinol, which undergoes loss of the elements of water on distillation. (The product was therefore heated with a little iodine, to complete this loss of water.) In this way, dibutylideneacetone was isolated.

E. E. T.

The Sodium Compound of Dextrose and the Hydrolysis of Acylated Sugars. GÉZA ZEMPLÉN and ALFONS KUNZ (*Ber.*, 1923, 56, [B], 1705—1710).—A sodium compound of dextrose has been described frequently in the literature and has generally been regarded as a substituted alkoxide. It does not, however, react in the manner characteristic of this class of compounds. Investigation of it has shown that it is an additive compound of molecular proportions of dextrose and sodium ethoxide.

When dextrose penta-acetate is treated with a cold, absolute alcoholic solution of sodium ethoxide, a sodium derivative speedily separates which yields ethyl acetate when treated with water. The formation of this intermediate compound gives the clue to the mechanism of the hydrolysis of acetylated sugars by sodium methoxide, for which, as noted previously by Fischer and Bergmann, considerably less ethoxide is required than is necessary according to theory with the acetyl groups which are present. The reaction is represented by the scheme :



The action of sodium ethoxide on acetobromoglucose in absolute alcoholic solution has also been examined. A precipitate similar to that obtained from dextrose penta-acetate is formed in small amount, but the bulk of the dextrose remains in solution and is converted into β -ethylglucoside; this is shown by its transformation into β -ethylglucoside tetra-acetate. The by-products of the change appear to be much more complex than those derived from the penta-acetate.

H. W.

Fermentative Hydrolysis of β -Alkyl Glucosides. Indices for Emulsin. Estimation of Molecular Weights. H. COLIN and (Mlle) A. CHAUDUN (*Bull. Soc. Chim. biol.*, 1923, 5, 382—388).—The method previously described (A., 1921, ii, 225) for estimating the molecular weights of certain polysaccharoses has been extended to the estimation of the molecular weights of β -alkyl glucosides. The method depends on the fact that the amount of glucoside fixed by a given quantity of emulsin is proportional to its molecular weight.

E. S.

Action of Ferments on Sulphuric and Phosphoric Acid Esters of Sugars and their Derivatives. BURCKHARDT HELFERICH, ALBRECHT LÖWA, WALDEMAR NIPPE, and HANS RIEDEL (*Z. physiol. Chem.*, 1923, 128, 141—153).—By the action of sulphuryl chloride or of phosphoryl chloride on various sugar derivatives, the corresponding esters have been obtained and isolated as their barium salts as follows. *Barium α -methylglucoside sulphate*, $[\alpha]_D^{19} + 81.16^\circ$. *Barium β -methylglucoside sulphate*, $[\alpha]_D^{23} - 19.12^\circ$. *Barium methylmaltoide sulphate*, $[\alpha]_D^{18} + 53.8^\circ$. *Barium trehalose sulphate*, $[\alpha]_D^{18} + 128.75^\circ$. *Barium amygdalic acid sulphate*, $[\alpha]_D^{18} - 45.1^\circ$. *Barium methylcelloside sulphate*, $[\alpha]_D^{18} - 16.2^\circ$. *Barium β -methylglucoside phosphate*, $[\alpha]_D^{18} - 31.0^\circ$. *Barium β -phenylglucoside phosphate*, $[\alpha]_D^{18} - 51.1^\circ$. *Barium trehalose phosphate*, $[\alpha]_D^{19} + 135.5^\circ$. *Barium methylcelloside phosphate*, $[\alpha]_D^{23} - 14.98^\circ$. *Barium amygdalic acid phosphate*, $[\alpha]_D^{23} - 49.0^\circ$. All the rotations are measured in aqueous solution. Hepta-acetylmethylcelloside, m. p. 186.5° , $[\alpha]_D^{19} - 26.03^\circ$ in tetrachloroethane, $[\alpha]_D^{17} - 31.61^\circ$ in acetic acid, is obtained from acetobromocellose and methyl alcohol in presence of silver oxide. When hydrolysed with methyl-alcoholic ammonia, it yields *methylcelloside*, bevelled prisms, m. p. 193° , $[\alpha]_D^{17} - 18.69^\circ$ in water. The action of α - and β -glucosidases on these esters has been investigated, but in every case they have been found inactive.

W. O. K.

Preparation of Rare Sugars [Arabinose, Rhamnose, Xylose, Galactose, Melezitose, Raffinose, and Maltose]. T. SWANN HARDING (*Sugar*, 1922, 406; 1923, 82—83, 124—125, 175—176, 240—241, 308—310, 350—352).—*Arabinose*: 300 g. of beet pulp are hydrolysed by boiling for one and a half hours with 6 litres of 1% sulphuric acid, neutralised with 175 g. of barium hydroxide, and allowed to subside; the supernatant liquid is clarified with basic lead acetate, the excess removed as sulphide, decolorising carbon added, and the whole filtered; after concentration to about $\frac{1}{4}$ litre, 500 c.c. of 95% alcohol are added for the elimination of organic acids, colouring matter, and salts, and crystallisation is effected from alcoholic solution containing 1% of nitric acid, the yield being 4—5% of the weight of raw material. *Rhamnose*: black oak bark is boiled with water, and the extract concentrated for the crystallisation of the quercitrin, which glucoside is hydrolysed with 0.4% sulphuric acid; the resulting liquid is filtered, clarified with basic lead acetate, delead, and evaporated to a syrup of about 80% solids, which readily crystallises, the yield being about 1% of the raw material. *Xylose*: 1 kg. of corn cobs is boiled for two hours with 6 litres of 4% sulphuric acid, and the liquid is filtered, neutralised with barium carbonate, filtered, and evaporated to a thick syrup, from which the sugar crystallises by the addition of alcohol, the yield being about 12%. *Galactose*: Clark's method (*A.*, 1921, i, 647) is preferred, the yield in the author's hands being 35—37%. *Melezitose*: honey collected from the Douglas fir is dissolved in water, the extract cooled, and the wax separated; after clarifying with kieselguhr and decolorising

carbon, and concentrating, the trisaccharide crystallises out, the yield on recrystallisation being about 22%. *Raffinose*: 6 kg. of cotton-seed meal are extracted with 30 litres of water containing 750 g. of aluminium sulphate, filtered, and evaporated to 3 litres, to which are added 6 litres of 80% alcohol; after subsiding, the liquid is clarified with basic lead acetate, filtered, delead, treated with decolorising carbon, and filtered; the alcohol is eliminated, and the residue concentrated to 300 c.c., from which syrup after adding 95% alcohol the sugar will crystallise out on keeping, the yield thus obtained being about 2%. *Maltose*: soluble starch is saccharified with barley flour, the resulting dextrins being very much less soluble in alcohol than when malt extract is used. Previous work on the elaboration of methods for the preparation of these sugars is summarised.

J. P. O.

System Sucrose-Sodium Chloride-Water and the Combination of these Constituents. N. SCHOORL (*Rec. trav. chim.*, 1923, 42, 790—799).—A method is described which allows the existence of one or more compounds of two components being established. The method consists in the determination of the vapour pressure of the saturated solution of various mixtures of the two solid components. If the curve shows an *euhygroscopic* point, or if there is a special branch in the curve, then the existence of a compound is indicated. The term *euhygroscopic* denotes a point of minimum vapour pressure, and is analogous to the term eutectic. Vapour-pressure curves and solubility curves of mixtures of sucrose and sodium chloride have been determined at 25°, and it is shown that an equimolecular compound, crystallised with 2 molecules of water, $C_{12}H_{22}O_{11} \cdot NaCl \cdot 2H_2O$, exists.

J. F. S.

Starch. VIII. The Characterisation of the Polyamyloses. HANS PRINGSHEIM and KURT GOLDSTEIN (*Ber.*, 1923, 56, [B], 1520—1526).—The authors' conception that β -hexa-amylose is a dimeric tri-amylose and α -hexa-amylose is a trimeric diamylose has not met with universal acceptance. It is, however, strengthened by the observations that the molecular weight of methylated β -hexa-amylose in benzene solution agrees with the theoretical value, whereas that of methylated tri-amylose is somewhat high in benzene but normal in phenol. The molecular weight of methylated α -hexa-amylose confirms its conception as a trimeric diamylose.

β -Hexa-amylose is converted by methyl sulphate and potassium hydroxide solution or by this mixture followed by silver oxide and methyl iodide into *dodecamethyl- β -hexa-amylose*, $[C_6H_8O_5Me_2]_6$, $[\alpha]_D^{20} + 143.20^\circ$ in ethyl-alcoholic solution; attempts to methylate the product further were not generally successful, although in one instance a more highly methylated product was obtained. Methylation of triamylose gives *hexamethyltriamylose*, $(C_6H_8O_5Me_2)_3$, hexagonal plates, $[\alpha]_D^{20} + 138.38^\circ$ in ethyl-alcoholic solution. *Dodecamethyl- α -hexa-amylose* crystallises in well-defined rhombohedra, $[\alpha]_D^{20} + 148.73^\circ$ when dissolved in ethyl alcohol.

β -Hexa-amylose and α -tetra-amylose are converted by phos-

phoryl chloride in the presence of pyridine at -15° into *phosphoric esters*, which appear to contain one phosphoric acid residue for each dextrose residue; for some unexplained reason, the carbon content of these compounds is considerably lower than that demanded by theory.

The benzylation of the polyamyloses has been investigated further (cf. Pringsheim and Eissler, A., 1913, i, 1156; Karrer, A., 1922, i, 1119). Tetra-amylose is converted by benzoyl chloride and sodium hydroxide solution (1%) at -2° into dibenzoyldiamylose, whereas in the presence of more concentrated sodium hydroxide solution at the atmospheric temperature it is transformed into tetrabenzoyldiamylose. Under similar conditions, β -hexa-amylose yields tribenzoyltriamylose and hexabenzoyltriamylose. H. W.

The Action of Concentrated Hydrochloric Acid on Different Celluloses. E. C. SHERRARD and A. W. FROEHLKE (*J. Amer. Chem. Soc.*, 1923, **45**, 1729—1734).—The hydrolysis of celluloses from cotton, white spruce, Douglas fir, and yellow birch, by means of 41% hydrochloric acid at 20° , has been followed by measuring the specific rotation, and by estimating the reducing sugars by means of Fehling's solution, the results being shown graphically. The specific rotation curves for cotton and white spruce cellulose are practically identical, although the latter contains mannose, but Douglas fir cellulose, and more particularly yellow birch cellulose, are hydrolysed more rapidly; since yellow birch contains about 28% of pentosan, this is not surprising. Each curve shows two breaks, one after about two hours (cf. Willstätter and Zechmeister, A., 1913, i, 955), and the other after about six or seven hours. Possibly the three steps in the curves represent successive stages in the degradation of the cellulose; they may also be due to changes in the optical activity of the sugars produced, or perhaps three sugars are formed from the start of the reaction. The relative merits of the three hypotheses cannot be decided from the evidence available. No direct relationship exists between the optical curves and those obtained by estimations of the reducing sugars. The latter show that the reaction slackens, a maximum of dextrose, 85.6—97.8%, being obtained after about twenty-five hours. It is concluded (cf. Cunningham, T., 1918, **113**, 173) that the optical method of determining the quantitative conversion of cellulose into sugar is of little value. It does, however, indicate that considerable differences exist between celluloses from different sources. W. S. N.

The Viscosity of some Cellulose Acetate Solutions. ERNEST WALTER JOHN MARDLES (T., 1923, **123**, 1951—1957).

Lignin. EMIL HEUSER and ARNE WINSVOLD (*Cellulosechemie*, 1923, **4**, 49—58, 62—68).—On treatment with fused potassium hydroxide, lignin prepared from wood by the method of Willstätter and Zechmeister yielded up to 28% of phenolic derivatives. This suggests a constitution with a benzene nucleus and oxidisable

side-chains. Under similar conditions, cellulose yields only negligible quantities of aromatic derivatives. The most favourable temperature for the fusion is between 240° and 280° . Various substantial amounts of lignic acids are recovered from the products of the fusion; the phenolic products consist of protocatechuic acid (16—19%) and pyrocatechol (1—3%). If the fusion be conducted in the presence of air, secondary oxidation takes place with formation of oxalic acid (up to 20%). In an indifferent atmosphere, such as hydrogen or nitrogen, the formation of oxalic acid is practically suppressed and the yield of pyrocatechol increases up to 9%. Protocatechuic acid is the primary product of the fusion; the pyrocatechol is formed from it by elimination of carbon dioxide. If the fusion be conducted in an iron vessel, there is a catalytic destruction of the protocatechuic acid, but the formation of pyrocatechol, if air be excluded, is increased up to 23%.

J. F. B.

Methyl- and Ethyl-ammonium Mercuribromides. RAYMOND M. HANN (*J. Amer. Chem. Soc.*, 1923, **45**, 1763—1764).—Alkylammonium mercuribromides, $\text{NR}_4\text{Br.HgBr}_2$, and alkylammonium dimercuribromides, $\text{NR}_4\text{Br.2HgBr}_2$, where $\text{R}=\text{H}$, or alkyl, are formed in alcoholic solution from mercuric bromide, an alkyl bromide, and the hydrobromide of an amine. They are far more soluble in organic solvents than the corresponding chlorides and iodides. The presence of chloride-ion, as from an amine hydrochloride, decreases the solubility, but gives products containing both chlorine and bromine.

Dimethylammonium dimercuribromide, m. p. $171\text{--}172^{\circ}$.
Diethylammonium dimercuribromide, heavy, brilliant white plates, m. p. 158° .
Trimethylammonium mercuribromide, m. p. 102° .
Triethylammonium dimercuribromide, m. p. $124\text{--}125^{\circ}$.
Tetraethylammonium mercuribromide, m. p. 72° .

W. S. N.

Tetramethylammonium Tri- and Tetra-chloroiodides. WILLIAM NORMAN RAE (*J. Amer. Chem. Soc.*, 1923, **45**, 1725).—Since no polyhalides of the alkali metals or ammonium corresponding with the di-, tri-, and tetra-chloroiodides of tetramethylammonium are known, the author has repeated the work of Weltzien (*Annalen*, 1856, **99**, 1), in which the preparation of these compounds is described. Using the same method as Weltzien, it is shown that the compound described as the trichloroiodide is of variable composition, and that in all probability this substance is a mixture of the di- and tetra-chloroiodides produced by the decomposition of an unstable trichloroiodide. Weltzien's tetra-chloroiodide is judged from the analyses also to have been partly decomposed. The author has obtained a solid which approaches much more closely to the composition demanded by NMe_4ICl_4 by the long-continued action of dry chlorine on tetramethylammonium iodide at 28° . This compound is an orange-coloured substance which requires about fifty days' treatment as above for its preparation.

J. F. S.

The Complex Ions formed by Silver Salts and Ammonia or Substituted Ammonias. P. JOB (*Compt. rend.*, 1923, 176, 1805—1808; cf. this vol., i, 307).—The methods used in the author's previous work have now been applied to the cases of diethylamine and hexamethylenetetramine. The former yields a complex ion of the formula $\text{Ag}(\text{NHEt}_2)_2^+$ which is slightly less stable than the corresponding ethylenediamine complex. On dilution, the complex ion breaks down and the properties of the resulting solution indicate the formation of NHEt_2Ag^+ ions. Hexamethylenetetramine also yields two complex univalent ions, $\text{Ag}[\text{C}_6\text{H}_{12}\text{N}_4]_2^+$ and $\text{Ag}[\text{C}_6\text{H}_{12}\text{N}_4]^+$. Concentrated ammonia yields an ion of the formula $\text{Ag}(\text{NH}_3)_2^+$, but the changes undergone by the latter on dilution are less capable of a simple interpretation than with the ions previously mentioned. A brief account is given of the action of change of temperature on the various argentodiamino-ions.
H. J. E.

Preparation of Carbamide from Ammonia and Carbon Dioxide. JEAN LÉON MAURICE FRÉJACQUES (Fr. Pat. 527733; from *Chem. Zentr.*, 1923, ii, 631—632).—Ammonium carbamate is heated under pressure at 145—200°. For example, by the action of ammonia on carbon dioxide with cooling or by the action of liquid ammonia on carbon dioxide, ammonium carbamate is obtained, and heated in an autoclave for two to four hours at 150°. The temperature is allowed to fall to 65—100°, and the ammonia, carbon dioxide, and water from undecomposed ammonium carbamate are removed. Carbamide remains in the autoclave.

G. W. R.

The Carbamide Dearrangement. II. TENNEY L. DAVIS and KENNETH C. BLANCHARD (*J. Amer. Chem. Soc.*, 1923, 45, 1816—1820).—The formation of phenylcarbamide and of *s*-diphenylcarbamide occurs when carbamide and aniline hydrochloride are boiled in aqueous solution. Phenylcarbamide dearranges into diphenylcarbamide when its aqueous solution is boiled, and, if steam is passed through, the distillate contains aniline. This dearrangement of carbamide and its substitution derivatives, which has not previously been observed to occur in solution (but cf. this vol., i, 22), is used in the preparation of various alkyl- and aryl-carbamides.

s-Dimethylcarbamide and *s*-diethylcarbamide are formed when carbamide is heated at 160—170° with methylamine hydrochloride or ethylamine hydrochloride, respectively. *s*-Diphenylcarbamide and *s*-phenylethylcarbamide are both produced when diethylcarbamide and aniline are heated at 160—170°; at this temperature, *s*-phenylethylcarbamide passes into *s*-diphenylcarbamide, with evolution of ethylamine. *s*-Di-*n*-butylcarbamide, white flakes, m. p. 70.5—71.0°, is formed when carbamide is boiled in aqueous solution with *n*-butylamine or its hydrochloride. When heated with aniline at 160—170°, it yields *s*-diphenylcarbamide, and a small quantity of a substance, white flakes, m. p. 65°, possibly *s*-phenyl-*n*-butylcarbamide. *s*-Di-*n*-amylcarbamide, white flakes,

m. p. 92·8°, is produced when carbamide and *n*-amylamine hydrochloride are heated at 160—170°; the use of *iso*amylamine hydrochloride gives a *substance*, transparent plates, m. p. 37·5°, evidently *s-diisoamylcarbamide*. Benzylcarbamide is formed when carbamide and benzylamine are heated at 160—170°, or boiled together in aqueous solution, but dibenzylcarbamide is produced only by the first method. Benzylcarbamide does not undergo rearrangement when boiled in aqueous solution. Carbamide does not react in boiling aqueous solution with methylaniline, or when heated with dibutylamine hydrochloride. *as*-Phenylethylcarbamide is produced when carbamide and ethylaniline hydrochloride are boiled in aqueous solution, whilst the use of methylaniline hydrochloride gives *as*-phenylmethylcarbamide.

It is held that these facts support the hypothesis (*loc. cit.*) that unsymmetrically disubstituted carbamides dearrange in only one way, $RR'N \cdot CO \cdot NH_2 \rightleftharpoons RR'NH + HNCO$, whilst symmetrically disubstituted carbamides dearrange in two ways, $R \cdot NH_2 + R' \cdot NCO \rightleftharpoons RNH \cdot CO \cdot NHR' \rightleftharpoons R' \cdot NH_2 + R \cdot NCO$. W. S. N.

Preparation of Alkylguanidines. ROSS PHILLIPS and H. T. CLARKE (*J. Amer. Chem. Soc.*, 1923, **45**, 1755—1757).—Methyl isothiocarbamide reacts with methylamine or dimethylamine in warm aqueous solution, with evolution of methyl mercaptan, and formation of, respectively, *methylguanidine sulphate*, m. p. 239—240°, yield 82%, and *α-dimethylguanidine sulphate*, m. p. 285—288° (decomp.), yield 82%. It is found incidentally that *sodium methyl sulphide*, $2MeSNa \cdot 9H_2O$, long, flat needles, decomp. 200°, crystallises from an aqueous 25% solution of sodium hydroxide when the gas is passed in for purposes of isolation.

W. S. N.

Alkaline Solutions of Copper Hydroxide [and Silver Oxide]. III. WILHELM TRAUBE (*Ber.*, 1923, **56**, [B], 1653—1656).—Complex salts of copper hydroxide with amines and polyhydroxy-compounds have already been shown to exist and to possess a reddish-violet colour characteristic of the presence of copper in both the anion and the kation. It is now shown that similar salts can be obtained containing silver, copper, biuret, and an amine.

Silver diamminecupribiuret, $[Ag(NH_3)_2]_2[Cu(C_2H_3O_2N_3)_2]$, is prepared by adding freshly prepared silver oxide to a solution of biuret in aqueous ammonia. When the oxide has dissolved, copper hydroxide is added and dissolves to a purple solution which deposits the cupribiuret as red, obliquely truncated prisms.

Silver ethylenediaminecupribiuret, $[Ag(en)_2]_2[Cu(C_2H_3O_2N_3)_2]$, is prepared in a similar manner, and forms short, ruby-red prisms, easily soluble in water. H. H.

Reactions of Thiocyanates on Ferric Salts and of Ferric Salts on Thiocyanates. J. CLARENS (*Bull. Soc. chim.*, 1923, [iv], **33**, 988—991).—Red ferric thiocyanate is easily soluble in aqueous ether and can be extracted from a dilute aqueous solution

by that solvent. The extract possesses a deep violet colour which may be completely discharged by the addition of ferric chloride. The explanation of this effect put forward by the present author is that an excess of thiocyanate is necessary for the formation of ferric thiocyanate, which is soluble in ether. When a ferric salt is added, this excess of thiocyanate is removed, and a salt of dithiocyanic acid, insoluble in ether, is formed. H. H.

An Intercepted Hydrolysis. OLIVER C. DE C. ELLIS and LESLIE B. GIBBINS (*J. Amer. Chem. Soc.*, 1923, **45**, 1727—1728).—In an attempt to prepare phosphonium cyanide by heating potassium cyanide with phosphorus and a little water, an extremely pure sample of ammonium cyanide was collected in the cooled receiver. The reaction is explained as follows: the equilibrium $\text{KCN} + \text{H}_2\text{O} \rightleftharpoons \text{KOH} + \text{HCN}$ is destroyed at higher temperatures by the disappearance of the hydrogen cyanide; this is due to a further hydrolysis, $\text{HCN} + 2\text{H}_2\text{O} = \text{HCO}_2\text{NH}_4$, and $\text{HCO}_2\text{NH}_4 = \text{NH}_3 + \text{HCO}_2\text{K} + \text{H}_2\text{O}$. The total reaction of boiling potassium cyanide in water is $\text{KCN} + 2\text{H}_2\text{O} = \text{NH}_3 + \text{HCO}_2\text{K}$. When phosphorus is present, the hydrolysis is interrupted to an extent defined by the reaction of the phosphorus with the potassium hydroxide present, an equivalent amount of hydrogen cyanide being liberated. Thus the two main reactions of the preparation are $\text{KCN} + 2\text{H}_2\text{O} = \text{NH}_3 + \text{HCO}_2\text{K}$ and $3\text{KCN} + 4\text{P} + 6\text{H}_2\text{O} = 3\text{KH}_2\text{PO}_2 + \text{PH}_3 + 3\text{HCN}$. If the phosphorus is replaced by aluminium, the yield of ammonium cyanide is greater, particularly if a suitable quantity of sulphuric acid be added. In some cases, the product was coloured, due to presence of azulmic acid, thus showing the great readiness with which ammonia is oxidised. $2\text{NH}_4\cdot\text{CN} + \text{O} = 2\text{NH}_3 + \text{C}_2\text{N}_2 + \text{H}_2\text{O}$; $\text{NH}_4\cdot\text{CN} \rightleftharpoons \text{NH}_3 + \text{HCN}$; $2\text{NH}_3 + 2\text{C}_2\text{N}_2 = \text{C}_4\text{H}_6\text{N}_6$; $\text{C}_4\text{H}_6\text{N}_6 + \text{H}_2\text{O} = \text{C}_4\text{H}_5\text{N}_5\text{O} + \text{NH}_3$. Ammonium cyanide is readily ignited, burning with a pale fawn-coloured flame. It immediately decolorises neutral potassium permanganate solution; it reacts with a chloroform solution of sulphur, yielding ammonium thiocyanate. J. F. S.

Oxidation Phenomena among the Complex Cyanides of Nickel; Valency, Co-ordination, Colour. ANDRÉ JOB and ANDRÉ SAMUEL (*Compt. rend.*, 1923, **177**, 188—191).—The red solution obtained on reducing a nickelocyanide by means of an alkali metal amalgam contains the compound $\text{K}_2[\text{Ni}(\text{CN})_3]$, where nickel is univalent and has a co-ordination number of 3. The formation, simultaneously, of potassium cyanide is proved by the fact that nickelous cyanide dissolves in the solution to give dipotassium nickelocyanide, $\text{K}_2[\text{Ni}(\text{CN})_4]$. The red solution, moreover, absorbs carbon monoxide (and also acetylene), forming an almost colourless solution containing univalent nickel with co-ordination number 4, *i.e.*, containing the complex group $[\text{Ni}(\text{CN})_3\text{CO}]$, no potassium cyanide being liberated in this case. Similarly, cobaltous cyanide, potassium cyanide, and carbon monoxide combine to form the *carbonylcobaltocyanide*.

The instability ascribed in the literature to the above red solution

is due to the presence of free cyanide-ions, and is more marked if an excess of potassium cyanide is added. Again, on shaking the red solution with air it becomes pale yellow and nickelous cyanide is precipitated: $2K_2[Ni(CN)_3] + O + H_2O = Ni(CN)_2 + K_2[Ni(CN)_4] + 2KOH$, so that the dissolved nickel remaining is bivalent, with co-ordination number 2.

The yellow nickelocyanide solution becomes bright red when treated with an excess of potassium cyanide, owing to the formation of *tetrapotassium nickelocyanide*, $K_4[Ni(CN)_6]$, containing bivalent nickel with co-ordination number 6. The doubt hitherto cast on the existence of this salt is due to the fact that evaporation leads to the separation of potassium cyanide and nickelocyanide. Similarly, in dilute solutions, the complex dissociates, so that conductivity measurements are then equally untrustworthy.

When nitric oxide is passed into a solution of potassium nickelocyanide, the colour first fades and then becomes an intense violet. This is due to reduction of nitric oxide to hydroxylamine. Thus, the violet solution is obtained by dissolving potassium nickelocyanide (1 mol.) in water, adding a suspension of nickelous cyanide (1 mol.), and then 3 molecules of hydroxylamine and 6 molecules of potassium hydroxide. To the violet *compound* (nickel tervalent, co-ordination number 6) is given the provisional formula $K_2[Ni(CN)_3(OH)_2(NH_2\cdot OH)]$.
E. E. T.

Dissociation of Complex Cyanides. GEORGE JOSEPH BURROWS (T., 1923, 123, 2026—2029).

Reaction of Hydroxylamine with Nitroprussides. J. GIRAL PEREIRA (*Anal. Fis. Quim.*, 1923, 21, 236—244).—When hydroxylamine hydrochloride is allowed to react with a solution of sodium nitroprusside in the presence of sodium hydroxide, free from carbonate, under conditions described, a red coloration is given accompanied by evolution of nitrogen with effervescence. On addition of ethyl alcohol, a red, glutinous mass separates. A description is given of its reactions with various substances. Its formation is discussed and the formula $Fe \begin{smallmatrix} C(NNa)\cdot C(NNa) \\ C(NNa)\cdot C(NNa) \end{smallmatrix} > C:N\cdot NO$ is suggested.
G. W. R.

The Catalytic Reduction of Semicarbazones. K. A. TAIPALE and S. A. SMIRNOFF (*Ber.*, 1923, 56, [B], 1794—1798).—1-Alkylsemicarbazides are prepared by the catalytic hydrogenation of the semicarbazones of aliphatic aldehydes in the presence of platinum black and alcohol or, preferably, glacial acetic acid. The β -isomerides have, in general, lower melting points than the corresponding α -compounds. Like the latter, they reduce ammoniacal silver solution at the atmospheric temperature; Fehling's solution is reduced slowly when cold, rapidly when heated.

α -Ethylsemicarbazide, $NH_2\cdot CO\cdot NH\cdot NH\cdot Et$, crystallises in small, transparent prisms, m. p. 97—98°; the corresponding *hydrochloride*, a microcrystalline powder, m. p. 148—150°; the *hydrogen oxalate*, $C_5H_{11}O_5N_3$, matted needles, decomp. 165.5°; the *benzoyl*

derivative, $C_{10}H_{13}O_2N_3$, m. p. 205—206°, and the *acetyl* compound, m. p. 218·5°, are described; a nitroso-derivative could not be obtained. The action of saturated barium hydroxide solution on the acetyl derivative leads to the formation of 3-*hydroxy-5-methyl-1-ethyl-1:2:4-triazole*, $\begin{array}{c} N=CMe \\ | \\ C(OH):N \end{array} > NEt$ or $\begin{array}{c} N=CMe \\ | \\ CO-NH \end{array} > NEt$, aggregates of needles, m. p. 123°; the corresponding amorphous *silver* salt and the *hydrochloride*, m. p. about 220—221° (decomp.) when rapidly heated, are described. 1-*n-Propylsemicarbazide* has m. p. 79·5—80° (*hydrochloride*, m. p. 160·5—161°). H. W.

The Application of Colloidal Platinum as Catalyst in the Reduction of Azines, Semicarbazones, and Phenylhydrazones. H. L. LOCHTE and J. R. BAILEY (*Ber.*, 1923, 56, [B], 1799—1800; cf. A., 1922, i, 329; this vol., i, 26).—A claim for priority against Taipale (this vol., i, 547).

The reduction of dimethylketazine to β -hydrazopropane has been effected by Taipale in glacial acetic acid solution. The reaction is more conveniently effected in the presence of hydrochloric acid when a mixture of acetone and hydrazine hydrate can be used, thus avoiding the preliminary isolation of dimethylketazine. The oxidation of β -hydrazopropane by hydrogen peroxide yields the azo-compound, $CHMe_2 \cdot N:N \cdot CHMe_2$, and not acetoneisopropylhydrazone as indicated by Taipale. The latter substance has been prepared as a colourless, mobile liquid with a pronounced odour of menthol, b. p. 132—134°/750 mm. H. W.

Manufacture of Hydroxylated Aliphatic Arsinic Acids.

LES ÉTABLISSEMENTS POULENC FRÈRES and CARL OECHSLIN (Brit. Pat. 191028).—Compounds such as $HO \cdot CH_2 \cdot CH_2 \cdot AsO_3H_2$, $C_3H_5(OH)_2 \cdot AsO_3H_2$, $OH \cdot C_3H_5(AsO_3H_2)_2$, are obtained by the action of an alkali arsenite on an aliphatic hydrocarbon containing one or more halogen atoms and one or more hydroxyl groups (*e.g.* glycol chlorohydrin, glycerol mono- and di-chlorohydrin, epichlorohydrin) and decomposing the alkali salt by acidification. W. T. K. B.

A New Organo-metallic Compound: Diplumbic Hexaethyl. THOMAS MIDGLEY, jun., CARROLL A. HOCHWALT, and GEORGE CALINGAERT (*J. Amer. Chem. Soc.*, 1923, 45, 1821—1823).—Lead triethyl hydroxide is prepared by the action of sodium hydroxide solution on lead triethyl chloride; a 30% solution in 95% ethyl alcohol is electrolysed, using lead electrodes and a current density of 0·01 amp./sq. cm. *Diplumbic hexaethyl*, a heavy, yellow oil, b. p. about 100°/2 mm., is formed at the cathode, much gas being evolved at the anode, $2PbEt_3 \cdot OH = Pb_2Et_6 + H_2O + O$. The oil is easily decomposed by air, giving a yellow powder which rapidly darkens; d 1·94. The oil is bimolecular in concentrated benzene solution, but unimolecular in very dilute solution. It reacts with hydrochloric acid, giving lead triethyl chloride, lead chloride, and a gas, probably according to the equation $Pb_2Et_6 + 3HCl = PbEt_3Cl + PbCl_2 + 3C_2H_6$. W. S. N.

The Low-temperature Tar obtained from the Zeche Fürst Hardenberg Coal and, in Particular, the Content of Benzene, Phenol, and Acetone. HANS BROCHE (*Ber.*, 1923, 56, [B], 1787—1791).—According to Schütz (this vol., i, 195, 452), the low-temperature tar derived from Zeche Fürst Hardenberg coal contains a much greater proportion of benzene, carbolic acid, and acetone than has been observed previously in low-temperature tars by Fischer and his co-workers. The author has therefore re-examined the tar produced from this coal in experimental, rotary furnaces, and finds that it does not contain more than 0.04% of benzene (calculated on the tar) and 0.16% of carbolic acid. It does not yield more than 50 g. of acetone per ton of coal. The low-temperature tar from the Hardenberg coal therefore closely resembles other low-temperature tars. H. W.

Naphthenes in their Behaviour towards Catalytic Dehydrogenation. The Nature of Petroleum. N. ZELINSKI (*Ber.*, 1923, 56, [B], 1718—1723).—Octanaphthene is practically unchanged by platinum black at 300—310°; treatment of the specimen with fuming sulphuric acid containing 10% of sulphur trioxide shows that it contains at least 15—20% of octanes. *iso*-Octanaphthene is similarly unchanged in the presence of platinum black at 300°; the natural hydrocarbon appears to be closely related to that obtained from heptanaphthenecarboxylic acid. The similarity in the behaviour of octanaphthene and *isooctanaphthene* towards catalytic dehydrogenation justifies the conclusion that their ring systems are identical or very closely related. Nonanaphthene undergoes only slight dehydrogenation in the presence of palladium black at 300—310°; after removal of other cyclic compounds by fuming sulphuric acid, the residual hydrocarbon is a mixture containing not less than 50% of open-chain compounds.

1 : 4-Dimethyl-2-ethylcyclopentane is partly dissolved by fuming sulphuric acid (10% SO₃) to yield a dark-coloured solution; the change occurs without marked development of heat and without evolution of sulphur dioxide. *cyclo*Pentane is passive under similar conditions, whereas the hexahydroaromatic hydrocarbons become oxidised. The behaviour towards fuming sulphuric acid appears to be a trustworthy criterion for discriminating between *cyclopentanes* and *cyclohexanes*. The author is drawn to the conclusion that naphthenes prepared from naphthenic acids and the natural naphthenes of petroleum consist mainly of cyclic compounds and not of hexahydroaromatic hydrocarbons. H. W.

The Behaviour of 1 : 1-Dimethylcyclohexane towards Catalytic Dehydrogenation. N. ZELINSKI [with (FRL.) N. DELZOVA] (*Ber.*, 1923, 56, [B], 1716—1718).—1 : 1-Dimethylcyclohexane, b. p. 118.5—120°, d_4^{20} 0.7820, n_D^{18} 1.4342, is not affected by passage over extremely active, platinised asbestos at 300°. Since the hydrocarbon does not belong to the hexahydroaromatic series (owing to the presence of the two methyl groups attached to the same carbon atom), this observation is in harmony with the authors'

theory of the pronouncedly selective nature of catalytic dehydrogenation and of its exclusive applicability to hexahydroaromatic compounds.
H. W.

Parallelism between the Mobility of the Hydrogen of the Benzene Nucleus and that of Chlorine of the Side Chain. S. C. J. OLIVIER (*Rec. trav. chim.*, 1923, 42, 775—778).—A résumé and discussion of previously published work on the ease with which the halogens are removed from the benzene nucleus and from side chains in the presence of other substituting groups (A., 1922, i, 646; this vol., i, 179, 769).
J. F. S.

The Sulpho-chromic Oxidation of Aromatic Hydrocarbons and the Structural Conception of Graphite. L. J. SIMON (*Compt. rend.*, 1923, 177, 265—268; cf. this vol., i, 81; also Simon and Guillaumin, this vol., ii, 432).—Sulpho-chromic oxidation of a series of hydrocarbons shows that with the use of silver dichromate good values are obtained with those of aromatic structure. Chromic anhydride yields an "oxidation deficit" in each case; this varies within comparatively small limits except in the cases of naphthalene and phenanthrene and differs for isomerides, e.g., diphenyl and acenaphthene. Other hydrocarbons are clearly distinguished from those in the aromatic series by giving results which are very considerably below the theoretical value. A table of the figures obtained with different varieties of carbon is given (cf. this vol., ii, 506), from which the conclusion is drawn that as the "oxidation deficit" of graphite is about one-third, it is possible to oxidise it in three stages. This, added to the fact that the results with graphite are of the same order as those given by aromatic hydrocarbons, is regarded as furnishing additional evidence in support of the hexagon-ring structure of graphite and possibly indicating that two carbon atoms in the ring are somewhat different in their properties from the remaining four.
H. J. E.

Influence of Substitution in the Components on Equilibrium in Binary Solutions. XLI. Equilibrium in Binary Solutions of the Isomeric Dinitrotoluenes with Amines and Hydrocarbons. ROBERT KREMANN, EUGEN HÖNIGSBERG, and OTTO MAUERMANN (*Monatsh.*, 1923, 44, 65—81).—The tendency of dinitrotoluenes to form additive compounds with amines and with hydrocarbons is, as would be expected, intermediate between that of the mono- and tri-nitrotoluenes. Of the four dinitrotoluenes (2:4-, 2:6-, 3:5-, and 3:4-), the 3:5-derivative most readily, and the 2:6-derivative least readily forms additive compounds, thus illustrating Kremann's theory of steric valency hindrance.

3:4-Dinitrotoluene forms simple eutectics with the following compounds (a percentage given, throughout this abstract, is that of the second, variable, component in the different series): aniline, (—17°, 69%), *p*-toluidine (11°, 41%), β -naphthylamine (33°, 28%), α -naphthylamine (—10°, 54%), acenaphthene (39°, 30%), anthracene (55°, 2%), and fluorene (37°, 29%).

2:6-Dinitrotoluene forms simple eutectics with *p*-toluidine

(18°, 55%), α -naphthylamine (7.5°, 62%), β -naphthylamine (45°, 24%), anthracene (54°, 6%), fluorene (46°, 30%), and acenaphthene (46°, 27%).

3:5-Dinitrotoluene is best prepared by slowly adding acetone-*p*-toluidide to eight times its weight of nitric acid (*d* 1.79), at a temperature not exceeding 0°, purifying the dinitro-derivative by hot benzene extraction, hydrolysing it with concentrated sulphuric acid (not above 90°), diazotising the resulting base at -10° in concentrated sulphuric acid—absolute alcohol solution, warming, and purifying the dinitrotoluene by extraction with alcohol.

The additive power of 3:5-dinitrotoluene is shown by the following: Aniline, equimolecular compound, m. p. 46.5°, eutectics with the two components at 46°, 32% and at -13°, 92% (cf. A., 1906, ii, 268); compound formation is not well indicated by the results obtained. *p*-Toluidine, equimolecular compound, m. p. 25°, eutectic with *p*-toluidine at 22°, 61%; the indications of compound formation are indefinite in this case also. α -Naphthylamine, equimolecular compound, m. p. 107—108°, eutectic with the two components at 75°, 12%, and at 40°, 87%. β -Naphthylamine, equimolecular compound, m. p. about 53°, undergoing extensive dissociation in the fused state: eutectics at 53°, 27%, and at 53°, 40%. Acenaphthene, equimolecular compound, m. p. 94°, eutectics with the two components at 72°, 15%, and at 79°, 73%. Fluorene and anthracene give simple eutectics only, at 42°, 39%, and at 76°, 14%, respectively.

2:4-Dinitrotoluene and *p*-toluidine form only a simple eutectic at 15°, 50%. E. E. T.

Freezing-point Diagram of Mixtures of Trinitrotoluene and Picric Acid. C. A. TAYLOR and W. H. RINKENBACH (*Ind. Eng. Chem.*, 1923, **15**, 795).—The freezing-point curve of mixtures of pure trinitrotoluene and pure picric acid is given. There is a eutectic point at 69.8% of trinitrotoluene (59.4°). No molecular compounds are formed. H. C. R.

***p*-Chlorodiphenylsulphone.** HAEHL (*Compt. rend.*, 1923, **177**, 194—195).—The author shows that the product obtained by Beckurts and Otto (cf. A., 1886, 1031, etc.) by the action of benzene-sulphonyl chloride on chlorobenzene in presence of aluminium chloride is *p*-chlorodiphenylsulphone. Sulphanilic acid is converted into *p*-chlorobenzenesulphonic acid, the chloride of this acid being condensed, in presence of aluminium chloride, with benzene. The product is identical with that described by the older workers. E. E. T.

Hydrogenation of the Diphenyl Nucleus. J. RANEDO and A. LEON (*Anal. Fis. Quím.*, 1923, **21**, 270—279).—The catalytic hydrogenation by the Willstätter method of diphenyl and *p*-diphenyl-carboxylic acid was studied, using platinum black as catalyst. With partial hydrogenation, mixtures were produced in each case. Complete hydrogenation of diphenyl gives a liquid, b. p. 226—228°, presumably dodecahydrodiphenyl. *p*-Diphenylcarboxylic acid, by complete hydrogenation, yields a mixture of two isomeric acids, one

having m. p. 105° (needles) and the other m. p. $76-78^{\circ}$ (scales). The *amide* of the acid of m. p. 105° was prepared; it forms crystals, m. p. 197° .
G. W. R.

Bromodiphenylmethane and the Grignard Reaction. L. BERT (*Compt. rend.*, 1923, **177**, 324—326; cf. Gomberg and Cone, A., 1906, i, 414).—Magnesium, if previously activated by means of ethyl bromide, readily reacts with bromodiphenylmethane in ethereal solution to give a precipitate of *s*-tetraphenylethane [yield, 70%; m. p. 212.5° (cf. Biltz, A., 1893, i, 718)]. Mere traces of magnesium diphenylmethyl bromide are formed, and in order to utilise the bromo-compound for Grignard reactions, the second component must be present from the outset. Thus, when carbon dioxide is allowed to pass through a reacting mixture of the bromo-compound, magnesium, and ether, and the product is decomposed in the usual manner, a mixture of diphenylacetic acid and tetraphenylethane results.
E. E. T.

Chromoisomerism in the Stilbene Series. NICHOLAS MICHAEL CULLINANE (*T.*, 1923, **123**, 2053—2060).

Decahydronaphthalene and its Behaviour towards Catalytic Dehydrogenation. N. ZELINSKI (*Ber.*, 1923, **56**, [B], 1723—1724).—Decahydronaphthalene is smoothly prepared by passing tetrahydronaphthalene and hydrogen over platinised asbestos at $150-160^{\circ}$ or palladium black at 120° . It is very readily dehydrogenated by palladium black at the atmospheric pressure and 300° , whereby naphthalene is produced. The formation of intermediate substances of unsaturated character could not be observed.
H. W.

The Structure of the Benzene Nucleus. IV. The Reactivity of Bridged Linkings. CHRISTOPHER KELK INGOLD (*T.*, 1923, **123**, 2081—2088).

The Structure of the Benzene Nucleus. III. Synthesis of a Naphthalene Derivative involving a Bridged Phase of the Nucleus. The Constitution of Naphthalene and Anthracene. WILLIAM ARTHUR PERCIVAL CHALLENGER and CHRISTOPHER KELK INGOLD (*T.*, 1923, **123**, 2066—2081).

Catalytic Oxidation of Naphthalene at High Temperatures. TOKISHIGE KUSAMA (*J. Chem. Soc. Japan*, 1923, **44**, 605—651).—In preparing phthalic anhydride from naphthalene by catalytic oxidation, the author has studied the effect on the catalyst of the temperature of reaction, the ratio of the oxidisable compound and the oxygen, the time of contact of the mixed gas and vapour and the catalyst, and the addition of an inert gas to the mixture. As catalysts, oxides of vanadium and molybdenum were found to be most suitable, and they act better when mixed with other oxides than when used singly. The best results were obtained by the use of vanadium oxide containing a small amount of molybdenum oxide. During the course of reaction, the temperature of the catalyst varies locally, the front part of the catalyst having usually a higher

temperature than the rear. The course of the reaction is indicated by a temperature curve drawn by taking the temperatures as ordinates and the distance of the catalyst from one end as abscissæ; If there is a sharp maximum in the front portion of the curve, complete combustion predominates, but if the curve shows a gradual elevation with a maximum at the rear, it indicates that the reaction is proceeding smoothly, and that a good yield is being obtained. From the form of the temperature curves, the relative value of the different catalysts can be compared and the course of the reactions is indicated. When a mixture of vanadium and molybdenum oxides is used as the catalyst and air as the source of oxygen, complete combustion is minimal at 280–400°. When the catalyst is used in a continuous layer, good yields are obtained by lowering the temperature of the front part of the catalyst and increasing the velocity of a mixture of naphthalene vapour and air. By a discontinuous arrangement of the catalyst, complete combustion is prevented and a good yield is obtained.

K. K.

Rules of Substitution in the Naphthalene Nucleus. V. VESELY and M. JAKEŠ (*Bull. Soc. chim.*, 1923, [iv], 33, 955–962).—An attempt to apply to the naphthalene molecule a modified form of the Crum Brown and Gibson rule for substitution in the benzene nucleus. Two types of directive substituent are distinguished:

(a) The quinonoid type corresponding with the ortho-para type in the benzene series and including the same radicles. In this class, a quinonoid derivative is always formed if possible. That is to say, if the original substituent is in the 1 position, the second group will enter the 2, 4, 5, or 7 position. If the original group is in the 2 position, the entering group will occupy the 1, 3, 6, or 8 position. As the 1:4- and 1:2-derivatives are the most stable quinonoid forms, so it is found that these preponderate, if possible, in the mixture of isomerides formed.

(b) The non-quinonoid type, corresponding with the meta directing substituents in the benzene series and including the same groups. In this class, there is a predisposition to form 1:3-, 1:6-, 1:8-, and 2:7-derivatives.

The above rules do not apply to tri-substitution, and are not rigid even for di-substitution. Examples are given to show how far they are followed, and conversely.

H. H.

Some Substitution Reactions of 2-Nitronaphthalene. V. VESELY and M. JAKEŠ (*Bull. Soc. chim.*, 1923, [iv], 33, 952–955).—Direct bromination of 2-nitronaphthalene leads to the formation of 5-bromo-2-nitronaphthalene, the identity of which with the compound obtained by the Sandmeyer reaction on the diazonium sulphate of 2-nitro-5-naphthylamine is established. Nitration of 2-nitronaphthalene in sulphuric acid solution is unsuitable for the preparation of dinitro-derivatives because considerable quantities of 1:3:8-trinitronaphthalene are formed, and, in addition, some of the original nitro-compound undergoes sulphonation. A mixture of 2:5- and 2:8-dinitronaphthalenes is obtained by nitration of 2-nitronaphthalene in boiling glacial acetic acid. The mixture

of isomerides so obtained may be separated by crystallisation from concentrated sulphuric acid. H. H.

Studies in the Anthracene Series. V. EDWARD DE BARRY BARNETT, JAMES WILFRED COOK, and MARCUS AURELIUS MATTHEWS (T., 1923, 123, 1994—2008).

The Action of Grignard's Compounds on Anthrone. F. KROLLPFEIFFER and F. BRANSCHIED (*Ber.*, 1923, 56, [B], 1617—1619).—The action of an excess of Grignard's reagents in cold ethereal solution on anthrone leads to the formation of substituted 9-hydroxy-9 : 10-dihydroanthracenes, $C_6H_4 \begin{smallmatrix} CR(OH) \\ CH_2 \end{smallmatrix} > C_6H_4$, which are converted when the mixtures are heated to gentle boiling into substituted *ms*-anthracenes, $C_6H_4 \begin{smallmatrix} CR \\ CH \end{smallmatrix} > C_6H_4$.

The following individual substances are described: 9-Methylanthracene, pale, greenish-yellow needles, m. p. 79—80°. 9-Hydroxy-9-ethyl-9 : 10-dihydroanthracene, coarse, colourless crystals, m. p. 87°. 9-Ethylanthracene, colourless leaflets with blue fluorescence, m. p. 59°. 10-Chloro-9-ethylanthracene (prepared by chlorination of a solution of 9-ethylanthracene in ice-cold chloroform), pale greenish-yellow needles, m. p. 111°. 9-Hydroxy-9-isoamyl-9 : 10-dihydroanthracene, coarse, colourless crystals, m. p. 94—95°. 9-isoAmylanthracene, pale green needles with blue fluorescence, m. p. 61°. 9-Hydroxy-9-phenyl-9 : 10-dihydroanthracene, coarse, colourless crystals, m. p. 112—113°. 9-Phenylanthracene, lustrous, pale yellow leaflets, m. p. 151—152°. H. W.

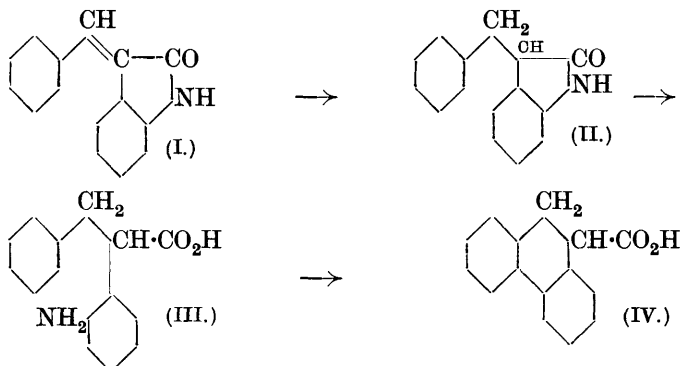
The Action of Grignard's Compounds on Anthrone. A. SIEGLITZ and R. MARX (*Ber.*, 1923, 56, [B], 1619—1621).—The action of magnesium alkyl halides on anthrone has been examined under conditions which differ somewhat from those adopted by Krollpfeiffer and Branschied (preceding abstract). A lukewarm solution of anthrone in anhydrous, thiophen-free benzene is added gradually to a cold solution of three molecular proportions of the Grignard reagent in ether. The product is decomposed with ice-cold water and dilute sulphuric acid. The benzene-ether layer is washed with sodium hydroxide solution and the solvent is allowed to evaporate slowly; by-products such as anthraquinone and dianthrone separate first, followed by the alkylanthracene derivatives.

The following individual substances are described: 9-Methylanthracene, pale yellow prisms or needles, m. p. 81·5°, b. p. 196—197°/12 mm. [*picrate*, dark, brownish-red needles, m. p. 137° (decomp.)]. 9-Methyl-9 : 10-dihydroanthracene, prepared by reduction of 9-methylanthracene by sodium and alcohol, long, colourless needles, m. p. 61·5—62°. 9-Hydroxy-9-ethyl-9 : 10-dihydroanthracene, large, transparent rhombohedra, m. p. 88—89°. 9-Ethylanthracene, colourless leaflets, m. p. 59°, b. p. 189—191°/11 mm. 9-n-Propylanthracene, colourless needles, m. p. 69—70° [*picrate*, brownish-red needles, m. p. 113·5—114·5° (decomp.)].

9-*n*-Propyl-9:10-dihydroanthracene, a colourless liquid, b. p. 175—176°/11 mm. 9-*n*-Butylanthracene, long, colourless needles, m. p. 49—50° (picrate, $2C_{18}H_{18}, C_6H_3O_7N_3$, dark, brownish-red needles, m. p. 82°). 9-*n*-Butyl-9:10-dihydroanthracene, a colourless liquid with blue fluorescence, b. p. 191—192°/11 mm. H. W.

A New Synthesis of Dihydrophenanthrene Derivatives.

E. KIRCHNER (*Nachr. K. Ges. Wiss. Göttingen*, 1921, 154—161; from *Chem. Zentr.*, 1923, i, 944—945).—In order to study the constitution of colchicine, the author has devised a new synthesis of dihydrophenanthrenecarboxylic acid. Benzylidenexindole (I) from benzaldehyde and oxindole, is hydrogenated to benzylloxindole, (II), which forms white needles, m. p. 130°. By heating with barium hydroxide α -benzyl-*o*-aminophenylacetic acid (III) is obtained. This is diazotised and the product heated at 50°. By the action of ammonia, a product is obtained from which, on distillation under reduced pressure at 170—270°, dihydrophenanthrenecarboxylic acid (IV) is obtained. It has m. p. 127—130° and gives phenanthrene by distillation with calcium oxide.

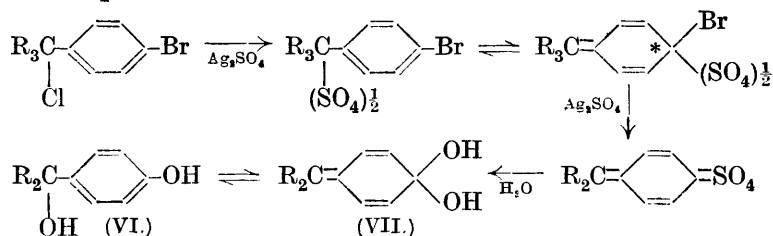


The acid portion also contains benzylisocoumaranone, $C_{13}H_{12}O_2$, m. p. 58—59°. The neutral portion contains a compound, $C_{15}H_{10}O_2$ (?), which forms yellow crystals, m. p. 225°. In the place of benzaldehyde as a starting point, its hydroxy- and methoxy-derivatives may be used. In similar manner, starting from α -phenyl- β -*o*-aminophenylpropionic acid, the lactone of α -phenyl- β -*o*-hydroxyphenylpropionic acid, and from that 3-phenyldihydrocoumarin, m. p. 122—123°, may be obtained. From nitrobenzaldehyde, by condensation, *o*-aminobenzylloxindole is obtained at first and then periquindoline (annexed formula).

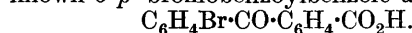
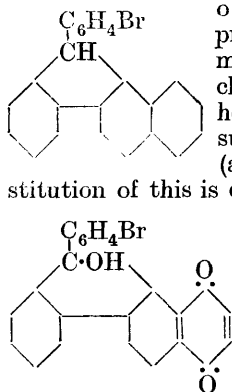
The latter has m. p. above 290°. The acetyl derivative forms white needles, m. p. 185°. *o*-Nitrobenzylidenexindole forms reddish-yellow needles, m. p. 225°. Its hydrochloride has m. p. 280°. G. W. R.

Triphenylmethyl. XXXIII. Quinoidation of the Triaryl-methyls. M. GOMBERG and F. F. Blicke (*J. Amer. Chem. Soc.*, 1923, 45, 1765—1779).—*p*-Bromodiphenyl- α -naphthylcarbinol, di-

halogen. Moreover, the highly coloured reaction mixture yields, on hydrolysis, the corresponding *p*-hydroxytriarylcarbinol, which may be isolated either as the benzenoid form (VI), or as the anhydro-form of the quinonoid modification (VII). These results are interpreted as follows :



The general conclusion is that, in the coloured triarylmethyls, and in the coloured, salt-like derivatives of triarylcarbinols, colour results from a quinonoid structure. *p*-Bromodiphenyl- α -naphthylcarbinol, m. p. 132—133°, is prepared in 80% yield from magnesium α -naphthyl bromide and *p*-bromobenzophenone in warm ether-benzene solution. It gives an intense green coloration with concentrated sulphuric acid or perchloric acid. By passing dry hydrogen chloride into its warm, concentrated, benzene solution, *p*-bromodiphenyl- α -naphthylmethyl chloride, m. p. 182—183°, is obtained; this forms intensely green, additive products with the chlorides of zinc, tin, iron, mercury, and aluminium. The carbinol, or the chloride, loses water, or hydrogen chloride, when heated with glacial acetic acid and concentrated sulphuric acid, giving *p*-bromophenylchrysofluorene (annexed formula), m. p. 233—235°. The constitution of this is established by oxidising it by means of sodium dichromate in glacial acetic acid solution; the first product is a *fluorenequinone* (annexed formula), m. p. 172—173°, which dissolves in concentrated sulphuric acid with a blood-red coloration. By further oxidation it gives the known *o*-*p'*-bromobenzoylbenzoic acid,



4-Bromo- α -naphthylamine hydrochloride is diazotised in cold glacial acetic acid solution by the addition of amyl nitrite, 4-bromonaphthalene- α -diazonium chloride being isolated as a pale yellow, crystalline product, by pouring into cold ether. It is then gradually added in aqueous solution to a cold solution of cuprous cyanide, whereby 4-bromo- α -cyanonaphthalene, m. p. 102—103°, is obtained in 80% yield. This gives 4-bromonaphthalene- α -carboxylic acid, m. p. 217—220° (cf. Mayer and Sieglitz, A., 1922, i, 740), when hydrolysed by means of acetic acid and sulphuric acid. The *ethyl* ester reacts in boiling toluene solution with magnesium phenyl bromide, giving diphenyl-4-bromo- α -naphthylcarbinol, m. p. 130°, yield 60%. Diphenyl-4-bromo- α -naphthyl-

methyl chloride, m. p. 160—161°, gives a deep green coloration with sulphuric acid. Attempts to isolate free radicles have not been successful, but the following peroxides are described. Those of the simple radicles are obtained by the atmospheric oxidation of the solution in which the carbonyl chloride has been agitated with finely divided silver for twenty minutes; if the reaction is allowed to continue for forty-eight to sixty hours, peroxides of the complex radicles are obtained. *p-Bromodiphenyl- α -naphthylmethyl peroxide* has m. p. 146° (decomp.). The flocculent *peroxide* of the second-order radicle, $[\text{CPh}(\text{C}_6\text{H}_4\text{Br})(\text{C}_{10}\text{H}_7)\cdot\text{C}_6\text{H}_4\cdot\text{CPh}(\text{C}_{10}\text{H}_7)]_2\text{O}_2$, decomposes indefinitely at about 120°. *Diphenyl-1-bromo- α -naphthylmethyl peroxide* has m. p. 153—154° (decomp.). The amorphous *peroxide*, $(\text{C}_{10}\text{H}_6\text{Br}\cdot\text{CPh}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{CPh}_2)_2\text{O}_2$, decomposes at 135°, and melts indefinitely. W. S. N.

Attempted Syntheses of Meta-related Ring Systems.

F. REINDEL and F. SIEGEL (*Ber.*, 1923, 56, [B], 1550—1557).—Attempts to prepare *m*-dibenzylbenzene and to cause *m*-xylylene bromide to react with amines, phenols, and thiophenols are described. The experiments have not up to the present led to the isolation of compounds containing rings closed in the meta-position of the benzene nucleus.

The action of aluminium chloride on *m*-xylylene bromide in the presence of benzene yields mainly diphenylmethane accompanied by smaller amounts of *p*-dibenzylbenzene, anthracene, and mixtures of very viscous, fluorescent liquids. It is very improbable that the latter contain *m*-dibenzylbenzene or that the product isolated by Smythe (T., 1922, 121, 1270), which has been tentatively considered to be *m*-dibenzylbenzene, consists actually of this substance. *iso*Phthalyl chloride, m. p. 42—43°, b. p. 143—144°/13 mm., is conveniently prepared from *isophthalic* acid and thionyl chloride, and is converted by the Friedel-Crafts reaction into *isophthalophenone*. The latter substance is unexpectedly resistant towards reduction with amalgamated zinc and hydrochloric acid; under similar conditions terephthalophenone is transformed only to a very small extent into *p*-dibenzylbenzene.

m-Xylylene bromide reacts with *o*-nitroaniline in the presence of boiling chloroform to give an almost quantitative yield of *di-o'-nitrophenyl-m-xylylenediamine*, $\text{C}_6\text{H}_4(\text{CH}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2)_2$, yellow needles, m. p. 146—148°. *Di-m'-nitrophenyl-m-xylylenediamine*, yellow leaflets, m. p. 142—145°, is prepared in a similar manner, but in very poor yield.

m-Xylylene bromide is transformed by phenol in alcoholic solution in the presence of sodium ethoxide into *m-xylylenyl diphenyl ether*, $\text{C}_6\text{H}_4(\text{CH}_2\cdot\text{OPh})_2$, colourless leaflets, m. p. 71—76°. Under similar conditions, *m*-nitrophenol yields *m-xylylenyl di-m'-nitrophenyl ether*, almost colourless needles, m. p. 100—102°. Attempts to isolate the corresponding *m'*-amino-compound were unsuccessful; its *acetyl* derivative, colourless leaflets, m. p. 165—170°, is prepared by acetylation of the crude base or by the action of *m*-xylylene bromide on *m*-acetylaminophenol.

m-Xylylenedithioglycol diphenyl ether, $C_6H_4(CH_2 \cdot SPh)_2$, colourless leaflets, m. p. 78—82°, is quantitatively prepared from *m*-xylylene bromide and thiophenol. The compound, as also *m*-xylylenyl diphenyl ether, is very resistant towards oxidising agents, but is converted by sodium dichromate and dilute sulphuric acid at 170—180° into the corresponding disulphone, $C_6H_4(CH_2 \cdot SO_2Ph)_2$, long, colourless rods, m. p. 163—165°, phenylbenzylsulphone-*m*-carboxylic acid, $CO_2H \cdot C_6H_4 \cdot CH_2 \cdot SO_2Ph$, m. p. 188—192°, and isophthalic acid. H. W.

Action of Ammonia and Amines on 3 : 4-Dinitrodimethylaniline and 3 : 4-Dinitrodiethylaniline. P. VAN ROMBURGH (*Rec. trav. chim.*, 1923, 42, 804—807).—Alcoholic ammonia heated at 120° for several hours in a sealed tube with 3 : 4-dinitrodimethylaniline yields 4-nitro-3-aminodimethylaniline in yellow crystals, m. p. 135°. Similar treatment with an alcoholic solution of methylamine at 125° yields 4-nitro-3-methylaminodimethylaniline in yellow crystals, m. p. 115°. This compound crystallises with half a molecule of methyl alcohol in lustrous orange needles, m. p. 88—90°. When dimethylamine is similarly treated with 2 : 4-dinitrodimethylaniline, 4-nitrotetramethyl-*m*-phenylenediamine is formed in large, reddish-orange plates, m. p. 81°; 4-nitro-3-ethylaminodimethylaniline, orange needles, m. p. 98°; 4-nitro-3-amino-diethylaniline, clear, yellow crystals, m. p. 139°; 4-nitro-3-methylaminodiethylaniline, yellow crystals, m. p. 96—97°; 4-nitro-3-dimethylaminodiethylaniline, orange-yellow crystals, m. p. 63—64°, and 4-nitro-3-ethylaminodiethylaniline, pale yellow crystals, m. p. 78·5°, are all obtained by heating the appropriate amine with the appropriate dialkylaniline. J. F. S.

Phenyltaurine and its Higher Homologues. R. DEMARS (*Bull. Sci. Pharmacol.*, 1922, 29, 492—495; from *Chem. Zentr.*, 1923, i, 1019).—Phenyltaurine, $NHPh \cdot CH_2 \cdot CH_2 \cdot SO_3H$, is prepared by the action of aniline (2 mols.) on a mixture of chloroethanesulphonic acid (1 mol.) and aniline (1 mol.) at 130—140°. After repeated recrystallisation, large, dark brown crystals of the aniline salt are obtained. Hydrolysis by means of steam distillation yields the free acid. *N*-Phenylmethyltaurine, $C_6H_5 \cdot CH_2 \cdot SO_3NS$, similarly prepared, forms violet crystals, m. p. 239—240°. *N*-Phenylethyltaurine, $C_{10}H_{15}O_3NS$, forms greenish-white crystals. *N*-Phenylmethyltaurine and *N*-phenylethyltaurine both dissolve cupric hydroxide (cf. Delépine and Demars, A., 1922, i, 923). G. W. R.

Preparation of Condensation Products of the Aromatic Series containing Nitrogen and Sulphur. LEOPOLD CASSELLA & Co., G. M. B. H. (D.R.-P. 367344 and 367345; from *Chem. Zentr.*, 1923, ii, 572).—Supplementary to numerous earlier patents. *N*-Acyl derivatives of *N*-monoalkylated aromatic amines, for example, *N*-acetylmethyl-*p*-toluidide, $C_6H_4Me \cdot NMeAc$, give with sulphur monochloride condensation products containing nitrogen and sulphur, with formation of the alkyl chloride and the corresponding acid (acetic acid). The compound obtained in the case

of *N*-acetylmethyl-*p*-toluidide is identical with that obtained by the action of sulphur monochloride on *p*-toluidine. G. W. R.

Nitration of Aceto- β -naphthalide. V. VESELY and M. JAKES (Bull. Soc. chim., 1923, [iv], 33, 942—952).—When aceto- β -naphthalide is nitrated in acetic acid solution, the nitro-group enters the nucleus first of all in the 1 or 8 position. The present authors have succeeded in isolating, in addition, a considerable proportion of 6-nitro-2-acetylaminonaphthalene, which forms clear yellow, felted needles, m. p. 224°. The corresponding 6-nitro- β -naphthylamine crystallises from alcohol in clear orange flakes, m. p. 203°, and gives both a normal and an acid sulphate. 6-Nitro- β -naphthol crystallises in yellow needles, m. p. 158°. Direct dinitration of aceto- β -naphthalide gives, besides the 1:8-dinitro-compound, 1:5-dinitroaceto- β -naphthalide, which crystallises from acetic acid in yellow needles, m. p. 200—201°. By the Gattermann reaction with copper powder and sodium nitrite on the diazonium sulphate of 6-nitro- β -naphthylamine is obtained 2:6-dinitronaphthalene, crystallising in reddish plates, m. p. 268°. H. H.

The Nitration of 1-Bromoaceto- β -naphthalide. VITĚZSLAV VESELY and KAREL DVOŘAK (Chem. Listy, 1923, 17, 163—165).—Nitration with excess of cold nitric acid, *d* 1.525, of 1-bromoaceto- β -naphthalide yields 1:8-dinitroaceto- β -naphthalide, identical with the nitration product of 8-nitroaceto- β -naphthalide. Using only sufficient nitric acid to form a mononitro-derivative, together with sulphuric acid, the chief product is a dinitrobromoacetone-naphthalide, m. p. 250—251° (the position of the nitro-groups not being determined), together with a small quantity of 1-bromo-5-nitroaceto- β -naphthalide, yellow, silky needles, m. p. 194°. In order to prove the orientation of this compound, it was prepared by the bromination of 5-nitroaceto- β -naphthalide, and the products thus obtained were found to be identical. 1-Bromo-5-nitro- β -naphthylamine, orange needles, m. p. 161—162°, is obtained by the hydrolysis of this substance. 1-Bromo-8-nitroaceto- β -naphthalide, yellow needles, m. p. 180°, 1-bromo-4-nitroaceto- β -naphthalide, lemon-yellow needles, m. p. 175—176°, and 1-bromo-6-nitroaceto- β -naphthalide, yellow needles, m. p. 206—207°, were also prepared by the bromination of the corresponding nitroacetone-naphthalides, the corresponding 1-bromonitronaphthylamines melting at 142—143°, 155°, and 222—223°, respectively. R. T.

Preparation of 2-Hydroxy-1-arylamino-naphthalenes. SOCIÉTÉ ANONYME DES MATIÈRES COLORANTES ET PRODUITS CHIMIQUES DE SAINT DENIS, ANDRÉ WAHL, and ROBERT LANTZ (Brit. Pat. 182084, Fr. Pat. 548440, and D.R.-P. 365367; from Chem. Zentr., 1923, ii, 997—998).—Primary aromatic amines are allowed to react with 1-halogen- β -naphthols. For example, 1-chloro- β -naphthol is heated with aniline under a reflux apparatus. 1-Phenylamino- β -naphthol thereby obtained forms needles, m. p. 153—154°, which become reddish-grey on exposure to air. By the action on it of methyl sulphate the corresponding methyl

ether is formed; prisms, m. p. 80.5°. *p*-Toluidine heated with 1-bromo- β -naphthol at 125–130° yields 1-*p*-tolylamino- β -naphthol, which forms crystals, m. p. 137–138°. G. W. R.

The Chemistry of Naphthalene and its Derivatives. II. New Derivatives of Nitro- β -naphthylamine. N. N. VOROSHOV and K. A. GRIBOV (*Bull. Inst. Poly. Ivanovo-Voznesensk*, 1923, 7, 109–115).—The nitration of Brenner's acid (β -naphthylamine-6-sulphonic acid) leads to a good yield of 8-nitro- β -naphthylamine-6-sulphonic acid which forms a light grey powder almost insoluble in water. It is characterised by the formation of orange ammonium and sodium salts; the colour of these salts is probably due to the auxochromic effect of the amino-group in the *amphiposition* to the salt-forming sulphonic group, whilst in the free acid these two groups probably form an internal salt. The structure assigned to the new acid is confirmed by its conversion into 1:3-nitronaphthalenesulphonic acid and the corresponding amino-acid and also 1:3-dichloronaphthalene. On reduction with iron and acetic acid, the nitro-acid passes into 2:8-naphthylenediamine-6-sulphonic acid, an insoluble powder which can be tetrazotised and gives rise to substantive cotton dyes.

The nitration of amino-R-acid (β -naphthylamine-3:6-disulphonic acid) proceeds normally, but all attempts to isolate the nitration product lead to the partial or complete hydrolysis of the amino-group; the crude nitration product dyes wool and silk an intense brownish-yellow.

The nitration of amino-C-acid (β -naphthylamine-4:8-disulphonic acid) leads to the formation of the 6-nitro-derivative, which is also easily hydrolysed, but can nevertheless be isolated in the form of its sodium salt, which is a dark yellow powder; its structure follows from its conversion into 2:6-naphthylenediamine. The instability of this and the preceding compound is attributed to the effect of the sulphonic group attached to the ring carrying the amino-group. G. A. R. K.

Catalytic Preparation of Aminocyclohexanols. J. B. SENDERENS and J. ABOULENC (*Compt. rend.*, 1923, 177, 158–160).—At 90° and 50 kg. pressure, *p*-nitrophenol (in alcoholic solution) absorbs hydrogen, in presence of nickel, producing *p*-aminophenol. At 180° and 60 kg. pressure, aminocyclohexanol is formed in an impure state. It, however, *p*-aminophenol is reduced at the higher temperature and pressure, the aminocyclohexanol is obtained as white crystals, with m. p. 64–65° and b. p. 235–245° (hydrochloride, m. p. 90°).

In the corresponding reduction of *o*-nitrophenol, an even less pure product is obtained, whereas, by reducing *o*-aminophenol, the aminocyclohexanol is obtained as white crystals, m. p. 47° and b. p. 220–240° (hydrochloride, m. p. 75°). Brunel (*A.*, 1903, i, 680) recorded for the three corresponding temperatures, 66°, 219°, and 175°, but whereas his cyclohexanol was an individual, that now obtained is a mixture of the *cis*- and *trans*-forms. E. E. T.

Osmotic Pressures of Aqueous Solutions of Phenol at 30°. ARTHUR GROLLMAN and J. C. W. FRAZER (*J. Amer. Chem. Soc.*, 1923, **45**, 1705—1710).—The osmotic pressures of solutions of phenol have been determined throughout the solubility range at 30°. From the results so obtained the degree of association of phenol in aqueous solution has been calculated, and it is found that the percentage of simple molecules existing in the bimolecular condition varies from 86% in 0.1*M* solution to 99% in 0.9*M* solution. The pure material is entirely associated. It is suggested that the difference in the nature of the chemical compounds formed on direct bromination of aqueous phenol solutions of varying concentration is to be attributed to the different molecular combinations present. The great absorption of heat attending the dissolution of phenol in water is due to the partial dissociation of the higher molecular forms, the reaction $(C_6H_5 \cdot OH)_2 \rightarrow 2C_6H_5 \cdot OH$ being endothermic. J. F. S.

Preparation of Aryl Phosphates. CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (EDUARD TSCHUNKUR and ERNST KNIEPEN) (D.R.-P. 367954; from *Chem. Zentr.*, 1923, ii, 915—916).—Aromatic cyclic or heterocyclic hydroxy-compounds or their substitution products are treated with phosphoryl halides in the presence of suitable catalysts, for example, magnesium, calcium, aluminium, their chlorides, or the chlorides of iron or chromium. The following compounds are prepared: *triphenyl phosphate*, from phenol and phosphorus oxychloride; *tri-p-tolyl phosphate*; *tri-β-naphthyl phosphate*, m. p. 110—111°; *resorcinyll phosphate*, $(C_6H_4O_2)_3(PO)_2$, crystals, m. p. above 300°; *tri-8-quinolyl phosphate*, a granular substance, m. p. 175—176°; *phenyl-di-β-naphthyl phosphate*, a viscid mass solidifying on cooling, and having b. p. above 300°/9 mm. G. W. R.

Chloral-*p*-acetylaminophenol. O. HINSBERG (*Ber.*, 1923, **56**, [B], 1734).—The action of chloral on *p*-acetylaminophenol leads to the formation of a substance, (?) $CCl_3 \cdot CH(OH) \cdot O \cdot C_6H_4 \cdot NHAc$, a colourless, tasteless, crystalline solid, m. p. about 160° (decomp.) according to the rate of heating. It decomposes with evolution of chloral slowly at the atmospheric temperature, but rapidly when heated. The possibility that it is a molecular compound in which the components are united by subsidiary valencies is not excluded. H. W.

The Action of Bromine on *p*-Hydroxy- and *p*-Methoxy-sulphonic Acids. ANDREW NORMAN MELDRUM and MADHAVLAL SUKHLAL SHAH (*T.*, 1923, **123**, 1982—1986).

[The Isomerism of β-Naphthol Sulphides and the Analogous Isomerism of Aromatic *o*-Hydroxysulphides]. R. LESSER and G. GAD (*Ber.*, 1923, **56**, [B], 1802; cf. this vol., i, 561). The failure of dehydrosulphides which contain a substituent in the ortho-position to the hydroxy-group to react with phenyl- or *p*-nitrophenyl-hydrazine is not necessarily a proof that they have the spiran constitution with a double thionylum ring. H. W.

The Isomerism of β -Naphthyl Sulphide and its Derivatives.

O. HINSBERG (*Ber.*, 1923, 56, [B], 1735—1736).—The author agrees with Lesser and Gad (this vol., i, 561), that the assumption of a peculiar sulphur isomerism is no longer necessary to explain the relationship of β -naphthyl sulphide and *iso*- β -naphthyl sulphide. This is, however, not the case with certain of their derivatives, notably the corresponding sulphones and, in particular, the naphthathioxines (Nolan and Smiles, T., 1913, 103, 901). H. W.

The Ternary Eutectic Point of the Three Systems: Resorcinol- α -Nitronaphthalene-Pyrocatechol; Quinol-Resorcinol-Pyrocatechol; Quinol- α -Nitronaphthalene-Pyrocatechol. PIERRE SENDEN (*Bull. Soc. chim. Belg.*, 1923, 32, 281—285).—A continuation of work previously described (this vol., i, 461). Diagrams based on the experimental values obtained are given. The respective eutectic temperatures are 40.9°, 37.5°, and 48°. H. J. E.

Alkali Metal as a Reagent for Weakened Valencies in Organic Compounds. KARL ZIEGLER and FRITZ THIELMANN (*Ber.*, 1923, 56, [B], 1740—1745).—An alkali metal is very suitable for the detection of the presence of weakened valencies in widely-differing groups of organic compounds. Up to the present, this has been shown to be true for potassium and for the highly active alloy of sodium and potassium, but the action of metallic sodium has not been investigated.

$\alpha\gamma\gamma$ -Tetraphenylallyl ethyl ether, triphenylmethyl ethyl ether, phenyl triphenylmethyl ether, benzhydryl ethyl ether, dibenzhydryl ether, benzophenonedimethylacetal, and phenyl triphenylmethyl sulphide undergo fission in accordance with the scheme, $R\cdot O\cdot R' + 2K = RK + K\cdot O\cdot R'$, when shaken with potassium powder or with sodium-potassium alloy in the presence of anhydrous ethyl ether at the atmospheric temperature; the occurrence of the reaction under so mild experimental conditions is remarkable. The ethers are characterised by the presence of weakened valencies between the hydrocarbon radicles and the oxygen atom. Similar fission is unexpectedly observed with $\alpha\alpha\beta\beta$ -tetraphenylethane and $\alpha\alpha\alpha\beta$ -tetraphenylethane. Since the latter compounds are completely stable individuals which do not exhibit any tendency towards dissociation into radicles even at a much higher temperature than that used in these experiments, it is impossible to assume that the reaction with potassium is due primarily to a dissociation into radicles and subsequent union of the latter with the metal.

Triphenylmethyl peroxide when similarly treated yields the potassium derivative of triphenylcarbinol, fission occurring therefore between the oxygen atoms. H. W.

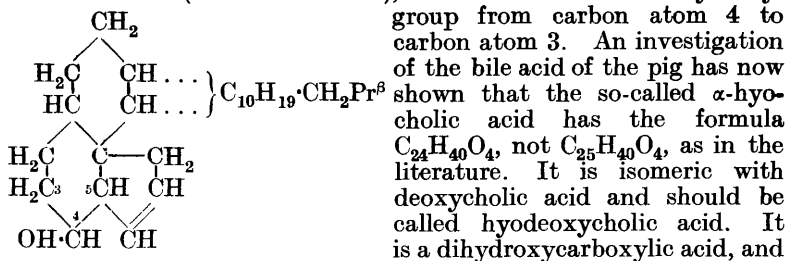
Diphenylphenylacetylenylcarbinol, $CPh\equiv C-CPh_2-OH$. CHARLES MOUREU, CHARLES DUFRAISSE, and COLIN MACKALL (*Bull. Soc. chim.*, 1923, [iv], 33, 934—942; cf. A., 1921, i, 35).—The substitution of the phenylacetylenyl group for one of the phenyl
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groups of triphenylcarbinol does not markedly affect the alcoholic properties of the compound. Although attempts to prepare the benzoate and the acetate of the alcohol failed, the Grignard reagent reacts with it with evolution of gas. Phosphorus trihalides react with the alcohol to form the *chloride*, m. p. 70—71°, and the *bromide*, m. p. 72—73°. Attempts to prepare the ethyl ether were unsuccessful, a yellow substance, m. p. 87°, being obtained by the action of ethyl alcohol and sulphuric acid on diphenylphenylacetylenylcarbinol. This yellow substance may be brominated to give three products, of which two melt at 130—131° and 183—184°, respectively. The alcohol itself does not behave towards halogens as an acetylenic substance. Bromine and iodine attack it and its halides very slowly, and always with the evolution of hydrogen halide, in spite of the fact that all the hydrogen in the molecules of the halides is situated in the phenyl groups. No crystalline derivatives were isolated from the last reactions. H. H.

Application of the Strain Theory to the Ring System of Cholesterol. A. WINDAUS and W. HÜCKEL (*Nachr. K. Ges. Wiss. Göttingen*, 1921, 162—183; from *Chem. Zentr.*, 1923, i, 850; cf. A., 1922, i, 658; this vol., i, 220).—The application of Blanc's reaction to the determination of the constitution of the polycyclic hydroaromatic acids formed from the degradation of cholesterol and the bile acids is discussed. It is shown that in the case of cholestanol contradictory results may be obtained. In the hydroaromatic systems examined, the rings are either in the *cis*- or *trans*-position to each other, according as the hydrogen atoms attached to the common carbon atoms lie on the same side or on opposite sides in the two rings. The rules which hold for the monocyclic systems are only applicable to *cis*-systems. With *trans*-systems different conditions obtain. From a study of models, the authors calculate the valency deflections for different systems. It is concluded that Blanc's reaction may be inapplicable to cholestanol. Whilst such exceptions are improbable for rings of three or four carbon atoms in complicated hydroaromatic compounds, the conditions are different for the 1 : 5- and 1 : 6-positions of the carbon atoms. With open chains and free rotation, the first and fifth (or sixth) carbon atoms approximate to the normal relative position of two carbon atoms. This is impossible with *trans*-ring systems, where ring closure is consequently difficult or impossible. G. W. R.

Relationships between Cholesterol and Bile Acids. A. WINDAUS (*Z. angew. Chem.*, 1923, 36, 309—310).—The relationship of cholic acid, from ox galls, to cholesterol has already been established (A., 1920, i, 41), and it is probable that there is a genetic relationship between the two in the animal organism. The transformation of cholesterol into deoxycholic acid, one of the three specific acids of ox bile, for example, necessitates the replacement of an *isobutyl* group by a carboxy-group, the addition of water at the double bond, the spatial inversion of the asymmetric

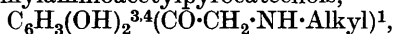
carbon atom 5 (annexed formula), and the removal of the hydroxyl



group from carbon atom 4 to carbon atom 3. An investigation of the bile acid of the pig has now shown that the so-called α -hyocholic acid has the formula $\text{C}_{24}\text{H}_{40}\text{O}_4$, not $\text{C}_{25}\text{H}_{40}\text{O}_4$, as in the literature. It is isomeric with deoxycholic acid and should be called hyodeoxycholic acid. It is a dihydroxycarboxylic acid, and gives on reduction hyocholanic acid, the decomposition product of cholanic acid. It has therefore the same configuration, as regards carbon atom 5, as cholesterol, and is more closely related to this than the deoxycholic acid from ox bile. The chenocholic acid from goose gall also contains twenty-four carbon atoms and can be transformed into cholanic acid. E. H. R.

Preparation of Nucleus-substituted Hydroxyl Derivatives of β -Chloro- α -hydroxy- α -arylethanes and β -Chloro- α -bisarylethanes. OSCAR HINSBERG (D.R.-P. 364039; from *Chem. Zentr.*, 1923, ii, 912—913).—Monochloroacetal is allowed to react on phenol, substituted phenols, dihydroxyphenols, trihydroxyphenols, or naphthols in the presence of acids. β -Chloro- α -hydroxy- α -hydroxyphenylethane, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2\text{Cl}$, from phenol and chloroacetal in the presence of acetic acid and strong hydrochloric acid, is a powder with high m. p. which loses hydrogen chloride at 130° . β -Chloro- α -hydroxy- α -(4-hydroxy-2-methyl-3-isopropylphenyl)ethane, from chloroacetal and thymol, is a yellow, crystalline powder decomposing at 160° with evolution of hydrogen chloride. From chloroacetal (1 mol.) and thymol (2 mols.) β -chloro- α -bis(4-hydroxy-2-methyl-3-isopropylphenyl)ethane is obtained; it is crystalline. β -Chloro- α -hydroxy- α -di-o-hydroxyphenylethane, from chloroacetal and pyrocatechol, is a powder of high m. p., darkening on exposure to air. β -Chloro- α -hydroxy- α -trihydroxyphenylethane from pyrogallol and chloroacetal is a similar compound. β -Chloro- α -di-2-hydroxynaphthylethane, from chloroacetal and β -naphthol, forms small needles, m. p. 174° . G. W. R.

Preparation of Optically Active Aromatic Amino-alcohols. SOCIETY FOR CHEMICAL INDUSTRY IN BASLE (Swiss Pat. 92298 and Brit. Pat. 187129; from *Chem. Zentr.*, 1923, ii, 572).—Optically active salts of α -alkylaminoacetylpyrocatechols,



are reduced and the mixture of the salts of the optically active dihydroxyphenylethanol alkylamines, after separation of the isomerides, are changed into the free bases. For example, an aqueous solution of methylaminoacetylpyrocatechol (or ethylaminoacetylpyrocatechol) and *d*-tartaric acid is reduced by hydrogen in the presence of colloidal platinum. The platinum is precipitated and the solution, after its removal, concentrated. A crystalline by-product is removed and the filtrate evaporated to dryness. The

residue is then dissolved in methyl alcohol. After seeding with a crystal, *l-o-dihydroxyphenylethanolmethylamine-d-hydrogen tartrate* crystallises out whilst *d-o-dihydroxyphenylethanolmethylamine-d-hydrogen tartrate* remains in solution. The *l-o-dihydroxyphenylethanolmethylamine* obtained by the action of ammonia on an aqueous solution of the *d-tartrate* is identical with naturally prepared adrenaline. In the case of the corresponding derivatives of ethylamine, *d-o-dihydroxyphenylethanolmethylamine d-hydrogen tartrate* crystallises out from the mixture of salts, whilst *l-o-dihydroxyphenylethanolmethylamine d-hydrogen tartrate* remains in solution. *d-o-Dihydroxyphenylethanolmethylamine* has m. p. 197°. *l-o-Dihydroxyphenylethanolmethylamine* has also m. p. 197°. G. W. R.

Preparation of an Optically Active Aromatic Amino-alcohol. SOCIETY FOR CHEMICAL INDUSTRY IN BASLE (Swiss Pat. 92299; from *Chem. Zentr.*, 1923, ii, 572—573).—Racemic *o-dihydroxyphenylethanolmethylamine* is separated into the salts of its optically active isomerides by means of optically active α -halogenocamphorsulphonic acids in the presence of suitable organic solvents. The free base is obtained from the salt of *l-o-dihydroxyphenylethanolmethylamine* by the usual methods. *l-o-Dihydroxyphenylethanolmethylamine d- α -bromocamphorsulphonate* has m. p. 161° (decomp.) after discoloration at 155°. G. W. R.

Trichloro-*tert.*-butyl Nitrobenzoate. T. B. ALDRICH (U.S. Pat. 1451357).—On being heated together, trichloro-*tert.*-butyl alcohol and *m*-nitrobenzoyl chloride yield trichloro-*tert.*-butyl *m*-nitrobenzoate, white plates, m. p. 86—88°.

CHEMICAL ABSTRACTS.

Preparation of Urethane Derivatives of Benzoic Acid. SOCIETY FOR CHEMICAL INDUSTRY IN BASLE (Swiss Pats. 93436 and 93750; from *Chem. Zentr.*, 1923, ii, 746).—*m*- or *p*-Aminobenzoic acid is treated with ethylene chlorohydrin chloroformate and the chlorourethanebenzoic acid thereby formed allowed to react with primary aliphatic alcohols. The esters thus obtained are treated with diethylamine. By the action of ethylene chlorohydrin chloroformate on sodium *p*-aminobenzoate, *p-chlorourethanebenzoic acid*, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl}$, is obtained as crystals. By the action of thionyl chloride, the corresponding *acid chloride* is obtained. This, by treatment with ethyl alcohol at 100°, gives *ethyl chlorourethanebenzoate*, a crystalline substance which with diethylamine at 100° gives *ethyl diethylaminourethanop-benzoate*, $\text{CO}_2\text{Et}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NEt}_2$. The free base has m. p. about 40°. The *hydrochloride* is crystalline and has m. p. 210° (decomp.). *Allyl diethylaminourethano-m-benzoate* has m. p. about 50°. The *hydrochloride* forms crystals, m. p. 149—150°. G. W. R.

Preparation of Urethane Derivatives of Benzoic Acid. SOCIETY FOR CHEMICAL INDUSTRY IN BASLE (Swiss Pats. 94568 and 94983; from *Chem. Zentr.*, 1923, ii, 746; cf. preceding abstract).—Ethyl diethylaminourethano-*p*-benzoate may be prepared by

the action of ethyl *p*-aminobenzoate on ethylene chlorohydrin chloroformate and treatment of the urethane thereby obtained with diethylamine. By a similar reaction, *amyl diethylamino-urethano-p-benzoate* is obtained. It has m. p. about 40°. The *hydrochloride* forms crystals, m. p. 138—139°. G. W. R.

Preparation of Urethane Derivatives of Benzoic Acid. SOCIETY FOR CHEMICAL INDUSTRY IN BASLE (Swiss Pats. 94569 and 94984; from *Chem. Zentr.*, 1923, ii, 746; cf. preceding abstracts).—Ethyl diethylaminourethano-*p*-benzoate may be prepared by treating ethyl *p*-aminobenzoate with carbonyl chloride and allowing the *ethyl phenylcarbimide-p-carboxylate* (odourless crystals, m. p. about 60°) thereby obtained to react with diethylaminoethyl alcohol. Using dimethylaminoethyl alcohol, *ethyl dimethylaminourethano-p-benzoate* is obtained. Its *hydrochloride* is crystalline and has m. p. 224—225°. G. W. R.

Preparation of Benzyl Esters of *p*-Dialkylaminomethylbenzoic Acids. F. HOFFMANN-LA ROCHE & Co., AKT. GES. (Swiss Pats. 93500 and 93501; from *Chem. Zentr.*, 1923, ii, 573).—Benzyl esters of ω -halogenomethylbenzoic acids are condensed with secondary aliphatic amines. By heating cyanobenzyl chloride with hydrobromic acid and warming the *p-bromomethylbenzoic acid* (needles, m. p. 224°) thereby formed with thionyl chloride, *p-bromomethylbenzoyl chloride* is obtained. This gives with benzyl alcohol *benzyl p-bromomethylbenzoate*, m. p. 62°, which when heated with diethylamine, dimethylamine, or piperidine, respectively, at 100°, gives the following compounds. *Benzyl p-diethylaminomethylbenzoate hydrochloride*, $C_6H_4(CO_2 \cdot CH_2Ph)(CH_2 \cdot NEt_2) \cdot HCl$, crystals, m. p. 166°. *Benzyl p-dimethylaminomethylbenzoate hydrochloride*, colourless needles, m. p. 192°. *Benzyl p-piperidinomethylbenzoate hydrochloride*, leaflets, m. p. 183°. The products find use as local anæsthetics. G. W. R.

Diacyl Derivatives of *o*-Hydroxybenzylamine. L. CHAS. RAIFORD and E. P. CLARK (*J. Amer. Chem. Soc.*, 1923, 45, 1738—1743).—It is shown that the benzylation of *o*-hydroxybenzylacetamide does not cause migration of the acetyl radicle, and that the introduction of the acyl radicles in different orders gives isomeric acetyl-benzoyl derivatives. This is entirely different from the behaviour of such compounds in which both the reacting radicles are attached directly to the aromatic nucleus (A., 1922, i, 931).

The action of boiling acetic anhydride on *o*-hydroxybenzylamine in the presence of concentrated sulphuric acid gives *o-acetoxymethylacetamide*, hexagonal plates, m. p. 102—103°, which is hydrolysed by means of cold aqueous alcoholic potassium hydroxide, with formation of *o*-hydroxybenzylacetamide; the latter gives the benzoate, m. p. 116° (cf. Auwers and Eisenlohr, who give m. p. 108—109°; *Annalen*, 1909, 369, 236), on benzylation. The benzoate is reconverted into the *N*-acetyl derivative by hydrolysis by means of cold aqueous alcoholic potash. *o-Acetoxymethylbenzamide*, needles, m. p. 85°, is obtained by the action of boiling

acetic anhydride and sodium acetate on *o*-hydroxybenzylbenzamide, into which it is reconverted by the action of cold alcoholic potassium hydroxide. The *N*-benzoyl derivative is obtained from the free base by benzylation, but is more conveniently prepared by the hydrolysis by means of alcoholic potassium hydroxide of its *benzoate*, long, slender needles, m. p. 142–143°, which is produced from the free base by the action of benzoyl chloride and aqueous potassium hydroxide solution. W. S. N.

Condensation of Nitriles with Thioamides. II. Acetonitrile with Thiobenzamide; and Benzonitrile with Thioacetamide. SEIICHI ISHIKAWA (*J. Chem. Soc. Japan*, 1923, 44, 382–391; cf. A., 1921, i, 728).—Benziminoisothiobenzamide, $\text{NH}:\text{CPh}:\text{N}:\text{CPh}:\text{SH}$, was obtained by the condensation of benzonitrile and thiobenzamide. By passing dried hydrogen chloride into an ethereal solution of acetonitrile and thiobenzamide (A) or of benzonitrile and thioacetamide (B), the same condensation product, benziminoisothiobenzamide, is obtained, the yield being, however, poor. In the case of (A), thioacetamide is produced in the reacting solution, and in the case of (B) thiobenzamide was detected. A reversible reaction, $\text{PhCN} + \text{NH}:\text{CMe}:\text{SH} \rightleftharpoons \text{NH}:\text{CPh}:\text{SH} + \text{MeCN}$, has therefore occurred in the solution. The benzonitrile and thiobenzamide thus produced condense with one another. Two intermediate products, $\text{NH}:\text{CMe}:\text{N}:\text{CPh}:\text{SH}$ and $\text{NH}:\text{CPh}:\text{N}:\text{CMe}:\text{SH}$, may be produced before the condensation, but were not isolated. K. K.

The Action of Bases on $\alpha\beta$ - and $\alpha\beta\beta$ -Tribromo- β -phenylpropionic Acids and their Esters. P. RAMASWAMI AYYAR and J. J. SUDBOROUGH (*J. Ind. Inst. Science*, 1923, 6, 69–92).—In continuation of previous work on $\alpha\beta$ -dibromo- β -phenylpropionic acids (T., 1903, 83, 666), a study has been made of the action of bases on $\alpha\beta\beta$ -tribromo- β -phenylpropionic acid, and $\alpha\beta\beta$ -tribromo- β -phenylpropionic acid. On boiling the $\alpha\beta\beta$ -acid with water, carbon dioxide is split off almost quantitatively, the product being $\alpha\beta$ -dibromostyrene. Alkali hydroxides in alcoholic solutions eliminate hydrobromic acid from both the tribromo-acids, yielding mixtures of the two stereoisomeric $\alpha\beta$ -dibromocinnamic acids. With the $\alpha\beta\beta$ -acid or its ester, the ratio of *cis*- to *trans*-acid is 1 : 3·0, whilst with the $\alpha\beta\beta$ -acid or ester the ratio is 1 : 1·4, but when much dibromostyrene is formed, the ratio may fall to 1 : 9 or even 1 : 12. In addition to the formation of the dibromocinnamic acids, dibromostyrene is also formed to some extent, favouring conditions being the replacement of alcohol by water, the use of dilute alkali, and high temperature. Hydrogen bromide is eliminated more readily from the $\alpha\beta\beta$ -acid and its ester than from the $\alpha\beta\beta$ -acid or ester, and the $\alpha\beta\beta$ -acid is also that which most readily loses carbon dioxide to give dibromostyrene. The tribromo-acids react with organic bases such as aniline, quinoline, and dimethylaniline, the chief reaction being elimination of carbon dioxide and hydrogen bromide, and formation of dibromostyrene, together with mixtures of (probably) mono- and di-bromocinnamic acids. With the esters, however, the main

reaction consists in elimination of bromine and production of *p*-bromodimethylaniline: $\text{CHPhBr} \cdot \text{CBr}_2 \cdot \text{CO}_2\text{Me} + \text{NMe}_2 \cdot \text{Ph} = \text{CHPh} \cdot \text{CBr} \cdot \text{CO}_2\text{Me} + \text{HBr} + \text{C}_6\text{H}_4\text{Br} \cdot \text{NMe}_2$ and $\text{CPhBr}_2 \cdot \text{CHBr} \cdot \text{CO}_2\text{Me} + \text{NMe}_2 \cdot \text{Ph} = \text{CBrPh} \cdot \text{CH} \cdot \text{CO}_2\text{Me} + \text{HBr} + \text{C}_6\text{H}_4\text{Br} \cdot \text{NMe}_2$.

At the same time, hydrogen bromide is also eliminated to some extent, the product being therefore chiefly a mixture of mono- and di-bromocinnamic esters. This is of some interest, as the elimination of bromine from $\alpha\beta$ -dibromo-compounds under the influence of bases is not usual (cf. T., 1922, 121, 1314). F. A. M.

The so-called Distyrenic Acid of Fittig and Erdmann. R. STOERMER and WALTER BECKER (*Ber.*, 1923, 56, [B], 1440—1448).—Examination of “distyrenic acid” obtained by Fittig and Erdmann by the action of boiling sulphuric acid (50%) on cinnamic acid has shown that it is a mixture of substances which contains two saturated acids, for which the names distyranic and distyrenic acids are proposed, and unsaturated distyrenic acids from which a homogeneous material could not be isolated. Evidence is adduced to show that distyrenic acid is to be regarded as a 1 : 2-diphenylcyclobutane-3-carboxylic acid, whereas distyranic acid is probably a 1 : 3-diphenylcyclobutanecarboxylic acid, the constitution of which has not been completely elucidated owing to the difficult accessibility of the material.

The crude product of the action of sulphuric acid on cinnamic acid is purified from distyrene by treatment with alkali and ether and converted into the methyl esters by treatment with sodium hydroxide and methyl sulphate. The methyl esters are distilled in high vacuum, whereby mainly the saturated esters are volatilised whereas the unsaturated compounds cannot be removed without decomposition. The distillate is hydrolysed, giving mainly a mixture of saturated acids from which the removal of small quantities of unsaturated acid is effected only with great difficulty. The final mixture of saturated acids is separated by extraction with alcohol at 0° into *distyranic acid*, $\text{C}_{17}\text{H}_{16}\text{O}_2$, matted needles, m. p. 176°, and *distyrenic acid*, $\text{C}_{17}\text{H}_{16}\text{O}_2$, long, thin rodlets, m. p. 147°; the yield of the former compound is 0.3%, that of the latter 2.6% of the weight of the cinnamic acid used. Distyranic acid is converted into the corresponding *chloride*, a liquid which could not be caused to solidify, the *amide*, long, thin, colourless needles, m. p. 215°, the *anilide*, lustrous, slender needles, m. p. 194°, and the *methyl ester*, rhombic leaflets, m. p. 53°. The acid is not isomerised by pyridine at 160—170°; it is oxidised by permanganate to benzoic acid and a substance, m. p. 120°, which does not give the reactions of benzil. Distyrenic acid yields the corresponding *chloride*, $\text{C}_{17}\text{H}_{15}\text{OCl}$, a liquid which is very sensitive towards moisture, the *amide*, colourless, thin prisms, m. p. 205°, the *anilide*, colourless rodlets, m. p. 198°, and the *methyl ester*, long, thin rodlets, m. p. 72°, which regenerates the acid, m. p. 147°, when hydrolysed. The acid does not undergo isomerisation when treated with pyridine at 160—170°, with fuming hydrochloric acid at 150—160°, or when fused with potassium hydroxide. The *calcium*, *strontium*, *copper*, *zinc*, and *potassium*

salts have the unusual property of dissolving readily in chloroform, carbon disulphide, or acetone. Distyrenic acid is oxidised by potassium permanganate to benzoic acid and benzil. When calcium distyrenate is distilled with soda-lime, it yields $\alpha\beta$ -diphenyl- Δ^{α} -butene, $\text{CHPh:CPh}\cdot\text{CH}_2\cdot\text{CH}_3$, m. p. $56\cdot5^\circ$.

The methyl esters which remain after distillation of the final mixture (see above) yield on hydrolysis an inseparable mixture of distyrenic acids. The impossibility of hydrogenating these acids by the customary methods and their inability to yield lactones appear to indicate the absence of $\Delta^{\alpha\beta}$ - and $\Delta^{\beta\gamma}$ -unsaturated acids, respectively. The original soft mass gradually passes into a hard, resinous material which appears to be a polymeride in which the carboxy-group takes part in the union of the individual molecules.

H. W.

The Constitution of Sulphosalicylic Acid and of Related Substances. ANDREW NORMAN MELDRUM and MADHAVLAL SUKHLAL SHAH (T., 1923, 123, 1986—1993).

Preparation of New Carbonyl Derivatives of α -Naphthol. SOCIETY OF CHEMICAL INDUSTRY IN BASLE (Brit. Pat. 181009; cf. U.S. Pat. 1387596).—Esters of α -naphthol-4-carboxylic acid or of α -naphthol-2 : 4-dicarboxylic acid, as well as of 4 : 4'-dihydroxy-1 : 1'-dinaphthyl ketone, are obtained, in addition to the dyes previously described (*loc. cit.*), by the interaction of α -naphthol and a tetrahalogen derivative of methane, in the presence of a substance capable of neutralising an acid and of an aliphatic alcohol.

W. T. K. B.

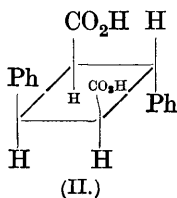
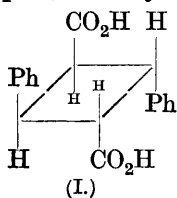
α -Quinones and 1 : 2-Diketones. VII. The Benzilic Acid Transformation in Cold Solution in the Absence of Air. The Cause of the Migration of the Radicle in the Benzilic Acid Transformation. A. SCHÖNBERG and K. T. KELLER (*Ber.*, 1923, 56, [B], 1638—1642).—The production of benzoic acid during the benzilic acid transformation is due to atmospheric oxidation, $\text{COPh}\cdot\text{COPh} + \text{O} + \text{H}_2\text{O} = 2\text{Ph}\cdot\text{CO}_2\text{H}$. Its formation can be completely avoided by working in cold solution in the absence of air. The process has the further advantage that it is applicable to substituted benzils many of which do not yield benzilic acids under the usual conditions of the transformation. The presence of more than one molecular proportion of potassium alkylxide is not necessary for the conversion of benzil into benzilic acid; the intermediate compound is therefore the mono-derivative $\text{OEt}\cdot\text{CPh(OK)}\cdot\text{COPh}$, and not the di-derivative. The cause of the transformation is sought in the tendency of the unequally loaded carbon atoms to equalise their valency demands.

Benzilic acid is conveniently prepared by the addition of a filtered solution of sodium hydroxide in alcohol (97%) to benzil dissolved in ether. The flask is filled to the neck, securely stoppered, and allowed to remain at the atmospheric temperature during twelve hours. The mixture is subsequently shaken with water, and benzilic acid is precipitated from the aqueous solution. 2 : 2'-Dimethoxybenzilic acid crystallises in colourless needles,

m. p. 160°. 4:4'-*Diethoxybenzilic acid*, colourless needles, m. p. 99°, and 3:3'-*dimethoxybenzilic acid*, colourless needles, m. p. 105°, are also described. H. W.

The Molecular Configurations of Polynuclear Aromatic Compounds. IV. 6:6'-Dichlorodiphenic Acid; its Synthesis and Resolution into Optically Active Components. GEORGE HALLATT CHRISTIE, CUTHBERT WILLIAM JAMES, and JAMES KENNER (T., 1923, 123, 1948—1951).

The Stereochemistry of the Truxillic Acids. VII. R. STOERMER [with CHRISTIAN WEGNER and ALFRED CARL] (*Ber.*, 1923, 56, [B], 1683—1695).—When a carboxyl group of the (five theoretically possible) truxillic acids is converted into the group CO·NHPh, the carbon atoms of the *cyclobutane* ring become, in part, actually asymmetric and hence certain of the anilic acids are resolvable into their optical antipodes whereas others have the indivisible meso-configuration. α - and γ -Truxillanilic acids have been resolved into their optical antipodes; it is therefore possible to represent with certainty the configurations of α - and γ -truxillic acid by the annexed formulæ, I and II.



The action of aniline on α -truxillic anhydride leads to the formation of α -truxillic acid, α -truxillanilic acid, $C_{24}H_{21}O_3N$, lustrous needles, m. p. 235°, and α -truxillodianilide, m. p. 286°. *Methyl α -truxillanilate*, prepared from the acid and methyl sulphate in alkaline solution, crystallises in slender needles, m. p. 173°, and the *ethyl* ester forms similar crystals, m. p. 151.5°. The acid is converted by thionyl chloride into α -truxillanilyl chloride, almost colourless crystals, m. p. 168° (decomp.), which is transformed by aniline into the dianilide mentioned above and by dry ammonia into α -truxillanilamide, m. p. 244°.

The resolution of *r*- α -truxillanilic acid into its optical antipodes is accomplished by means of strychnine in the presence of methylal. *Strychnine 1- α -truxillanilate* crystallises in aggregates of needles, m. p. 162° (decomp.). *1- α -Truxillanilic acid*, slender needles, m. p. 205°, has $[\alpha]_D^{20} = -23.0^\circ$, when dissolved in acetone. *d- α -Truxillanilic acid*, slender needles, m. p. 205°, $[\alpha]_D^{20} +21.8^\circ$ in acetone, is obtained by the aid of brucine in methylal solution from the mixture of *r*- and *d*-acids isolated from the mother-liquors obtained during the resolution of the *r*-acid by strychnine. *Methyl 1- α -truxillanilate*, slender needles, m. p. 176°, $[\alpha]_D^{20} -22.4^\circ$ in acetone and *ethyl d- α -truxillanilate*, m. p. 153°, $[\alpha]_D^{20} +18.75^\circ$, when dissolved in acetone, are also described. *d- α -Truxillanilyl chloride* has m. p. 135°, $[\alpha]_D^{20} +12.42^\circ$ in acetone (the specimen was probably not perfectly homogeneous); it is converted by aniline into the optically inactive di-anilide, m. p. 286° (see above), whereas the *laevorotatory chloride* is transformed by ammonia into *1- α -truxillanilamide*, m. p. 233°, $[\alpha]_D^{20} -28.8^\circ$ in acetone. *r- α -Truxillodianilide* is hydrolysed by

alcoholic potassium hydroxide solution only with extreme difficulty; the hydrolysed portion consists of a very difficultly separable mixture of α - and γ -truxillanic acids. A similar mixture is obtained by heating the α -anilic acid with alcoholic potassium hydroxide solution at 120° , whereas the conversion of α - into γ -truxillic acid is never observed under these conditions.

α -Truxillic anhydride dissolved in benzene is converted by dry, gaseous ammonia into α -truxilldiamide, m. p. 267° , α -truxillic acid and α -truxillanic acid, slender, colourless needles, m. p. 261° ; the copper, manganese, nickel, and lead salts of the latter acid are insoluble in water, in which the alkali and alkali-earth salts dissolve readily. Attempts to resolve the acid by means of strychnine or brucine in the presence of methylal or alcohol were unsuccessful. α -Truxilldiamide is highly stable towards alcoholic potassium hydroxide solution.

γ -Truxillanic acid, small, matted needles, m. p. 228° , is conveniently prepared by the action of aniline on γ -truxillic anhydride in the presence of boiling alcohol; the methyl ester, slender, colourless needles, m. p. 184.5° ; the ethyl ester, slender needles, m. p. 202° , and the *n*-propyl ester, small, colourless needles, m. p. 172° , are described. γ -Truxillanilic chloride, thick, colourless needles, m. p. 156° , prepared from the acid by means of thionyl chloride, but not by phosphorus pentachloride, is converted by dry, gaseous ammonia into γ -truxillanilamide, long, colourless needles, m. p. 255° , and by aniline into the dianilide, colourless needles, m. p. 267.5° . γ -Truxillanil, $C_{16}H_{14}<\begin{smallmatrix} CO \\ CO \end{smallmatrix}>NPh$, leaflets, m. p. 194° , is

most conveniently prepared by heating γ -truxillanic acid with anhydrous sodium acetate and acetic anhydride at 200° ; it is indifferent towards aqueous potassium hydroxide solution but readily hydrolysed by the alcoholic reagent.

γ -Truxillanic acid is resolved into its optical antipodes with unusual readiness by means of cinchonine in absolute ethyl-alcoholic solution. Cinchonine d- γ -truxillanilate crystallises in slender needles, m. p. 247° (decomp.). d- γ -Truxillanic acid, aggregates of slender needles, has m. p. 228° , $[\alpha]_D^{25} + 48.73^\circ$, when dissolved in acetone. Cinchonine l- γ -truxillanilate is an almost colourless, crystalline mass, m. p. 112° (decomp.). l- γ -Truxillanic acid, slender needles, has m. p. 228° , $[\alpha]_D^{25} - 49.54^\circ$ in acetone. Methyl l- γ -truxillanilate forms lustrous, woolly needles, m. p. 202° , $[\alpha]_D^{25} - 38.55^\circ$ in acetone. Ethyl d- γ -truxillanilate, needles, m. p. 206° , $[\alpha]_D^{25} + 25.19^\circ$ in acetone; l- γ -truxillanilic chloride, lustrous needles, m. p. 164° (decomp.), $[\alpha]_D^{25} - 9.53^\circ$ in acetone (which is converted by aniline into the *r*-dianilide, m. p. 267.5°), and d- γ -truxillanilamide, needles, m. p. 253° , $[\alpha]_D^{25} + 35.6^\circ$ in acetone, are also described.

H. W.

Production of Imidothio-esters by the Condensation of Thiocarbimides with Resorcinol or Phloroglucinol. R. J. KAUFMANN and ROGER ADAMS (*J. Amer. Chem. Soc.*, 1923, **45**, 1744—1752).—Alkyl- and aryl-thiocarbimides are condensed with

resorcinol or phloroglucinol in the presence of anhydrous ether, dry hydrogen chloride, and anhydrous zinc chloride, with production of the hydrochlorides of imidothio-esters, $R \cdot C(SR') : NH, HCl$. These substances are converted by boiling with water into the corresponding thio-esters, $R \cdot CO \cdot SR'$, which are converted by means of alkali into carboxylic acids, $R \cdot CO_2H$. The free imidothio-esters, $R \cdot C(:NH)SR'$, are produced by the action of sodium hydrogen carbonate solution on the hydrochlorides; they readily react with alcohols, giving mercaptans and imido-esters, $R \cdot C(:NH) \cdot OR''$, which, on boiling with dilute hydrochloric acid, pass, through the hydrochloride, into the esters, $R \cdot CO_2R''$, identical with the product formed from the carboxylic acids and the alcohol, $R''OH$.

These reactions have been conducted using methyl-, ethyl-, and phenyl-carbimides and *n*-butylcarbimide, which has b. p. $184.5-185.5^\circ/743$ mm., d_{25}^{25} 0.9563, n_D^{25} 1.4636. In order to purify the imidothio-ester hydrochlorides, it is necessary to dissolve the crude product in cold hydrochloric acid and reprecipitate the free base, since much of the zinc in the crude product is present as the zinc salt of the condensation product. Such a zinc salt has actually been isolated from the experiment in which phenylthiocarbimide and resorcinol were used (see below). The condensations proceed much more slowly in the absence of zinc chloride, but the materials obtained are always much purer. The following compounds are described. *Methyl op-dihydroxythiobenzoate*, m. p. $97-98^\circ$ ($+H_2O$, m. p. $70-71^\circ$), and its *di-p-nitrobenzoate*, m. p. $214-216^\circ$. *Methyl op-dihydroxyimidobenzoate*, white needles, m. p. 210° , and its *hydrochloride*, m. p. $224-226^\circ$. *S-Methyl op-dihydroxyimidothiobenzoate*, small, yellow needles, m. p. $197-199^\circ$ (decomp.), *hydrochloride*, m. p. $244-245^\circ$ (decomp.), *sulphate*, m. p. $230-231.5^\circ$. *Methyl-2:4:6-trihydroxythiobenzoate*, m. p. 190° . *S-Methyl 2:4:6-trihydroxyimidothiobenzoate*, m. p. $223-226^\circ$, *hydrochloride*, m. p. $255-256^\circ$. *Ethyl op-dihydroxybenzoate*, m. p. $69-70^\circ$, b. p. $170-176^\circ/13-15$ mm. *Ethyl op-dihydroxyimidobenzoate*, m. p. 214° . *Ethyl op-dihydroxythiobenzoate*, m. p. $60-61^\circ$, and its *di-p-nitrobenzoate*, m. p. $190-191^\circ$. *S-Ethyl op-dihydroxyimidothiobenzoate*, yellow crystals, m. p. $196-197^\circ$ (decomp.), *hydrochloride*, m. p. $229.5-231.5^\circ$ (decomp.), *sulphate*, m. p. $214-217^\circ$. *n-Butyl op-dihydroxythiobenzoate*, a light brown oil, gives a *di-p-nitrobenzoate*, m. p. $115-116^\circ$. *S-n-Butyl op-dihydroxyimidothiobenzoate*, bright yellow needles, m. p. $173-174^\circ$ (decomp.), *hydrochloride*, m. p. $226-228^\circ$ (decomp.). *S-Phenyl op-dihydroxyimidothiobenzoate*, yellow crystals, m. p. $156-158^\circ$ (decomp.), *hydrochloride*, m. p. $220-222^\circ$ (decomp.). This hydrochloride gives a zinc salt, $C_{13}H_{10}O_2NClS_2Zn$, small, pale yellow crystals, m. p. $225-227^\circ$ (decomp.). W. S. N.

Phthalaldehyde. L. SEEKLES (*Rec. trav. chim.*, 1923, **42**, 706-709).—A method for the preparation of phthalaldehyde from naphthalene is described. Nine g. of naphthalene dissolved in 100 c.c. of dry ethyl acetate were treated with 160 litres of 9.6% ozonised oxygen, whereby the diozonide was produced. The solu-

tion was then shaken for twenty-four hours with 20 g. of ice and water and a little calcium carbonate and filtered. The yellow ethyl acetate solution of the aldehyde was separated from the aqueous layer and the latter extracted three times with ethyl acetate. The solution was dried over powdered fused sodium sulphate and the acetate distilled off at 40° in a vacuum. The orange-coloured syrup remaining was distilled in steam, when unchanged naphthalene and then phthalaldehyde passed over. The two distillates were collected separately. The aldehyde distillate was saturated with sodium sulphate and extracted twenty times with ethyl acetate. The extract was dried, the acetate removed in a vacuum at 40°, and the aldehyde crystallised from light petroleum. The aldehyde separated as short, hard, colourless crystals, m. p. 53·2, or as long, pale yellow needles, m. p. 56—57°. The* residue in the flask from the steam distillation on keeping yielded colourless, hard plates which melted at 97° to a turbid liquid that cleared at 100° and is phthalaldehydic acid. From 18 g. of naphthalene, 8·5 g. of unchanged naphthalene were obtained, 1 g. of phthalaldehyde, and 8 g. of phthalaldehydic acid. The system phthalaldehyde-water has been investigated, and it is shown that a monohydrate exists, m. p. 45·3°. J. F. S.

The Beckmann Transformation of Oximinoketones.

SHINTARO KODAMA (*J. Chem. Soc. Japan*, 1923, 44, 339—352).—When oximinoacetophenone in combination with 2 or 3 mols. of sodium hydrogen sulphite, $\text{COPh}\cdot\text{CH}\cdot\text{N}\cdot\text{OH}\cdot 3\text{NaHSO}_3$, is boiled with an equivalent amount, or excess, of 17—30% sulphuric acid for 1 minute, it is changed into an isomeride, colourless needles, m. p. 90—91°, which gives phenylglyoxylic acid when treated with an alkali hydroxide and is identical with the α -isomeride of benzoylformamide, $\text{COPh}\cdot\text{CO}\cdot\text{NH}_2$, and can be changed into β - and γ -isomerides. This is a new example of the Beckmann transformation in the presence of water, the rearrangement having occurred in a case of dehydration. The reaction does not occur in the absence of the sulphite, and may be explained as follows: $[\text{X}=\text{SO}_3\text{Na} \text{ and } \text{Y}=\text{SO}_3\text{H}]\text{COPh}\cdot\text{CH}\cdot\text{NOH} \rightarrow \text{OH}\cdot\text{CPhX}\cdot\text{CHX}\cdot\text{NHX} \rightarrow [\text{OH}\cdot\text{CPhY}\cdot\text{CHY}\cdot\text{NHY}] \rightarrow \text{COPh}\cdot\text{CO}\cdot\text{NH}_2$. K. K.

Preparation of Tetrahydroxyquinone. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (BENNO HOMOLKA) (D.R.-PP. 368741 and 370222; from *Chem. Zentr.*, 1923, ii, 911).—Tetrahydroxyquinone is prepared by the action of alkali carbonates or magnesium oxide on glyoxal in the presence of atmospheric oxygen. Glyoxal may also be used in the form of its polymerides or as the sodium hydrogen sulphite compound. For example, glyoxal sodium hydrogen sulphite is added to an aqueous solution of sodium carbonate at about 50°. The solution absorbs oxygen, becomes yellow, and finally the *disodium* salt of tetrahydroxyquinone separates as bluish-black crystals with metallic green lustre. *Tetrahydroxyquinone* may be obtained from the sodium salt by treatment with hydrochloric acid. It forms large, lustrous, bluish-black crystals. G. W. R.

Reduction Products of the Hydroxyanthraquinones. II.
JOHN HALL and ARTHUR GEORGE PERKIN (T., 1923, 123, 2029—2037).

Derivatives of Anthraquinone. Reactions of Anthraquinone Sulphonic Acids with Mercaptans. W. S. HOFFMAN and E. EMMET REID (*J. Amer. Chem. Soc.*, 1923, 45, 1831—1838).—An extension of the previous research (A., 1922, i, 154). The following compounds are described :

1-Benzylthiolanthraquinone, m. p. 242°; 1:5-dibenzylthiolanthraquinone, dull orange, m. p. 176°; 1:8-dibenzylthiolanthraquinone, orange-red, m. p. 189°. 1-Benzylthiolanthraquinone-5-sulphonic acid and 1-benzylthiolanthraquinone-8-sulphonic acid as the sodium salts, with 2 and 3 molecules of water of hydration, respectively. 5-Benzylthiol-1-alkylthiolanthraquinones : *methyl*, m. p. 276°; *ethyl*, m. p. 208°; *propyl*, m. p. 210°; *butyl*, m. p. 235°; *isopropyl*, m. p. 239°; *isoamyl*, m. p. 211°. 8-Benzylthiol-1-alkylthiolanthraquinones : *methyl*, m. p. 262°; *ethyl*, m. p. 164°; *propyl*, m. p. 181°; *butyl*, m. p. 185°; *isopropyl*, m. p. 229°; *isoamyl*, m. p. 189°. These dithioethers are all orange to red in colour. 1-Benzylsulphoneanthraquinone, m. p. 233°; 1:8-dibenzyldisulphoneanthraquinone, m. p. 202°. Anthraquinone-5-benzyl-1-alkyldisulphones : *methyl*, m. p. 280°; *ethyl*, m. p. 210°; *propyl*, m. p. 215°; *butyl*, m. p. 228°; *isopropyl*, m. p. 229°; *isoamyl*, m. p. 202°. Anthraquinone-8-benzyl-1-alkyldisulphones : *methyl*, m. p. 255°; *ethyl*, m. p. 242·5°; *propyl*, m. p. 227°; *butyl*, m. p. 210°; *isoamyl*, m. p. 201°. 1-isoPropylthiolanthraquinone, gold coloured, m. p. 134°; 1:5-diisopropylthiolanthraquinone, orange, m. p. 148°; 1:8-diisopropylthiolanthraquinone, orange-red, m. p. 181°. Sodium 1-iso-propylthiolanthraquinone-5-sulphonate, +2H₂O; sodium 1-isopropylthiolanthraquinone-8-sulphonate, +3H₂O. 1-Alkylthiol-5-isopropylthiolanthraquinones : *methyl*, orange coloured, m. p. 184°; *ethyl*, gold coloured, m. p. 163°; *propyl*, gold coloured, m. p. 133°; *butyl*, orange-yellow, m. p. 114°; *isoamyl*, brown, m. p. 97°. 1-Alkylthiol-8-isopropylthiolanthraquinones : *methyl*, crimson, m. p. 189°; *ethyl*, crimson, m. p. 176°; *propyl*, orange-red, m. p. 135°; *butyl*, orange-red, m. p. 131°; *isoamyl*, orange-red, m. p. 109°. Anthraquinone-1-isopropylsulphone, m. p. 182°. Anthraquinonealkyl-5-isopropylsulphones : *methyl*, m. p. 235°; *ethyl*, m. p. 213°; *propyl*, m. p. 203°; *butyl*, m. p. 186°; *isopropyl*, m. p. 222°; *isoamyl*, m. p. 172°. 5-Butylthiolanthraquinone-1-alkylsulphones : *methyl*, *ethyl*, *propyl*, *butyl*, *isoamyl* have m. p., respectively, 256°, 210°, 204°, 162°, 189°. 8-Butylthiolanthraquinone-1-alkylsulphones : *methyl*, *ethyl*, *propyl*, *butyl*, *isoamyl* have m. p., respectively, 162°, 140°, 132°, 126°, 121°. These sulphone-thioethers and the preceding disulphones are yellow solids. The following compounds have been prepared with the aid of monothioethylene glycol : 1-β-hydroxyethylthiolanthraquinone, orange, m. p. 178°, its *acetate*, yellow, m. p. 146°; 1:5-di-β-hydroxyethylthiolanthraquinone, orange, m. p. 224°, *diacetate*, yellow, m. p. 199°; 1:8-di-β-hydroxyethylthiolanthraquinone, red, m. p. 206°, *diacetate*, m. p. 159°. A pure thioether

has not been obtained by the aid of ethylene mercaptan; but from this reagent and anthraquinonemonosulphonate a *compound*, m. p. above 250° , possibly $S_2([CH_2]_2 \cdot S \cdot C_{14}H_7O_2)_2$, has been prepared. 1-Butylthiolanthraquinone-5-sulphonic acid is oxidised as the sodium salt by means of fuming nitric acid at 100° to *sodium 1-butylsulphoneanthraquinone-5-sulphonate*, $+ \frac{1}{2}H_2O$, from hot water, $+ H_2O$ from cold water. This reacts extremely rapidly with mercaptans, giving the following 5-alkylthiolanthraquinone-1-butylsulphones: *methyl*, *ethyl*, *propyl*, *butyl*, *isoamyl*, having m. p., respectively, 228° , 214° , 201° , 162° , 152° , which give known disulphones (*loc. cit.*) on oxidation. The butylsulphone-sulphonate also reacts with thiophenol, giving a *compound*, m. p. above 350° , and with *p*-nitrothiophenol, giving an impure *compound*, m. p. above 300° .

It is pointed out that the *isopropyl* thioethers may sometimes be oxidised to sulphones, but usually pass into sulphonic acids.

The formation of 1-butylsulphone-5-alkyl thioethers provides, it is claimed, a ready method for the identification of mercaptans.

W. S. N.

The Isomeric *l*-Menthyl Phenylchloroacetates. ALEX. MCKENZIE and ISOBEL AGNES SMITH (T., 1923, 123, 1962—1978).

New Halogen Derivatives of Camphor. III. $\alpha'\beta$ - and $\alpha'\pi$ -Dibromocamphor. HENRY BURGESS and THOMAS MARTIN LOWRY (T., 1923, 123, 1867—1878).

Investigations in the Camphor and Camphenilone Series. S. NAMEKIN [with (FRL.) A. CHUCHRIKOFF, (FRL.) M. SCHLESINGER, and (FR.) L. BRÜSSOFF] (*Annalen*, 1923, 432, 207—231).—A more detailed account of work already published (this vol., i, 586, 690), together with the following.

β -Methylcamphenilone gives an *oxime*, long needles, m. p. 172° ; a *hydrazone*, b. p. 245 — $247^{\circ}/770$ mm., m. p. 85 — 87° , and an *azine*, $C_{10}H_{16} \cdot N \cdot N : C_{10}H_{16}$, rhombohedra, m. p. 163 — 164° . The hydrazone is converted by heating with sodium ethoxide at 180 — 200° into β -methylcamphenilane, m. p. 116 — 117° . The reduction of β -methylcamphenilone, by the action of sodium on its alcoholic solution, gives β -methylcamphenilol, a camphor-like substance, m. p. 172 — 173° (*phenylurethane*, needles, m. p. 104 — 105° , *hydrogen phthalate*, rhombs, m. p. 174 — 175°), which is partly dehydrated by means of phosphorus pentachloride, giving a *hydrocarbon*, b. p. 150 — $151^{\circ}/744.5$ mm., d_4^{20} 0.8546, n_D^{20} 1.4589. The latter is probably a mixture; when it is oxidised by means of potassium permanganate, a small quantity of a solid remains, m. p. 110 — 112° , having an odour like that of a saturated dicyclic hydrocarbon. W. S. N.

Reactions Differentiating Pinene from Nopinene. I. Permanganate Oxidation, Pinonic and Nopinic Acids. G. DUPONT and G. BRUS (*Ann. Chim.*, 1923, [ix], 19, 186—198; cf. Dupont, A., 1922, i, 1042).—Oxidation of nopinene to nopinic acid by means of permanganate results in poor yields, so that the method is useless for estimation of the hydrocarbon. The acid obtained, however, is pure and of the active form. Similar treatment of

pinene results in a considerable amount of racemisation, the bulk of the product being inactive pinonic acid, although the amount racemised depends on the oxidation conditions. Yields of more than 50% of inactive pinonic acid were obtained by a method herein described, using inactive pinene as a starting point. The latter substance is prepared by optical neutralisation of *d*-pinene obtained in a pure condition from Aleppo turpentine with the *l*-isomeride from the Bordeaux product. [See *J.S.C.I.*, 1923, Sept.]

H. J. E.

The Oxidation of Sabinene with Hydrogen Peroxide.
GEORGE GERALD HENDERSON and ALEXANDER ROBERTSON (T., 1923, 123, 1849—1855).

Extraction of Piperitone from Essential Oils. JOHN READ and HENRY GEORGE SMITH (*J. Soc. Chem. Ind.*, 1923, 42, 339—340T; cf. T., 1921, 119, 779; 1922, 121, 1863).—Details are given for the extraction of pure *dl*-piperitone from the essential oil of *Eucalyptus dives*. Extraction of the oil with normal sodium sulphite in a mechanically agitated, steam-jacketed vessel yields a crystalline compound from which feebly active piperitone can be regenerated by the addition of strong sodium hydroxide solution to its hot aqueous solution. Complete racemisation of the product so obtained may be effected by treatment with small quantities of alcoholic sodium hydroxide solution. For the isolation of specimens of the ketone of high rotatory power, recourse must be had to cautious fractional distillation of the essential oil under diminished pressure.

H. H.

The Constituents of some Indian Essential Oils. IX. The Leaf Oil from *Pinus excelsa*. X. The Essential Oil from the Oleo-resin of *Pinus Gerardiana*, Wall. JOHN LIONEL SIMONSEN (*Indian For. Rec.*, 1923, 9, 341—344, 345—348).—The pale yellow oil from *Pinus excelsa* (cf. this vol., i, 47), obtained by distillation in steam of the green cones and leaves, consists mainly of *l*- α -pinene and *l*- β -pinene (about 84%), the higher boiling fractions containing *l*-limonene, *l*-terpineol, borneol, a sesquiterpene, and a sesquiterpene alcohol, the two latter substances being present in quantities insufficient for examination. The combined acids present are acetic, butyric or isobutyric, octoic and lauric (? m. p. 43°) acids.

The oleo-resin from *Pinus Gerardiana* gives (per maund) 2.86 gallons of turpentine, and 66.8% of rosin. The former consists to the extent of about 80% of *d*- α -pinene (73%) and β -pinene, small quantities of a sesquiterpene (probably bicyclic, b. p. 157°/55 mm., d_{20}^{20} 0.9122, n_D^{20} 1.4947, $[\alpha]_D^{20}$ +24.08°; the yellow solution in acetic anhydride and a little sulphuric acid becomes emerald green and finally sage-green) and of a sesquiterpene alcohol also being present.

E. E. T.

Action of Selenium Oxychloride on Pure Caoutchouc.
CARL E. FRICK (*J. Amer. Chem. Soc.*, 1923, 45, 1800—1804).—The action of selenium oxychloride, in ice-cold carbon tetrachloride solution, on synthetic caoutchouc from the polymerisation of

isoprene, or on the following natural *Hevea* rubbers, Pale Crepe, Smoked Sheet, Para, and Caucho Ball, leads to an amorphous powder, which is insoluble in the ordinary solvents for caoutchouc, and has lost its elasticity and swelling power. Slight differences in the composition of the product appear, depending on the source of the natural caoutchouc and the method of coagulation, but no essential difference can be detected between the behaviour of natural caoutchoucs and of the product synthesised from isoprene. This tends to support the view that their constitutions are essentially the same.

W. S. N.

The Products of the Hydrolysis of Centaurein : Dextrose and Centaureidin. BRIDEL and C. CHARAUX (*J. Pharm. Chim.*, 1923, [vii], 28, 5—13; cf. this vol., i, 122).—The sugar liberated by the hydrolysis of centaurein is shown, both by isolation and by the biochemical method of Bourquelot and Bridel (A., 1920, ii, 337), to be exclusively dextrose. An accurate estimation of the methoxyl groups in centaureidin by the Zeisel method is difficult, owing to the insolubility in hydriodic acid of the compound and its demethylation product, but the authors consider, from results obtained, that the molecule may contain three such groups and that the formula may thus be written $C_{15}H_7O_5(OMe)_3$.

W. T. K. B.

Constitution of Cerebrin. ALFONSO CRUTO (*Rassegna Clin. Terap. e Scienze Aff.*, 1922, 21, 257—259; from *Chem. Zentr.*, 1923, i, 1133).—Purified cerebrin has m. p. 182—183° and is free from ash. The fatty acid obtained from its hydrolysis with 3% sulphuric acid has m. p. 85—86° and is identical with hydroxycerotic acid (Marie). Sphingosin, also obtained, agrees with that described by Thudichum and Thierfelder.

G. W. R.

The Toxin of *Cicuta virosa*. E. ŠVAGR (*Chem. Listy*, 1923, 17, 166—169).—No alkaloids are found in the rhizome of *Cicuta virosa*, and the substance, which has been named cicutine, and its glucoside do not therefore exist. The substances extracted from *C. virosa* are very readily oxidised by enzymes, yielding at least two resinous products, which still possess to a large extent the toxic properties of the extract. Two toxic substances are isolated, *cicutoxin*, a yellow, amorphous acidic substance, slightly soluble in water, and forming a lead salt, and *cicutoxinin*, a neutral, less toxic substance. Cicutoxin exhibits absorption bands at λ 570—640 and λ 650—680.

R. T.

Adsorbed Moisture and Water of Crystallisation in certain Common Dyes. H. WALES and O. A. NELSON (*J. Amer. Chem. Soc.*, 1923, 45, 1657—1666).—Vapour pressure—composition curves have been constructed for methylene-blue, the zinc chloride compound of methylene-blue, crystal-violet, rosaniline hydrochloride, pararosaniline hydrochloride, erythrosine, and tartrazine for the purpose of ascertaining whether the water present in these dyes is adsorbed or is held as water of crystallisation. Crystal-violet and tartrazine alone furnish evidence of the existence of hydrates. In

the case of the former dye, the vapour-pressure curve at 26° indicates the existence of hydrates containing 9, 6, 4, 3, and 2 molecules of water, respectively, whilst tartrazine, which appears to form hydrates containing 14, 10, 6, and 3 molecules of water, apparently exists, after exposure to the air, as a hexahydrate. In the case of erythrosine, which is generally assumed to exist as a monohydrate, no indication of the existence of a hydrate could be found, but evidence is obtained that the equivalent of 1 molecule of water in erythrosine is present as part of the molecule and a new hypothesis of the structure of this compound is put forward.

J. F. S.

The State of Methyl-orange and Methyl-red at the Transition Point. A. THIEL and A. DASSLER (*Ber.*, 1923, 56, [B], 1667—1671).—The isoelectric points of these ampholytic indicators were determined by solubility methods and checked against indicators of known p_H . The isoelectric point of methyl-orange (the free acid) lies at $p_H=1.7$; for methyl-red it lies at $p_H=3.7$. It is pointed out that both these indicators change into a deep red form in strongly acid solution. Formulæ are suggested to represent the various changes involved.

H. H.

Furfurylidene- and Difurfurylidene-4-methylcyclohexanones. (MLLE) N. WOLFF (*Compt. rend.*, 1923, 177, 197—199; cf. A., 1922, i, 668).—4-Methylcyclohexanone condenses with one molecule of furfuraldehyde in presence of sodamide to give 2-furfurylidene-4-methylcyclohexanone, pale yellow crystals, m. p. 43°, and with 2 molecules of furfuraldehyde, in presence of sodium methoxide, to give 2:6-difurfurylidene-4-methylcyclohexanone, yellow needles, m. p. 94°.

E. E. T.

Sulphoacetic Acid as a Condensing Agent. V. Preparation of 2:4:6-Trimethylpyrylium Perchlorate from Mesityl Oxide. WILHELM SCHNEIDER and ALFRED SACK (*Ber.*, 1923, 56, [B], 1786—1787).—2:4:6-Trimethylpyrylium perchlorate, m. p. 242° (decomp.), is more conveniently prepared from mesityl oxide, acetic anhydride, and sulphuric acid monohydrate than from 2:6-dimethylpyrone, according to the method of Baeyer and Piccard (A., 1911, i, 901).

H. W.

Flavonols and Anthocyanins. KURT NOACK (*Z. Bot.*, 1922, 14, 1—74; from *Chem. Zentr.*, 1923, i, 964).—Flavonols occurring in the green parts of plants can be changed by reduction into anthocyanins. Formation of anthocyanin is associated with inhibition of assimilation or injury to chloroplasts. In normally assimilating cells, formation of anthocyanin from flavonols already present does not take place. In the system anthocyanin—flavonol, equilibrium is normally on the side of the flavonol. Anthocyanins are not attacked by emulsin. Cyanin, pelargonin, malvin, and chrysanthemin are readily decomposed by *Aspergillus* tannase into anthocyanidin and sugar. Mecocyanin is less readily decomposed, whilst violamin is unattacked. Flavonols are also decomposed by tannase. Cyanidine chloride, when heated with hydrochloric acid and a little formaldehyde, condenses to form a substance which is

similar to the tannin red obtainable from certain plant extracts which do not contain anthocyanins. G. W. R.

Xanthyl Derivatives of Amino-acids. R. FOSSE, PH. HAGÈNE, and R. DUBOIS (*Compt. rend.*, 1923, **177**, 331—334).—Various compounds containing one or more amino-groups have been condensed with xanthhydrol; an amino-group condenses with the hydroxyl group of xanthhydrol, water being eliminated. Ethyl hydantoate with xanthhydrol gives *ethyl xanthylhydantoate*, needles, m. p. 201.5° (*potassium* salt described). Ethyl carbamidoisohexoate gives *ethyl xanthylcarbamidoisohexoate*, white crystals, m. p. 162—163°, whilst hydantoamide gives *xanthylhydantoamide*, m. p., according to speed of heating, 228° to 244°. *Hydantoylhydrazide* (m. p., according to speed of heating, 172° to 177°; obtained by the action of hydrazine on ethyl hydantoate) condenses with xanthhydrol to give *dixanthylhydantoylhydrazide*, m. p., according to speed of heating, 206° to 217°. E. E. T.

Xanthylallantoin. R. FOSSE and A. HIEULLE (*Compt. rend.*, 1923, **177**, 199—202; cf. this vol., i, 860, and preceding abstract).—Xanthhydrol precipitates allantoin from very dilute solutions (diluted acetic acid) as *xanthylallantoin*, condensation occurring between the hydroxyl and amino-groups in the two compounds respectively. The product cannot be confused with xanthylcarbamide. It melts at 214—215° (becoming coloured at 210°) and is soluble in boiling methyl alcohol. On grinding with normal potassium hydroxide and then diluting, it affords a solution from which acetic acid precipitates xanthylallantoin. On keeping, or warming, the alkaline solution, *potassium xanthylallantoate* separates. Hot concentrated hydrochloric acid converts xanthylallantoin into the chloride of the hydrol and allantoin, which then undergoes hydrolysis. E. E. T.

Preparation of Heterocyclic Compounds of the Naphthalene Series. HERMANN STAUDINGER (Swiss Pats. 92688 and 93486—93489; from *Chem. Zentr.*, 1923, ii, 573).— β -Naphthol, β -thionaphthol, or a β -*N*-monoalkylaminonaphthalene, monoaryalkylaminonaphthalene, or arylaminonaphthalene, is allowed to react with oxalyl chloride in the presence of diluents or condensing reagents such as carbon disulphide, benzene, aluminium chloride, or sulphuric acid. The diphenyldi-imidochloride of oxalic acid may be used in place of oxalyl chloride. β -Naphthol and oxalyl chloride give β -*naphthafuran*-1 : 2-dione, a yellow, crystalline powder, m. p. 183° (decomp.). β -Thionaphthol similarly gives β -*naphthathiofuran*-1 : 2-dione, a red crystalline powder, m. p. 153°. β -*Ethyl*naphthindole-1 : 2-dione, from β -ethylaminonaphthalene and oxalyl chloride, is a red, crystalline powder, m. p. 174°. β -*Benzyl*naphthindole-1 : 2-dione, has m. p. 185° and β -*phenyl*naphthindole-1 : 2-dione, m. p. 227°, are red, crystalline powders. G. W. R.

New Derivatives of Synthetic Adrenaline (Suprarenine). CASIMIR FUNK and LOUIS FREEDMAN (*J. Amer. Chem. Soc.*, 1923, **45**, 1792—1795).—The action of boiling dry ethyl-alcoholic hydrogen

chloride on *r*-adrenaline hydrochloride gives the aliphatic ethyl ether, *r*- β -3 : 4-*dihydroxyphenyl*- β -ethoxyethylmethylamine hydrochloride, white crystals, m. p. 169°, in 65% yield, whilst with methylalcoholic hydrogen chloride the corresponding methyl ether, white, rectangular prisms, m. p. 175°, is produced in 26% yield. Both compounds give the same colour reactions. Addition of ferric chloride gives a dark green coloration, passing to maroon-red on keeping or addition of ammonia. An orange-red coloration is produced on addition of sodium acetate and mercuric chloride in aqueous solution. The free bases oxidise readily in the presence of alkali. During the preparation of the ethyl ether, *diadrenaline ether hydrochloride*, $O(CH[C_6H_3(OH)_2 \cdot CH_2 \cdot NHMe, HCl])_2$, thin, rectangular prisms, m. p. 180—183°, is formed as a by-product. It gives a deep green coloration with ferric chloride, changing to reddish-violet and violet on keeping, or addition of ammonia. With sodium acetate and mercuric chloride, a greyish-blue precipitate is formed, which darkens on keeping. With ammonia, a grey precipitate is formed, which dissolves in excess of ammonia, giving a purple solution. With phosphotungstic or phosphomolybdic acid, a greyish-white precipitate is formed.

W. S. N.

Preparation of Acetyl Compounds of Quinine Aromatic Hydroxycarboxylates. *FARBENFABRIKEN VORM. FRIEDR. BAYER & Co.* (D.R.-P. 365682; from *Chem. Zentr.*, 1923, ii, 916; cf. Merck, Diehl, and Mayen, A., 1922, i, 46).—Quinine aromatic hydroxycarboxylates are acetylated by the usual methods. *Quinine o-acetoxybenzoate hydrochloride* is prepared by the action of acetyl chloride on quinine salicylate. *Quinine o-acetoxybenzoate* is a light-coloured, resinous substance. By heating *quinine 3-hydroxy-m-toluate* (white platelets, m. p. 145°) with acetic anhydride, *quinine 3-acetoxy-m-toluate* is obtained; it forms small crystals, m. p. 169°.

G. W. R.

Dimethiodides in the Eserine Series. MAX POLONOVSKI and MICHEL POLONOVSKI (*Compt. rend.*, 1923, 176, 1813—1815; cf. this vol., i, 700).—Attempts to obtain dimethiodides were successful with eseroline, eserethole, and eseretholemethine, but failed in the case of eserine itself. In no case is the fixation of the second mol. of methyl iodide complete. On the other hand, the dihydroderivatives, especially those of the methine bases, give almost quantitative yields of stable dimethiodides. *Dihydroeserinemethine dimethiodide*, $C_{16}H_{25}O_2N_3 \cdot 2MeI, H_2O$, and *dihydroeseretholemethine dimethiodide*, $C_{16}H_{26}ON_2 \cdot 2MeI, H_2O$, are not attacked by dilute alkalis; hydrogenation has thus increased the basicity of the pyrrole nucleus. These substances were not obtained pure by the ordinary methods, but in presence of sodium ethoxide and excess of methyl iodide, crystalline products were formed. Eseroline yields an optically inactive dimethiodide, m. p. 235°; the same substance is obtained by using eserine or the methyl ester of eseroline as the starting point, thus indicating that the final product contains a methylated hydroxyl group. A further method of preparation is

from eseroline monomethiodide under similar conditions. This dimethiodide is apparently identical with that described by Stedman (T., 1921, **119**, 891); the authors, however, assign to it the formula $C_{19}H_{36}O_2N_2I_2$ or $C_{19}H_{34}O_2N_2I_2$. Eserethole yields an homologous dimethiodide, m. p. 207° , containing one more CH_2 group, and eseretholemethine gives an identical derivative showing that in the process of exhaustive methylation intermediate formation of the methine base occurs with subsequent iodomethylation. H. J. E.

The Alkaloids of the Calabar Bean. IX. The Nature of the Third Nitrogen Atom in Eserine. MAX POLONOVSKI and MICHEL POLONOVSKI (*Bull. Soc. chim.*, 1923, [iv], **33**, 970—977).—This paper is mainly identical with that abstracted in this vol., i, 700. α -Eseretholemethine methiodide is now stated to have m. p. 140 — 141° . By reduction with zinc and hydrochloric acid, etheseroline gives *hydroetheseroline*, a neutral oil with $\alpha_D - 30^\circ$ in 95% alcohol, $c = 0.07$; this gives a *methiodide* with $\alpha_D - 20^\circ$ in water. H. H.

The Alkaloids of the Calabar Bean. X. The Di-acid Nature of Eserine Derivatives. Dimethiodides. MAX POLONOVSKI and MICHEL POLONOVSKI (*Bull. Soc. chim.*, 1923, [iv], **33**, 977—988; cf. preceding abstracts and T., 1923, **123**, 758).—The fact that eserine, eseroline, eserethole, and eseretholemethine do not form dimethiodides, although they contain two basic nitrogen atoms in the molecule, is explained by the insolubility in methyl iodide of the monomethiodides first formed. By working in methyl-alcoholic solution, it is possible to increase the absorption of methyl iodide and to obtain products corresponding with mixtures of mono- and dimethiodides. The dihydro-derivatives of these compounds, on the other hand, form stable dimethiodides with ease. If methylation is carried out in a sealed tube in the presence of sodium ethoxide, it is found that eserine and its derivatives give dimethiodides, and, in addition, add on two methyl groups and one hydroxyl group. Thus, dihydroeseroline, dihydroeserine, or their methine bases, all give a *dimethiodide* which crystallises in colourless needles, m. p. 205° . H. H.

Preparation of Keto Derivatives of the Morphine Series. KNOLL & Co. (D.R.-P. 365683; from *Chem. Zentr.*, 1923, ii, 916—917).—Morphine or its alkyl ethers are hydrogenated in the presence of acids and comparatively large quantities of catalysts such as palladium or platinum or their salts. The reaction consists in simultaneous hydrogenation and rearrangement of the alcoholic hydroxyl group to form a keto group. The morphine *keto base* of composition $C_{17}H_{19}O_3N$ has m. p. 262 — 263° . With hydroxylamine sulphate, it gives an *oxime* which forms crystals having m. p. above 234° . The *semicarbazone* has m. p. above 250° . By methylation of the morphine keto base, the *codeine keto base*, $C_{18}H_{21}O_3N$, is obtained; it has m. p. 193 — 194° ; the *oxime* has m. p. 265 — 266° ; the *semicarbazone* has m. p. 247 — 248° ; and the *methiodide*, m. p. 273° . The bases give salts with acids such as diethylbarbituric acid and diallylbarbituric acid. G. W. R.

Preparation of Halogenoethyl Morphines. GEORG VON KERESZTY and EMIL WOLF (Austr. Pat. 88673; from *Chem. Zentr.*, 1923, ii, 809).—Morphine and alkali alkylloxides are treated with halogenoethyl esters of an arylsulphonic acid. For example, a solution of morphine in ethyl-alcoholic sodium ethoxide is added slowly at 20–25° with shaking to an ethyl-alcoholic solution of chloroethyl benzenesulphonate. *Chloroethylmorphine* has m. p. 75°. At higher temperatures it solidifies and has a second m. p. 105°. The *hydrochloride* is crystalline and has m. p. 150–151°.

G. W. R.

Strychnos Alkaloids. XXXIX. The Violet Sulphite from Cacotheline and other Derivatives Thereof. HERMANN LEUCHS and WALTER HEMPEL (*Ber.*, 1923, 56, [B], 1775–1780).—Cacotheline, $C_{21}H_{21}O_7N_3 \cdot HNO_3$, is converted by aqueous sodium sulphite under definite conditions into a *nitroquinol sulphite*, $C_{21}H_{21}O_7N_3 \cdot H_2SO_3$, dark violet platelets. The presence of a carboxyl group is proved by the formation of a *monomethyl ester*, $C_{22}H_{25}O_{10}N_3S$, bluish-violet prisms. The violet sulphite is oxidised by ferric chloride to a *nitroquinone sulphite*, $C_{21}H_{21}O_{10}N_3S$, which is reconverted into the initial material by sulphurous acid. The nitroquinone is reduced by tin and hydrochloric acid to the *sulphite* of the *aminoquinol*, $C_{21}H_{23}O_7N_3S$, prisms (corresponding *hydrochloride*, colourless prisms or needles). Oxidation of the violet sulphite dissolved in ammonia by means of air leads to the formation of the *oxide* of the *nitroquinol sulphite*, $C_{21}H_{21}O_{11}N_3S$, yellowish-brown plates, which is transformed by methyl alcohol and sulphuric acid into a *substance*, $C_{23}H_{27}O_{12}N_3S$, colourless, thin prisms or pale yellow, quadratic plates or domatic prisms, the formation of which appears to be due to the esterification of the carboxy-group and

conversion of the group $\begin{array}{c} \text{C} \text{---} \text{O} \text{---} \text{C} \\ \text{[]} \end{array}$ into $C(OH) \cdot C(OMe)$; it is converted by potassium hydrogen carbonate solution into the *monomethyl* compound, $C_{22}H_{25}O_{12}N_3S$, colourless, rectangular prisms or long needles.

The following substances have not been described previously. The *diethyl ester* of the nitroquinol of the cacotheline base, $C_{25}H_{31}O_7N_3$, reddish-violet needles, m. p. 182°, which is oxidised by air to the *monoethyl ester* of the quinone, small, yellow prisms, which become discoloured, but do not melt above 180°; the *dimethyl ester* of the nitroquinol, reddish-violet prisms, m. p. 211° (decomp.) after softening at 170°, and the *monomethyl ester* of the cacotheline base, $C_{22}H_{23}O_7N_3$, dark yellow needles; the *metho-sulphate* of the nitroquinol dimethyl ester, $C_{25}H_{33}O_{11}N_3S$, violet needles and the corresponding *methiodide*, $C_{24}H_{30}O_7N_3I$, dark violet needles, and *methochloride*, $C_{24}H_{30}O_7N_3Cl$, reddish-violet needles.

H. W.

Strychnos Alkaloids. XL. Esterification of Brucinonic and Related Acids. HERMANN LEUCHS and WERNER GLADKORN (*Ber.*, 1923, 56, [B], 1780–1785).—During the oxidation of brucine to brucinonic acid it has been assumed (A., 1908, i, 563) that a

group, $-\text{CH}:\text{CH}-$, is transformed into two carboxyl groups one of which is free whereas the other is neutralised within the molecule. Further attempts to prove the presence of the second carboxyl group are now described.

The crystalline lead salt, when prepared according to different methods, is derived invariably from the monobasic acid.

Brucinonic acid is converted by treatment with methyl alcohol and hydrogen chloride into *methyl brucinonate*, $\text{C}_{24}\text{H}_{26}\text{O}_8\text{N}_2$, long prisms, m. p. 221—224°, and further apparently into the dimethyl ester the amorphous chloroplatinate of which gives analytical results approximating to those required by a derivative of the dimethyl ester hydrate. The oxime of brucinonic acid, on the other hand, gives a *monomethyl ester*, $\text{C}_{24}\text{H}_{27}\text{O}_8\text{N}_3$, hexagonal leaflets, m. p. 265° (decomp.), $[\alpha]_D^{25} + 81.7^\circ$ in glacial acetic acid solution (a hydrated form, needles, is also described) and a *dimethyl ester hydrate*, $\text{C}_{25}\text{H}_{31}\text{O}_9\text{N}_3$, short prisms, m. p. 144—146° after softening at 140° (*hydrochloride*, $\text{C}_{25}\text{H}_{31}\text{O}_9\text{N}_3\cdot\text{HCl}$, colourless, rectangular leaflets; *methiodide*, $\text{C}_{26}\text{H}_{34}\text{O}_9\text{N}_3\text{I}$, colourless leaflets or oblique prisms, m. p. 185—187° [decomp.] after softening at 175°); the possibility that the group $:\text{N}\cdot\text{CO}\cdot$ is converted into $:\text{NH}/\text{CO}_2\text{H}\cdot$, with the formation of a new carboxyl group, renders the demonstration of the presence of the original second carboxyl group uncertain. The *ethyl ester* of brucinonic acid oxime, $\text{C}_{25}\text{H}_{29}\text{O}_8\text{N}_3$, crystallises in long, thin prisms, m. p. about 280° (decomp.) after darkening at 260°. The monomethyl ester is transformed by hydrazine hydrate into the *hydrazide* of brucinonic acid oxime, $\text{C}_{23}\text{H}_{27}\text{O}_7\text{N}_5$, lustrous leaflets, m. p. about 265° (decomp.) after darkening at 245°, which is converted by sodium nitrite into the corresponding *azide*; the latter substance when treated with water at 100° gives nitrogen, formaldehyde, and a neutral compound, $\text{C}_{21}\text{H}_{23}\text{O}_6\text{N}_3$, lustrous needles which soften without melting at 210—290°.

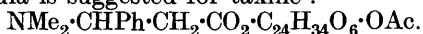
Dihydrobrucinonic acid is converted by gentle esterification into the corresponding *monoethyl ester*, $\text{C}_{25}\text{H}_{30}\text{O}_8\text{N}_2$, prisms, m. p. 227—229°, and *methyl ester*, $\text{C}_{24}\text{H}_{28}\text{O}_8\text{N}_2$, short prisms, m. p. 223—224° (a hydrated form is also described). More energetic treatment of the acid with methyl-alcoholic hydrogen chloride gives dimethyl brucinonate hydrate, which is characterised by the crystalline *methiodide*, $\text{C}_{26}\text{H}_{35}\text{O}_9\text{N}_2\text{I}$, colourless, domatic prisms, m. p. about 165° (decomp.), and the *hydrochloride*, $\text{C}_{25}\text{H}_{32}\text{O}_9\text{N}_2\cdot\text{HCl}$, transparent plates, m. p. 175—176° (decomp.).

Brucinolic acid is transformed similarly into the *monoethyl ester*, $\text{C}_{25}\text{H}_{30}\text{O}_8\text{N}_2$, colourless, rectangular leaflets, m. p. 121—123° (which is converted by alcoholic hydrogen chloride into brucinolone-b) and the *monomethyl ester*, $\text{C}_{24}\text{H}_{28}\text{O}_8\text{N}_2$, hexagonal plates, m. p. 205—207° after softening at 200°. The *methiodide of dimethyl brucinolate hydrate*, $\text{C}_{26}\text{H}_{35}\text{O}_9\text{N}_2\text{I}$, small leaflets, has m. p. 140—144° (decomp.) after much softening at 128°. H. W.

Taxine. II. E. WINTERSTEIN and A. GUYER (*Z. physiol. Chem.*, 1923, **128**, 175—229; cf. A., 1922, i, 572).—The quantity of taxine which may be extracted from the yew, *Taxus baccata*, is

apparently independent of the locality in which the tree is grown, although male trees contain on the average about twice the amount present in female trees. The boughs and young sprouts contain a very small amount.

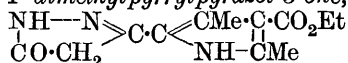
It has not yet been possible to obtain taxine, $C_{37}H_{51}O_{10}N$, in a crystalline condition. When distilled, it yields a small quantity of cinnamic acid, and on distillation with zinc dust styrene is obtained and when oxidised, benzoic acid, formaldehyde, cinnamic acid, acetic and oxalic acids are formed. Nitric oxide passed into an ethereal solution of taxine produces a mixture of the nitrate and the nitrite. When methylated with methyl iodide, a methiodide, $C_{37}H_{51}O_{10}N, MeI$, is formed, m. p. 123—125°; it is a rather unstable product which could not be obtained crystalline. When treated with water, or, better, with sodium hydroxide solution, this methiodide decomposes, forming trimethylamine and an amorphous compound of the formula $C_{35}H_{44}O_{10}$, a white powder, m. p. 120—140°, which on distillation or on treatment with acid yields cinnamic acid, and on oxidation with permanganate, benzaldehyde and benzoic acid, whilst by the action of sodium hydroxide solution in the cold, acetic and cinnamic acids and an insoluble product are formed. Taxine itself, when treated with sodium hydroxide solution, yields 1 molecule of acetic acid, a little cinnamic acid, and a basic amorphous compound containing nitrogen. If this compound, or taxine, is heated on the water-bath with 5% sulphuric acid for ten hours, a crystalline compound, $C_{11}H_{15}O_2N$, is obtained; hydrochloride, $C_{11}H_{15}O_2N \cdot HCl$, m. p. 173—174° (decomp.); hydrobromide, needles, m. p. 183°; chloroaurate, yellow needles, m. p. 135—136°; chloroplatinate, m. p. 208—210°. This compound, compact, spear-shaped crystals, yields, when heated, cinnamic acid and trimethylamine, and when oxidised benzoic acid and benzaldehyde and is probably β -dimethylamino- β -phenylpropionic acid. The following formula is suggested for taxine :



Substances different from those obtained by chemical means are produced from taxine by bacteria. The physiological properties of taxine have been further investigated. W. O. K.

Some Derivatives of Pyrrole. H. FISCHER and K. SCHNELLER (*Z. physiol. Chem.*, 1923, **128**, 240—253).—3-Acetyl-2 : 4-dimethylpyrrole reacts with chloroacetonitrile in ethereal solution in presence of hydrogen chloride to yield an imino-compound, which when treated with water yields 3-acetyl-5-chloroacetyl-2 : 4-dimethylpyrrole, colourless leaflets with a silky lustre, m. p. 173°. This compound, when treated with alcoholic ammonia, is converted into 3-acetyl-5-aminoacetyl-2 : 4-dimethylpyrrole, yellow crystals, which decomposes without melting, and when treated with alcoholic dimethylamine, is converted into 3-acetyl-5-dimethylaminoacetyl-2 : 4-dimethylpyrrole, fine needles, m. p. 104°. Similarly, ethyl 2 : 5-dimethylpyrrole-3-carboxylate condenses with dichloroacetonitrile to yield ethyl 4-dichloroacetyl-2 : 5-dimethylpyrrole-3-carboxylate, fine, white needles, m. p. 171°, and with methyl cyanoacetate to yield

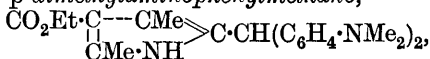
methyl 3-carbethoxy-2 : 4-dimethylpyrrole-5-acetate, $C_{13}H_{17}O_5N$, silky needles, m. p. 124° , whilst with cyanoacetic acid a similar condensation takes place, but carbon dioxide is evolved and ethyl 5-acetyl-2 : 4-dimethylpyrrole-3-carboxylate is formed. From carbonyl chloride and ethyl 2 : 4-dimethylpyrrole-3-carboxylate in toluene solution, 3-carbethoxy-2 : 4-dimethylpyrrole-5-carboxyl chloride, colourless leaflets, m. p. 192° , is obtained. If ethyl 3-carbethoxy-2 : 4-dimethylpyrrole-5-acetate is warmed with hydrazine hydrate, 3-3'-carbethoxy-2' : 4'-dimethylpyrrolpyrazol-5-one,



is formed, fine, silky, colourless needles, m. p. 268° .

If the imino-hydrochloride from ethyl 5-benzoyl-2 : 4-dimethylpyrrole-3-carboxylate is heated in alcoholic solution and freshly prepared sodium amalgam added, *phenylbis-3-carbethoxy-2 : 4-dimethylpyrrolmethane*, $\text{CHPh} \left(\text{C} \begin{array}{l} \text{CMe} \cdot \text{C} \cdot \text{CO}_2\text{Et} \\ \text{NH} \cdot \text{CMe} \end{array} \right)_2$, is formed, colourless leaflets turning red in the air, m. p. 182° .

Diazotised benzidine condenses with ethyl 2 : 4-dimethylpyrrole-3-carboxylate to yield an orange-red dye, m. p. 239° , and with 3-acetyl-2 : 4-dimethylpyrrole to yield a light orange dye, m. p. 298° . Tetramethyl-*pp'*-diaminobenzhydrol condenses on the boiling water-bath in presence of potassium hydrogen sulphite with ethyl 2 : 4-dimethylpyrrole-3-carboxylate to form 3-carbethoxy-2 : 4-dimethylpyrrolbis-*p*-dimethylaminophenylmethane,



colourless leaflets from alcohol, m. p. 176° , and with ethyl 2 : 5-dimethylpyrrole-3-carboxylate, and with 3-acetyl-2 : 4-dimethylpyrrole to form similar compounds, m. p. 142° and 165° , respectively.

An attempt to prepare β -acetic- β' -methyl maleic anhydride by the condensation of acetylsuccinic acid and potassium cyanide did not lead to the desired result. Instead, carbon dioxide was eliminated and dimethylmaleic anhydride was formed. W. O. K.

Some Pyridine Derivatives of Iridium. II. MARCEL DÉLÉPINE (*Ann. Chim.*, 1923, [ix], 19, 145—179; cf. this vol., i, 480).—Potassium iridotetrachloro-oxalate, prepared according to Vézes and Duffour's method (A., 1909, i, 762), experimental details of which are given, was used as a starting-point for new substitutions. Difficulties were experienced in preparing potassium *trans*-iridodichlorodioxalate, and investigation showed that this substance is always formed as a by-product in the preparation of the *cis*-isomeride, whilst it may also be obtained by intramolecular transformation of that substance. Experiment showed that, in the former case, each of the two isomerides is formed directly, no subsequent transformation taking place. The *cis*- may be converted into the *trans*-form by heating at 130° for one hour in the presence of potassium chloride, but the proportion of the substance which undergoes the change is small. The product, *potassium trans-iridodichlorodioxalate*, $\text{K}_3\text{IrCl}_2(\text{C}_2\text{O}_4)_2 \cdot 4\text{H}_2\text{O}$, forms either large, ruby-red, monoclinic

needles, or flattened, triclinic prisms. Both crystalline forms are hydrated to the same extent; the monoclinic crystals are deposited at temperatures above 40° , and in solution this form appears to be converted into the triclinic variety at about 30° . In the solid state, however, it is stable at the ordinary temperature. Although the *cis*- and *trans*-isomerides are similar in colour, the former possesses in solution twice the colour intensity of the latter for equal concentrations. Solutions of the two substances, which are equal in depth of colour, exhibit identical absorption spectra. The change from *cis*- to *trans*-configuration is reciprocal, but only takes place slowly in either direction. The resolution of the *cis*-isomeride into its optically active components was effected by means of the strychnine salts. Solutions of the separated components were kept for three years, when the *laevo*-form was found to have maintained its activity in full, whilst that of the *dextro*-form had somewhat diminished. This is considered to indicate the great stability of the molecule built up on a central iridium atom. Potassium *trans*-dioxalodipyridineiridate forms sulphur-yellow, octahedral crystals containing at least $6\text{H}_2\text{O}$, which rapidly effloresce, becoming yellowish-white and opaque. From hot concentrated solutions, crystals containing $2\text{H}_2\text{O}$ are deposited in the form of characteristic monoclinic needles. This substance may be transformed into the red tetrachlorodipyridine compound by the action of aqua regia, whilst with hydrochloric acid it yields a mixture of (a) two slightly soluble and (b) four readily soluble substances. The former consist of *iridium aquochlorodipyridine oxalate*, $\text{Ir}(\text{C}_5\text{H}_5\text{N})_2(\text{H}_2\text{O})\text{Cl}(\text{C}_2\text{O}_4)$, pale chamois-yellow needles, and *iridium diaquodichlorodipyridine dipyridinotetrachloride*, $[\text{Ir}(\text{C}_5\text{H}_5\text{N})_2\text{Cl}_4][\text{Ir}(\text{C}_5\text{H}_5\text{N})_2(\text{H}_2\text{O})_2\text{Cl}_2]$, rosy, orange crystals, which are hydrolysed by boiling water and converted by ammonia into ammonium dipyridinotetrachloroiridate and dichloroaquodipyridinoiridic hydroxide. The latter include iridodichlorodiaquodipyridine chloride and potassium hydrogen oxalate, with traces of potassium pentachloropyridineiridate and pyridine hydrochloride. In a discussion of the mechanism of this reaction with hydrochloric acid, the author draws the conclusion that the pyridine groups are highly resistant to attack, and are not changed in position in the series of reactions involved.

The entry of a third molecule of pyridine into iridium dipyridinotetrachloride is only effected after heating for four hours at 130° in a sealed tube. *Iridium 1 : 2 : 6-tripyridinotrichloride*, $\text{Ir}(\text{C}_5\text{H}_5\text{N})_3\text{Cl}_3$, yellow crystals, may be separated from its isomeride *iridium 1 : 2 : 3-tripyridinotrichloride*, yellow needles, which is formed simultaneously, by fractionation with chloroform, in which the former is considerably more soluble.

A general discussion of the application of Werner's co-ordination theory to the author's work is appended.

H. J. E.

The Action of Benzaldehydes on Free *o*-Aminophenylacetic Acid. P. W. NEBER and E. RÖCKER (*Ber.*, 1923, 56, [B], 1710—1716).—In a recent communication (A., 1922, i, 545), the condensation of *o*-nitrobenzaldehyde with *o*-aminophenylacetic acid

to form *o*'-nitrobenzylidene-*o*-aminophenylacetic acid has been described. The new acid passes by loss of water into a compound which has been formulated provisionally as a quinoline derivative. The unexpected properties of the latter substance have necessitated a revision of the reaction (effected with the more readily obtained benzylidene compound). The products are shown to be derivatives, not of quinoline, but of oxindole. The initial formation of *o*'-nitrobenzylidene-*o*-aminophenylacetic acid is confirmed. The acid when melted or heated in glacial acetic acid solution or in alcohol loses *o*-nitrobenzaldehyde and forms oxindole; the latter substance reacts with the liberated aldehyde to give 3-*o*-nitrobenzylidene-oxindole, $C_6H_4 \left\langle \begin{array}{c} C(CH \cdot C_6H_4 \cdot NO_2) \\ NH \end{array} \right\rangle CO$.

Benzylideneoxindole, sulphur-yellow needles, m. p. 176°, is obtained directly when benzaldehyde and *o*-aminophenylacetic acid are heated at 120–130°, without solvent, in boiling glacial acetic acid or in alcohol containing a little piperidine. It is converted by cautious treatment with barium hydroxide into α -*o*-aminophenylcinnamic acid, $CHPh \cdot C(C_6H_4 \cdot NH_2) \cdot CO_2H$, m. p. 131°, the constitution of which is established by its production from α -*o*-nitrophenylcinnamic acid (cf. Borsche, A., 1910, i, 35). α -*o*-2-Naphtholazophenylcinnamic acid, $C_{25}H_{18}O_3N_2$, coarse, dark red crystals, incipient decomp. 215°, is described. α -*o*-Aminophenylcinnamic acid condenses with *o*-nitrobenzaldehyde to give α -*o*'-nitrobenzylidene-*o*-aminophenylcinnamic acid, pale yellow needles, m. p. 157° after softening at 154°.

Mixtures of molecular quantities of *o*-aminophenylacetic acid and *m*-nitrobenzaldehyde, when heated at 150° or in boiling alcoholic solution in the presence of piperidine, give two products, golden-yellow leaflets, m. p. 227°, and slender, sulphur-yellow needles, m. p. 204°, whereas, according to Bagard and Wahl (A., 1909, i, 330, 735), *m*-nitrobenzylideneoxindole has m. p. 255–257°. 3-*p*-Nitrobenzylideneoxindole forms coarse, red crystals, m. p. 229° after softening at 227°. *o*'-Acetylaminobenzylidene-*o*-aminophenylacetic acid, colourless crystals, m. p. 143°, is converted at 145–150° or in boiling glacial acetic acid solution into 3-*o*-acetylaminobenzylidene-oxindole, small, pale yellow needles, m. p. 221°. *o*'-Chlorobenzylidene-*o*-aminophenylacetic acid, colourless needles, m. p. 127°, 3-*o*-chlorobenzylideneoxindole, lemon-yellow needles, m. p. 178°, 3-*m*-chlorobenzylideneoxindole, yellow needles, m. p. 166°, *p*'-chlorobenzylidene-*o*-aminophenylacetic acid, colourless crystals, m. p. 122°, and 3-*p*-chlorobenzylideneoxindole, sulphur-yellow needles, m. p. 184°, are also described.
H. W.

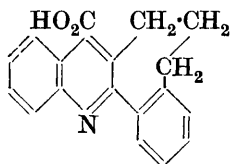
Preparation of Derivatives of 2-Methylquinoline. KNOLL & Co. (D.R.-PP. 363582 and 363583; from *Chem. Zentr.*, 1923, ii, 915).—Ketone anils are heated with or without the addition of condensing reagents or primary aromatic amines are heated with ketones in the presence of catalysts such as the hydrochlorides of the corresponding primary aromatic amines, zinc chloride, or iodine. The ketone anils used, or formed by the latter

reaction, decompose with evolution of a hydrocarbon and formation of 2:4-dialkylquinolines. By heating acetone anil, or acetone, aniline, and aniline hydrochloride in the presence of condensing reagents, 2:4-dimethylquinoline is obtained, with evolution of methane; it has b. p. 143°/15 mm. Similarly, from methyl ethyl ketoneanil 2-methyl-4-ethylquinoline, b. p. 150—153°/14 mm., is obtained with evolution of ethane. From the condensation product of acetone and *p*-toluidine, 2:4:6-trimethylquinoline, b. p. 146—148°/13.5 mm., m. p. 65.5°, is obtained. Acetophenoneanil gives 4-phenyl-2-methylquinoline with formation of aniline and benzene; it has m. p. 104°. G. W. R.

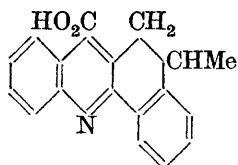
Benzopolymethylene Compounds. IX. Further Cyclic Analogues of Atophan. JULIUS VON BRAUN and AUGUST STUCKENSCHMIDT (*Ber.*, 1923, **56**, [B], 1724—1729).—Whereas tetraphan, obtained from isatin and 1-keto-1:2:3:4-tetrahydronaphthalene and its dihydro-derivative resemble strychnine in physiological action, the corresponding compound from α -hydrindone is inactive. It appears, therefore, that the naphthacridine nucleus is the physiologically active component. To test this point, benzosuberone has been converted into the ring-homologue of tetraphan. Unexpectedly, homotetraphan is found to resemble its lower homologue both quantitatively and qualitatively in physiological action. Its constitution has therefore been examined at considerable length, whereby its supposed structure is confirmed. It is possible, therefore, to lengthen the ethylene chain in tetraphan without appreciably changing its pharmacological action.

Benzosuberone, prepared according to the method of Kipping, Hall, and Hunter (*T.*, 1901, **79**, 602), is reduced by Clemmensen's method to benzosuberane, $C_6H_4<\begin{smallmatrix} CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \end{smallmatrix}>CH_2$, d_4^{25} 0.9693, n_D 1.5458. The latter substance cannot be dehydrogenated smoothly by sulphur and only with difficulty by lead oxide-pumice at 700°; naphthalene is thereby obtained, but the presence of methyl-naphthalenes could not be detected. *Homotetraphan* (annexed formula), almost colourless needles, m. p. 294°, is prepared by the action of benzosuberone on isatin in alkaline solution; the sodium salt is described.

γ -Phenyl-*n*-butyl bromide is converted by potassium cyanide into γ -phenyl-*n*-valeronitrile, a colourless liquid, b. p. 125—126°/13 mm., which is hydrolysed by hydrochloric acid at 120° into γ -phenyl-*n*-valeric acid, $CHMePh \cdot CH_2 \cdot CH_2 \cdot CO_2H$, a colourless, viscous liquid, b. p. 165°/12 mm. γ -Phenyl-*n*-valeryl chloride, b. p. 118—119°/13 mm., is converted by aluminium chloride in the presence of carbon disulphide into 1-keto-4-methyl-1:2:3:4-tetrahydronaphthalene, $C_6H_4<\begin{smallmatrix} CHMe \cdot CH_2 \\ CO \cdot CH_2 \end{smallmatrix}>$, b. p. 133—134°/12 mm. (*semi-carbazone*, m. p. 204°), which condenses with isatin in the usual



manner to form **4-methyltetrophan** (annexed formula), pale yellow needles, m. p. 262°. The latter substance is more active pharmacologically than tetraphan.



It is converted, when heated above its melting point, into **4-methyldihydronaphth-acridine**, a viscous liquid (*picrate*, m. p. 178°).

β -Benzylpropyl bromide is converted successively into β -benzylbutyronitrile, b. p. 121°/13 mm., and β -benzylbutyric acid, $\text{CH}_2\text{Ph}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, a colourless, viscous liquid, b. p. 161°/13 mm. β -Benzylbutyryl chloride, b. p. 123°/12 mm., is transformed into 1-keto-3-methyl-1:2:3:4-tetrahydronaphthalene, b. p. 127—128°/13 mm., d_4^{20} 1.0747, n_D^{20} 1.5590 (*semicarbazone*, m. p. 177°), which condenses with isatin to form **3-methyltetrophan**, m. p. 242—243°; the latter substance is physiologically more active than tetraphan. H. W.

The Constitution of the Dichlorohydroxyethylidenebis-nitroanilines. ALVIN S. WHEELER and SAMUEL C. SMITH (*J. Amer. Chem. Soc.*, 1923, **45**, 1839—1842).—The action of hot dichloroacetic acid and phosphorus pentoxide on *p*-nitroaniline, *o*-nitroaniline, or *m*-nitroaniline gives, respectively, *p*-nitrodichloroacetanilide, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{CHCl}_2$, pale yellow needles, m. p. 127°, *o*-nitrodichloroacetanilide, bright yellow plates, m. p. 70—72°, and *m*-nitrodichloroacetanilide, almost colourless needles, m. p. 103°. The *para*-compound appears, together with *p*-nitroaniline, as a decomposition product of the action of hot dilute sulphuric acid on the substance previously described (Wheeler and Glenn, *J. Elisha Mitchell Sci. Soc.*, 1903, **19**, 63), as having the constitution $\text{OH}\cdot\text{CCl}_2\cdot\text{CH}(\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2)_2$; the compounds having methoxyl (*loc. cit.*) and ethoxyl groups (Wheeler and Smith, *A.*, 1920, i, 93), in place of hydroxyl, give the same products. This reaction determines the position of the hydroxyl (alkoxyl) group in these compounds, which are now to be represented by the formula $\text{CCl}_2\text{H}\cdot\text{C}(\text{OR})(\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2)_2$. An exactly similar constitution is ascribed to the *ortho*-compounds (*loc. cit.*), which give *o*-nitroaniline and *o*-nitrodichloroacetanilide on treatment with hot dilute sulphuric acid. W. S. N.

The Isomerism of the Dinitrobenzidines. OSCAR LISLE BRADY and GERALD PATRICK McHUGH (*T.* 1923, **123**, 2047—2053).

Preparation of Derivatives of *para*-Substituted Phenylcarbamides. C. F. BOEHRINGER & SOEHNE (D.R.-P. 367611; from *Chem. Zentr.*, 1923, ii, 909—910).—Derivatives of *para*-substituted phenylcarbamides of the general formula



(where $\text{R}^2=\text{Me}$ or Et and $\text{R}^1=\text{Me}$, OMe , or OEt) are obtained by introducing the carbamino-group into bases of the formula $\text{R}^2\cdot\text{C}_6\text{H}_4\cdot\text{NHR}^1$ by known methods. *N*-Methyl-*p*-phenetidine and potassium cyanate in hydrochloric acid solution yield α -*N*-methyl-*p*-phenetylcarbamide; it forms prismatic crystals, m. p. 137°.

α -*N*-Methyl-*p*-anisylcarbamide, from *N*-methyl-*p*-anisidine, forms crystals, m. p. 154°. α -*N*-Methyl-*p*-tolylcarbamide is prepared from *N*-methyl-*p*-toluidine and carbamide nitrate, and forms small needles, m. p. 102—103°. α -*p*-Tolyl-*n*-ethylcarbamide has m. p. 65°. The introduction of an alkyl group such as methyl or ethyl into the imido-group of a monoarylcabamide increases both sweetness and solubility in water. G. W. R.

The Ternary System Antipyrine-Caffeine-Water. Migranine. ROBERT KREMANN and EMMERICH JANETZKY (*Monatsh.*, 1923, 44, 49—63).—The authors have studied, in the usual manner, the above ternary system. Antipyrine and caffeine form only a simple eutectic (103°, 13% of antipyrine). Antipyrine and water merely give a eutectic at -3.3° (37.5% of antipyrine). Water and caffeine monohydrate form a eutectic at -0.4°, 4% of caffeine, the transition temperature of caffeine monohydrate-caffeine probably being about 61°, since the solubility curve is broken at this temperature (31% of caffeine). From the ternary diagram constructed, the behaviour, on evaporation, of a mixture of antipyrine (85%), caffeine (8%), and water (7%) (that is, one having approximately the composition of migranine, with added water) is discussed. At 78°, such a mixture would deposit antipyrine. By isothermal evaporation at water-bath temperatures, antipyrine separation would continue, until the solution acquired the composition, antipyrine 81.5, caffeine 13, and water 5.5%. After this, as water was lost, the eutectic mixture of antipyrine and caffeine would separate.

Migranine consists, chemically, of a mixture of caffeine (8.2%) and antipyrine (89.4%), together with small quantities of citric acid (0.56%), combined with the antipyrine. Physically, it consists of the crystalline caffeine-antipyrine eutectic, in which are embedded crystals of antipyrine and of the ternary caffeine-antipyrine-antipyrine citrate eutectic (cf. A., 1920, i, 570). E. E. T.

Preparation of Halogen-substituted Barbituric Acid Derivatives. HERMANN STAUDINGER (Swiss Pats. 93435 and 93749; from *Chem. Zentr.*, 1923, ii, 748).—Diallylbarbituric acid or ethylallylbarbituric acid is treated with hydrobromic acid, preferably in the presence of diluents. The hydrogen bromide is added directly to the double linking in the side-chain with formation of the corresponding bromopropyl derivatives. For example, by the action of 25% hydrobromic acid in acetic acid on diallylbarbituric acid under pressure at 90—100°, *di*- β -bromopropylbarbituric acid is obtained. It is a microcrystalline, white powder with m. p. 237—239°. *Ethyl*- β -bromopropylbarbituric acid forms crystals, m. p. 171—173°. G. W. R.

Some Dialkylbarbituric Acids with Tertiary Amino-grouping. ARTHUR W. DOX and LESTER YODER (*J. Amer. Chem. Soc.*, 1923, 45, 1757—1762).—A number of ethyl dialkylmalonates have been prepared in which one alkyl group is ethyl or *iso*amyl and the other *n*-propyl with substitution of a tertiary amino-group

on the γ -carbon atom. From these esters the corresponding barbituric acids have been prepared. The latter, when tested by oral administration to dogs, or by intraperitoneal injection of the alkali solution into white mice, failed to show the hypnotic effect characteristic of the simpler barbituric acids. This inactivity is attributed in some cases to insolubility, in others to a reversal of the distribution coefficient between the two solvents, water and fat (or lipoids).

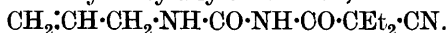
Ethyl ethyl- γ -bromopropylmalonate is prepared by the action of trimethylene bromide in hot benzene solution on the sodio-derivative of ethyl ethylmalonate, and has b. p. 169—174°/20 mm. It reacts with diethylamine to give *ethyl ethyl- γ -diethylaminopropylmalonate*, a yellow oil, b. p. 143—149°/6 mm., which is converted by heating at 108° with sodium ethoxide and carbamide into *5-ethyl-5- γ -diethylaminopropylbarbituric acid*, m. p. 165—166°. The following compounds are prepared in an analogous manner. *Ethyl ethyl- γ -acetanilidopropylmalonate*, a viscous, yellow oil, b. p. 244—250°/17 mm. *5-Ethyl-5- γ -acetanilidopropylbarbituric acid*, m. p. 180°. *Ethyl ethyl- γ -acetophenetidinopropylmalonate*, b. p. 237—240°/4 mm. *5-Ethyl-5- γ -acetophenetidinopropylbarbituric acid*, m. p. 158—159°. *Ethyl isoamyl- γ -bromopropylmalonate*, a viscous oil, b. p. 175—182°/13 mm. *Ethyl γ -diethylaminopropylisoamylmalonate*, b. p. 155—161°/5 mm. *5- γ -Diethylaminopropyl-5-isoamylbarbituric acid*, m. p. 133°. *Ethyl γ -ethylanilinopropylisoamylmalonate*, a yellow oil, b. p. 194—201°/4 mm. *5- γ -Ethylanilinopropyl-5-isoamylbarbituric acid*, needles, m. p. 135°. *Ethyl γ -acetophenetidinopropylisoamylmalonate*, a viscous, yellow oil, b. p. 245—250°/4 mm. *5- γ -Acetophenetidinopropyl-5-isoamylbarbituric acid*, m. p. 155°. W. S. N.

The Course of the Bromination of Allyl-substituted Imino-barbituric Acids. OTTO DIELS [with KURT WERNER, HUGO BERNHARDT, and RUDOLF RÖHRICHT] (*Annalen*, 1923, **432**, 115—136).—The condensation of allylcarbamide with ethyl diethylcyanoacetate by heating with sodium ethoxide at 102—105° leads to the formation of 4-imino-5:5-diethyl-3-allylbarbituric acid (I), m. p.

109°, to which the formula $\text{NH} \begin{array}{c} \text{CO} \text{---} \text{C} \text{Et}_2 \\ \text{CO} \text{---} \text{N} (\text{C}_3\text{H}_5) \end{array} > \text{C} \text{:NH}$ is assigned, in preference to the alternative structure, $\text{NH} \begin{array}{c} \text{C} (\text{NH}) \cdot \text{C} \text{Et}_2 \\ \text{CO} \text{---} \text{N} (\text{C}_3\text{H}_5) \end{array} > \text{CO}$.

It is converted by the action of bromine in cold glacial acetic acid solution into the *hydrobromide*, decomp. 250°, of 4-bromoimino-5:5-diethyl-3-allylbarbituric acid, glistening tablets, m. p. 184°. This compound does not contain the original $>\text{C} \text{:NH}$ group, because it is not hydrolysed by means of dilute mineral acids. Moreover, the allyl radicle is intact, since the compound gives *N-allylveronal*, long needles, m. p. 79—80°, on treatment with zinc dust in aqueous alcoholic solution. When reduced in ethereal solution by the aid of aluminium amalgam, the monobromide gives two products: the primary amine, $\text{NH} \begin{array}{c} \text{CO} \text{---} \text{C} \text{Et}_2 \\ \text{CO} \text{---} \text{N} (\text{C}_3\text{H}_5) \end{array} > \text{CH} \cdot \text{NH}_2$, $+ \frac{1}{2} \text{H}_2\text{O}$, m. p. 131°, and the corresponding secondary alcohol,

+ $\frac{1}{2}$ H₂O, m. p. 174°. The latter is also formed from the amine by the action of nitrous acid or of hot acetic acid, and gives, on oxidation by means of chromic acid in warm glacial acetic acid solution, *N*-allylveronal, together with a very small quantity of a compound, m. p. 185°. The amine forms an *oxalate*, and an additive compound, C₁₁H₁₉O₂N₃·PhNCO·H₂O, m. p. 220°, when ground with phenylcarbimide. When the monoimino-compound is brominated there is formed, in addition to the bromoimino-derivative, a dibromide, C₁₁H₁₇O₂N₃Br₂, m. p. 120°, which is regarded as *s*-cyanodiethylacetyl- β - γ -dibromopropylcarbamide, CH₂Br·CHBr·CH₂·NH·CO·NH₂·CO·CET₂·CN, for the following reasons. It does not suffer hydrolytic fission when treated with dilute acids, nor does it give *N*-allylveronal when reduced in boiling alcoholic solution by means of zinc dust. Actually the latter reaction gives a compound, C₁₁H₁₉O₂N₃, m. p. 120°, which is stable to hot dilute acids, and is therefore held to be *s*-cyanodiethylacetyl-*n*-propylcarbamide. The dibromide, m. p. 120°, is therefore a derivative, not of the iminobarbituric acid (I), but of the isomeric *s*-cyanodiethylacetylallylcarbamide,



The action of cold glacial acetic acid on the crude product from the condensation of allylcarbamide with ethyl cyanodiethylacetate gives the *acetate*, +2H₂O, glistening tablets, decomp. 245°, of a *base*, m. p. 90°, which is isomeric with iminodiethylallylbarbituric acid, into which it passes in the course of a few hours. The bromination of the acetate in glacial acetic acid solution does not, however, give the same product as when the imino-compound is used, but the *hydrobromide*, m. p. about 265° (decomp.), of a *monobromide*, thick needles, m. p. 151—152°, to which the con-

stitution $\begin{array}{c} \text{CO}\cdot\text{CBr}_2\cdot\text{C}\equiv\text{N} \\ \text{NH}\cdot\text{CO}\cdot\text{N}\cdot\text{CH}_2 \end{array} > \text{CH}\cdot\text{CH}_2\text{Br}$ is assigned. The production of this compound is assumed to proceed through the dibromide, $\begin{array}{c} \text{CO}\cdot\text{CET}_2\cdot\text{C}\cdot\text{NH} \\ \text{NH}\cdot\text{CO}\cdot\text{N}\cdot\text{CH}_2 \end{array} \cdot \text{CHBr}\cdot\text{CH}_2\text{Br}$, in the formation of which the allyl group is reactive. When it is reduced in aqueous alcoholic solution by means of zinc dust, the product is a *base*, C₁₁H₁₉O₂N₃, short, hard crystals, m. p. 246°, which is different from either of the preceding bases of this composition, and is represented by the formula $\begin{array}{c} \text{CO}\cdot\text{CET}_2\cdot\text{CH}\cdot\text{NH} \\ \text{NH}\cdot\text{CO}\cdot\text{N}\cdot\text{CH}_2 \end{array} > \text{CHMe}$. It is suggested that the isomerism of the compound (I) and the base, m. p. 90°, may depend on the spatial relationship between the allyl and imino-radicles.

A further example of the formation, in this series, of a dicyclic system is provided by the action of concentrated hydrobromic acid on the compound (I). In the cold, a *hydrobromide*, m. p. 205°, is formed, from which alkali liberates the original material, but if the reaction is conducted at 100°, the product is the *hydrobromide*, m. p. 285°, of an isomeric *base*, C₁₁H₁₇O₂N₃, m. p. 165°, which is formed by the addition of hydrogen bromide to the allyl group, and its subsequent elimination between this and the imino-

radicle. The structure of the bromine-free product will be $\text{CO}\cdot\text{CEt}_2\cdot\text{C}=\text{N}>\text{CHMe}$ or $\text{CO}\cdot\text{CEt}_2\cdot\text{C}=\text{N}\cdot\text{CH}_2$, according as $\text{NH}\cdot\text{CO}-\text{N}\cdot\text{CH}_2$ or $\text{NH}\cdot\text{CO}-\text{N}\cdot\text{CH}_2\cdot\text{CH}_2$, bromine becomes initially attached to the β - or the γ -carbon atom of the allyl radicle, but a choice has not yet been made between these formulæ.

4 : 6-Diimino-5 : 5-diethyl-3-allylbarbituric acid, m. p. 257°, hydrobromide, decomp. above 255°, is prepared by heating allylcarbamide and diethylmalononitrile with ethyl-alcoholic sodium ethoxide at 102—105°; it is gradually hydrolysed to *N*-allylveronal by means of cold dilute sulphuric acid. The action of bromine on a dilute aqueous suspension of the di-imino-derivative gives the hydrobromide, decomp. above 210°, of a monobromide, $\text{C}_{11}\text{H}_{17}\text{O}_4\text{N}_4\text{Br}$, in which, by analogy with the monoimino-compound, the bromine is probably attached to that imino-nitrogen atom which is nearer to the allyl group. In agreement with this view, the action of cold concentrated aqueous ammonia on the hydrobromide gives the original di-iminobarbituric acid.

The results clearly demonstrate a striking indifference, towards bromine, of the allyl radicle when in combination with the barbituric acid molecule, by reason of which the attempted preparation of the $\beta\gamma$ -dibromopropyl derivatives has failed.

Moreover, an effort to prepare such compounds, by condensing dibromopropylcarbamide with diethylmalononitrile or ethyl cyano-diethylacetate in the presence of alcoholic sodium ethoxide at 102—105°, has also been unsuccessful, because the sodium ethoxide causes elimination of hydrogen bromide from the dibromopropylcarbamide, with formation of a microcrystalline compound, $\text{C}_4\text{H}_7\text{ON}_2\text{Br}$, m. p. 146°, apparently the sole product of the reaction.

W. S. N.

5 : 5-Diarylbarbituric Acids. ARTHUR W. DOX and ADRIAN THOMAS (*J. Amer. Chem. Soc.*, 1923, **45**, 1811—1816).—*Ethyl diphenylmalonate*, white prisms, m. p. 58—59°, b. p. 180—200°/9 mm., is prepared by the interaction of benzene and ethyl mesoxalate in the presence of warm concentrated sulphuric acid. When it is heated with alcoholic sodium ethoxide and carbamide at 106—108°, diphenylbarbituric acid is not produced, but loss of carbon dioxide occurs, with formation of diphenylacetic acid, diphenylacetamide, and traces of diphenylmethane. Ethyl di-*p*-tolylmalonate behaves similarly, giving di-*p*-tolylacetic acid, and di-*p*-tolylacetamide, white needles, m. p. 190°. Phenol and ethyl mesoxalate react in the cold in the presence of dry hydrogen chloride, giving *ethyl di-p-hydroxyphenylmalonate*, flat, lustrous needles, m. p. 133—134°, which gives a blue coloration with ferric chloride, and readily condenses when heated with carbamide and sodium ethoxide, with formation of 5 : 5-di-*p*-hydroxyphenylbarbituric acid, small, slender needles, m. p. 288—290°. *Ethyl di-6-hydroxy-m-tolylmalonate*, short, white prisms, m. p. 107—108°, and 5 : 5-di-6'-hydroxy-m-tolylbarbituric acid, white prisms, m. p. 217—219°, are prepared similarly from *o*-cresol. 5 : 5-Diphenoxy-

barbituric acid, slender, white needles, m. p. 192°, is prepared from *ethyl diphenoxymalonate*, b. p. 195—204°/6 mm., which is prepared from sodium phenoxide and ethyl dibromomalonate in boiling alcoholic solution.

Since intraperitoneal injection of di-*p*-hydroxyphenylbarbituric acid or diphenoxybarbituric acid into white mice does not produce coma or even muscular inco-ordination, even when the dose is twice as large as that which produces profound coma within fifteen minutes when veronal is used, it is concluded that these substances are physiologically inert.

W. S. N.

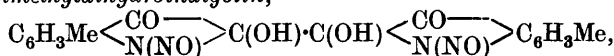
2-Ethylaminoindole Hydrochloride from Rutaecarpine.

YASUHIKO ASAHINA and the DAICHI SEIYAKU KABUSHIKI KAISHA (Japan Pat. 41593).—Five g. of rutaecarpine are boiled with 40 c.c. of amyl alcohol and 40 g. of powdered potassium hydroxide; after cooling, it is mixed with 50 c.c. of water, and the alcohol is separated. After filtration, the larger part of the solvent is distilled off and the liquid nearly neutralised with dilute phosphoric acid; white, silky crystals (about 3.1 g.) of 2-ethylaminoindole-carboxylic acid are deposited. By boiling these with 5% hydrochloric acid for two to three hours, the acid is decomposed into carbon dioxide and the amine, which is extracted with ether. Colourless scales of 2-ethylaminoindole hydrochloride, m. p. 245—246°, are obtained by passing hydrogen chloride into the ethereal solution.

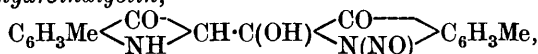
K. K.

The Indigo Group. III. The Action of Nitrous Fumes on 7:7'-Dimethylindigotin. THEODOR POSNER and WALTER HEUMANN (*Ber.*, 1923, 56, [B], 1621—1629).—The action of nitrous fumes on 7:7'-dimethylindigotin is, in general, precisely analogous to the action on indigotin itself; certain secondary changes which appear to differ in the two cases will be described in a subsequent communication.

The primary intermediate product, 1:1'-dinitroso-2:2'-dihydroxy-7:7'-dimethyldihydroindigotin,

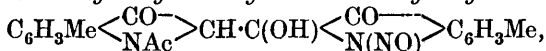


an unstable, yellowish-brown powder, is obtained by the action of nitrous fumes on a suspension of 7:7'-dimethylindigotin in ether. It is converted by alcohol into 1-nitroso-2-hydroxy-7:7'-dimethyldihydroindigotin,



a pale yellow, crystalline powder, m. p. 198—200° (decomp.), after darkening at about 185°. The yield of this substance is only 20—25% of the initial material, which is also decomposed into ethyl *m*-toluoylformate (see later) and 7-methylisatin, tile-red needles, m. p. 266° (*phenylhydrazone*, golden yellow needles, m. p. 242°). Nitrosohydroxydimethyldihydroindigotin is converted by aqueous ammonia into a compound, $\text{C}_{18}\text{H}_{13}\text{O}_3\text{N}_3$, pale, golden-yellow needles, m. p. 265—266°, the constitution of which has

not been definitely elucidated; this reaction differs from that observed with the corresponding derivative of indigotin. Nitroso-hydroxydimethyldihydroindigotin can be cautiously recrystallised from glacial acetic acid. Protracted treatment with the acid gives 1-nitroso-2-hydroxy-1'-acetyl-7:7'-dimethyldihydroindigotin,



golden-yellow crystals, m. p. 237—239° (decomp.) after darkening at about 200°, and ultimately 2-hydroxy-1:1'-diacetyl-7:7'-dimethyldihydroindigotin, $\text{C}_6\text{H}_3\text{Me} \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{N} \\ \diagdown \quad \diagup \\ \text{Ac} \end{array} \text{CH} \cdot \text{C}(\text{OH}) \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{N} \\ \diagdown \quad \diagup \\ \text{Ac} \end{array} \text{C}_6\text{H}_3\text{Me}$, a yellow, crystalline powder which darkens above 250°, but does not melt below 300°.

The action of nitrous fumes on 7:7'-dimethylindigotin suspended in glacial acetic acid proceeds similarly to that on indigotin. In this case, however, the intermediately-formed dinitrosodiacetoxy-7:7'-dimethyldihydroindigotin is too unstable to permit its isolation and nitrosohydroxy-7:7'-dimethyldihydroindigotin is obtained. If adequate cooling is not provided, 7-methylisatin is formed.

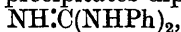
When nitrous fumes are passed into a suspension of 7:7'-dimethylindigotin in methyl or ethyl alcohol, 7-methylisatin is formed and ultimately converted into the ester of *m*-toluoylformic acid. *Methyl m-toluoylformate*, $\text{C}_6\text{H}_4\text{Me} \cdot \text{CO} \cdot \text{CO}_2\text{Me}$, has b. p. 137—138°/11—12 mm., 245—250° (slight decomp.)/763 mm. *Ethyl m-toluoylformate* has b. p. 140—142°/11—12 mm., 250—255° (partial decomp.)/atmospheric pressure. Hydrolysis of the esters gives *m-toluoylformic acid*, m. p. 80—82° (*phenylhydrazone*, m. p. 158°). H. W.

2-Pyridylpyrroles. A. E. TSCHITSCHIBABIN and J. E. BYLINKIN (*Ber.*, 1923, 56, [B], 1745—1749).—Attempts are described to prepare pyridylpyrroles from 2-aminopyridine on the lines developed by Pictet for the synthesis of nicotine from 3-aminopyridine.

N-2-Pyridylpyrrole, $\begin{array}{c} \text{CH} \cdot \text{CH} \\ \diagup \quad \diagdown \\ \text{CH} \cdot \text{CH} \end{array} > \text{N} \cdot \text{C}_5\text{H}_4\text{N}$, is obtained by distillation of a mixture of 2-aminopyridine, mucic acid, and aluminium oxide; it is conveniently separated from unchanged 2-aminopyridine by means of benzoic anhydride. It is an almost colourless liquid, b. p. 123°/11 mm., 250°/748 mm. It dissolves in cold aqueous sulphuric or hydrochloric acids to colourless solutions which become intensely purplish-red when warmed. The *chloroplatinate*, $(\text{C}_9\text{H}_8\text{N}_2)_2 \cdot \text{H}_2\text{PtCl}_6 \cdot 2\text{H}_2\text{O}$, a microcrystalline, yellow powder which slowly decomposes without melting when heated, and the *picrate*, needles, m. p. 141°, are described. The base is isomerised when passed through a heated tube to 2-pyridyl-2'-pyrrole, $\begin{array}{c} \text{CH} \cdot \text{CH} \\ \diagup \quad \diagdown \\ \text{CH} \cdot \text{NH} \end{array} > \text{CH} \cdot \text{C}_5\text{H}_4\text{N}$, small, colourless prisms, m. p. 87—88° [*chloroplatinate*, $(\text{C}_9\text{H}_8\text{N}_2)_2 \cdot \text{H}_2\text{PtCl}_6 \cdot 2\text{H}_2\text{O}$, small needles; *picrate*, yellow needles or prisms, m. p. 221°]. The latter substance is converted by the successive action of metallic potassium and

methyl toluene-*p*-sulphonate into *N*-methyl-2-pyridyl-2'-pyrrole [*α*-nicotyrin], $\begin{array}{c} \text{CH}-\text{CH} \\ | \quad \diagup \\ \text{CH} \cdot \text{NMe} \end{array} \text{C} \cdot \text{C}_5\text{H}_4\text{N}$, an almost colourless liquid which becomes dark red when preserved, b. p. 149—150°/22 mm. [*chloroplatinate*, $(\text{C}_{10}\text{H}_{10}\text{N}_2)_2 \cdot \text{H}_2\text{PtCl}_6$, dark, orange-coloured needles; *picrate*, small, yellow leaflets, m. p. 138—139°]. H. W.

Synthesis of Diphenylguanidine. J. D. BRUMBAUGH (*Chem. Age* (N.Y.), 1923, **31**, 175—176).—Ethyl alcohol (*d* 0.87) at 75° is saturated with ammonia, and a mixture of diphenylthiocarbamide and zinc oxide is added. Ammonia is passed through the stirred mixture at 75° for three hours, or until desulphurisation is complete. The hot solution is filtered and poured into dilute ammonia solution, which precipitates diphenylguanidine,



in 67% yield.

CHEMICAL ABSTRACTS.

Reduction of Uric Acid Glycols—A Contribution to the Characterisation of their Hydroxyls. HEINRICH BILTZ and RUDOLF LEMBERG (*Annalen*, 1923, **432**, 137—176).—This research is primarily concerned with the influence of the hydroxyl group in the position 4, in promoting the fission of the bond 3 : 4 in derivatives of uric acid.

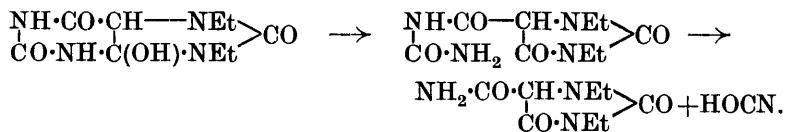
The reduction of uric acid glycols to uric acids by means of hydriodic acid was previously unsuccessful, apparently because the presence of the hydroxyl group in position 4 facilitates the disruption of the bond 3 : 4 (Biltz and Heyn, A., 1912, i, 589). This behaviour is unaffected by etherification of the 5-hydroxyl group, but the diethers are readily reduced to the uric acids. Since 3 : 7-dimethyl- and 4 : 5-dichloro-7 : 9-dimethyl-4 : 5-dihydrouric acids are readily reduced to the respective uric acids by means of strongly acid stannous chloride, an attempt has now been made to replace the hydroxyl groups of the glycols by halogen. 4 : 5-Dihydroxy-7 : 9-dimethyl-4 : 5-dihydrouric acid gradually dissolves in phosphorus oxychloride at 100°, with formation of 5-chloro-4-hydroxy-7 : 9-dimethyl-4 : 5-dihydrouric acid, together with traces of the 4 : 5-dichloro-derivative. The presence of the latter is evident from the formation of 7 : 9-dimethyluric acid by the reduction, by means of zinc dust and glacial acetic acid, of the residue left after distilling off the excess of phosphoryl chloride under reduced pressure; 7 : 9-diethyluric acid could not, however, be obtained in this way. The formation of the monochloro-compound is demonstrated by treating the phosphoryl chloride solution with methyl or ethyl alcohol, whereby the 4-hydroxy-5-alkoxy-derivative is produced. 5-Ethoxy- and 4-hydroxy-5-methoxy-7 : 9-dimethyl-4 : 5-dihydrouric acids have been prepared in this manner, also 4-hydroxy-5-ethoxy-7 : 9-diethyl-4 : 5-dihydrouric acid, large, four-sided, domed prisms, m. p. 179°, and 4-hydroxy-5-methoxy-7 : 9-diethyl-4 : 5-dihydrouric acid, hexagonal tablets, rhombohedra, or four-sided, domed prisms, m. p. 130—131°. These results confirm many previous observations which have demonstrated the reactivity

of the hydroxyl group in position 5 of the uric acid and *pseudouric* acid derivatives.

The action of phosphorus tribromide at 100° on 7:9-diethyl- or 4:5-dihydroxy-7:9-dimethyl-4:5-dihydrouric acids, followed by extraction by means of water, ethyl alcohol, or, better, methyl alcohol, gives, respectively, 4-*hydroxy*-7:9-diethyl-4:5-dihydrouric acid, slender needles, or elongated leaflets, m. p. 199—200° (*ammonium* salt), and 4-*hydroxy*-7:9-dimethyl-4:5-dihydrouric acid, rectangular leaflets, or flat prisms, m. p. 200—201° (*ammonium* salt). The same reaction ensues by the use of phosphorus trichloride or of commercial phosphorus oxybromide containing the trihalide; the use of phosphorus trihalides as reducing agents is discussed, and illustrated by many examples drawn from the literature. The reduction of the 4:5-dihydroxy-derivatives of 9-methyl-, 9-ethyl-, or 3:7-dimethyl-4:5-dihydrouric acids could not be effected, apparently because these substances only react at temperatures higher than the boiling point of phosphorus tribromide. When treated in the same way, 4:5-dihydroxy-4:5-dihydrouric acid is converted into *spirodihydantoin*. The monohydroxy-acids rapidly reduce cold ammoniacal silver nitrate solution (cf. following abstract). The diethyl-acid has a bitter taste, but is physiologically inactive when administered to frogs or dogs (Pohl). The action of chlorine in aqueous solution on the monohydroxy-acids gives the dihydroxy-acids, but in ethyl- or methyl-alcoholic solution, the product is the 4-hydroxy-5-ethoxy- or 4-hydroxy-5-methoxy-acid, respectively. Chlorination of 4-hydroxy-7:9-diethyl-4:5-dihydrouric acid in glacial acetic acid solution gives the monohydrate of 5-hydroxy-1:3-diethylhydantoylamine (see below). The action of hot concentrated hydrochloric acid on 4-hydroxy-7:9-dimethyl-4:5-dihydrouric acid converts it into carbamide and 1:3-dimethylhydantoin.

It is characteristic of the 4-hydroxy-4:5-dihydrouric acids that the hydroxyl group may readily be methylated by the action of diazomethane in cold, moist ethereal solution. In this way, the 7:9-diethyl acid and the 7:9-dimethyl acid give, respectively, 4-*methoxy*-7:9-diethyl-4:5-dihydrouric acid, glistening, flat prisms, m. p. 200°, and 4-*methoxy*-7:9-dimethyl-4:5-dihydrouric acid, m. p. 190—195° (*monohydrate*, long, glistening, four-sided prisms, m. p. 190—195° (*decomp.*), whilst 4-*methoxy*-3:7-dimethyl-4:5-dihydrouric acid, prisms, m. p. 194°, is similarly obtained from 4-hydroxy-3:7-dimethyldihydrouric acid. The preparation of the latter (Biltz and Damm, A., 1914, i, 1093), from the 5-chloro-4-hydroxy-acid, has been improved, the reduction now being effected by the use of zinc dust and glacial acetic acid. By the action of chlorine in absolute methyl-alcoholic solution, the 4-methoxy-7:9-diethyl- and 4-methoxy-7:9-dimethyl-dihydrouric acids are converted into 4-hydroxy-5-methoxy-7:9-diethyl- and 4-hydroxy-5-methoxy-7:9-dimethyl-4:5-dihydrouric acids, respectively, the introduction of the methoxyl radicle in position 5 being accompanied by the hydrolysis of the existing methoxyl group in position 4. This is partly avoided by working at a temperature below 0°.

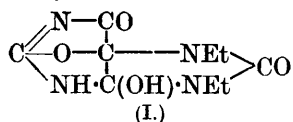
It is remarkable that elimination of water from the positions 4 and 5 of the 4-hydroxy-4 : 5-dihydrouic acids does not occur; this confirms a previous suggestion (Biltz and Damm, *loc. cit.*) that the hydrogen atom in position 5 and the hydroxyl group in position 4 are on opposite sides of the ring. Actually the influence of the 4-hydroxyl radicle promotes an entirely different kind of change. Thus, when 4-hydroxy-7 : 9-diethyl-4 : 5-dihydrouic acid is heated at 230—250°, instead of water, cyanic acid (isolated as cyanuric acid) is eliminated, with formation of 1 : 3-diethylhydantoylamide, hard, four- or six-sided prisms, m. p. 110°; this reaction undoubtedly proceeds through 1 : 3-diethylhydantoylcarbamide according to the scheme :



1 : 3-Diethylhydantoylamide has a bitter taste, and instantaneously reduces cold ammoniacal silver nitrate solution. It is oxidised in aqueous solution by means of chlorine, giving 5-hydroxy-1 : 3-diethylhydantoylamide, the *monohydrate* of which forms hard, hexagonal tablets, m. p. 90—100°. If the chlorination of diethylhydantoylamide is carried out in ethyl-alcoholic solution, 5-ethoxy-1 : 3-diethylhydantoylamide is formed. The thermal decomposition of the hydroxy-7 : 9-dimethyl acid at 230° gives cyanic (cyanuric) acid, and 1 : 3-dimethylhydantoylamide, leaflets, m. p. 181°, which is oxidised by the action of cold ammoniacal silver nitrate solution, and gives, on treatment with chlorine in aqueous solution, 5-hydroxy-1 : 3-dimethylhydantoylamide. The previous statement (Biltz, A., 1910, i, 521) that the latter reduces ammoniacal silver nitrate solution was erroneous. A *monohydrate* of this amide, hard, four-sided prisms (? monoclinic), m. p. 180—182°, is described. The thermal disruption of the bond 3 : 4 is apparently inhibited to some extent by substitution in position 3, since this decomposition is not effected when 4-hydroxy-3 : 7-dimethyl-4 : 5-dihydrouic acid is heated at 250°; the only pure product isolated is a *compound*, $\text{C}_6\text{H}_9\text{O}_3\text{N}_3$, prisms, or leaflets, m. p. 210°, isomeric with trimethyl isocyanurate. Fission of the bond 3 : 4 does, however, occur when 4 : 5-dihydroxy-3 : 7-dimethyl-4 : 5-dihydrouic acid is left in contact with pyridine and methyl alcohol, with formation of α -5-hydroxy-1-methylhydantoyl- β -methylcarbamide. 4 : 5-Dihydroxy-7 : 9-diethyl- and 4 : 5-dihydroxy-7 : 9-dimethyl-4 : 5-dihydrouic acids undergo the same reaction, giving, respectively, 5-hydroxy-1 : 3-diethylhydantoylcarbamide and 5-hydroxy-1 : 3-dimethylhydantoylcarbamide, m. p. 216° (Biltz, *loc. cit.*). W. S. N.

Dioxin Degradation of 4-Hydroxy-4 : 5-dihydrouic Acids.
HEINRICH BILTZ and RUDOLF LEMBERG (*Annalen*, 1923, 432, 177—207).—4-Hydroxy-7 : 9-diethyl-4 : 5-dihydrouic acid (cf. preceding

abstract) is oxidised by means of warm ammoniacal silver nitrate solution, or warm ferric chloride solution, or, better, by the action of air

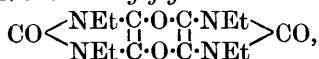


on its solution in methyl alcohol and pyridine, to 2 : 5-oxido-4-hydroxy-6 : 8-diketo-7 : 9-diethyl-3 : 4 : 5 : 6 : 8 : 9-hexahydropurine (I), leaflets, m. p. 209—210° (decomp.); but oxidation by means of potassium

dichromate gives 4 : 5-dihydroxy-7 : 9-diethyl-4 : 5-dihydrouric acid. That the hydrogen in position 5 is utilised in forming the oxido-compound is demonstrated by its indifference to ammoniacal silver nitrate solution, or aqueous or alcoholic chlorine. The compound (I) is readily methylated by means of moist ethereal diazomethane, giving 2 : 5-oxido-4-methoxy-6 : 8-diketo-7 : 9-diethyl-3 : 4 : 5 : 6 : 8 : 9-hexahydropurine, hexagonal prisms, m. p. 198° (slight decomp.). The same compound is obtained by oxidising 4-methoxy-7 : 9-diethyldihydrouric acid by means of warm ferric chloride solution; hence the compound (I) contains the original 4-hydroxy-group intact. That the second hydrogen atom comes from position 1, and not from position 3, is evident, since hydroxy-3 : 7-dimethyldihydrouric acid undergoes a similar series of changes. If the hydrogen were directly derived from position 1, a three-membered ring would be formed. This is unlikely; hence enolisation must intervene. The subsequent elimination of the two hydrogen atoms can then only lead to a compound having the structure (I). The compound (I) gradually dissolves in boiling water with elimination of carbon dioxide and ammonia, and formation of the lactone of 5-hydroxy-1 : 3-diethylglyoxalone-4-carbamic

acid, (II) $\text{CO} < \begin{array}{c} \text{O}-\text{C}\cdot\text{NEt} \\ \parallel \\ \text{NH}\cdot\text{C}\cdot\text{NEt} \end{array} > \text{CO}$, rhombohedra, m. p. 146—148°

(decomp.). This compound behaves as a lactone towards aqueous alkali hydroxides (titration). It may be methylated by means of moist ethereal diazomethane, giving the lactone of 5-hydroxy-1 : 3-diethylglyoxalone-4-methylcarbamic acid, four-sided prisms, m. p. 228—229°. Since this acid gives methylamine when boiled with sodium hydroxide solution, the entering methyl group must have become attached to nitrogen. In the production of the compound (II), therefore, the reactive 4-hydroxyl radicle has disappeared from the compound (I), being removed, together with hydrogen from position 5, as water, subsequent to the elimination of nitrogen (position 1) as ammonia and carbonyl (position 6) as carbon dioxide. The alternative removal of nitrogen from position 3 is excluded because (a) this would lead to the known lactimide of 5-hydroxy-1 : 3-diethylhydantoin-5-carboxylic acid, and, (b) in the corresponding degradation of the 3 : 7-dimethyl acid, ammonia, and not methylamine, is removed at this stage. The compound (II) is converted by the action of boiling aqueous alkali carbonate or hydroxide into bis-N : N'-diethylglyoxalonodioxin (III),



long prisms, m. p. 165—166°, which is also formed by the action of

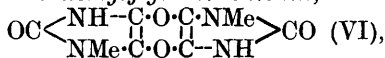
boiling sodium carbonate solution on 2 : 5-oxido-4-methoxy-6 : 8-diketo-7 : 9-diethylhexahydropurine, and is a by-product in the preparation of the lactone (II). This compound is extraordinarily stable; it is not acidic, and does not react with aqueous bromine, with boiling concentrated hydrochloric acid, or with aniline at 215—220°. It is, however, gradually decomposed by the action of boiling 50% aqueous potassium hydroxide, with elimination of ethylamine, but only a small quantity of a substance, m. p. about 80°, perhaps diethylcarbamide, is isolated. Nevertheless, the compound (III) is oxidised by means of chromic acid in boiling aqueous sulphuric acid solution, the product being diethylparabanic acid. The structure (IV), $\text{OC} \begin{array}{c} \text{NEt} \cdot \text{CO} \\ \text{NEt} \cdot \text{C} = \text{C} \end{array} \begin{array}{c} \text{CO} \cdot \text{NEt} \\ \text{C} \end{array} \text{CO}$, also ex-

presses this decomposition, but the dioxin formula is preferred by reason of the inertness of the substance towards bromine or boiling concentrated nitric acid. Its production from the lactone (II) by the union of two molecules, subsequently to the removal of the $-\text{OC} \cdot \text{NH}-$ group as carbon dioxide and ammonia, may more readily be reconciled with the formula adopted.

4-Hydroxy-7 : 9-dimethyl-4 : 5-dihydrouric acid suffers the same degradation, excepting that the intermediate lactone corresponding with (II) is not isolated. Oxidation of the 7 : 9-dimethyl acid may be accomplished with the aid of atmospheric oxygen, using the pyridine-methyl alcohol solution, or, very conveniently, by means of ferric chloride solution, and gives 2 : 5-oxido-4-hydroxy-6 : 8-diketo-7 : 9-dimethyl-3 : 4 : 5 : 6 : 8 : 9-hexahydropurine, cf. formula (I), domed prisms, m. p. 230° (decomp.), methyl ether, small rhombohedra, m. p. 230° (decomp.). The oxido-derivative gradually dissolves when boiled with dilute hydrochloric acid, giving a compound, rhombohedra, m. p. 317°, for which, however, no formula has been devised. By the action of boiling water alone, the oxido-compound passes into bis-N : N-dimethylglyoxalonodioxin, domed prisms, m. p. 228°, which gives dimethylparabanic acid on oxidation by means of chromic acid.

The analogous degradation of 4-hydroxy-3 : 7-dimethyl-4 : 5-dihydrouric acid has also been accomplished, but with difficulty. The action of atmospheric oxygen in the presence of pyridine and methyl alcohol, or the use of 10% ferric chloride solution, gives the 4 : 5-dihydroxy-acid, but the use of 5% ferric chloride solution leads to the formation of 2 : 5-oxido-4-hydroxy-6 : 8-diketo-3 : 7-dimethyl-3 : 4 : 5 : 6 : 8 : 9-hexahydropurine, $+1\frac{1}{2}\text{H}_2\text{O}$, small rhombohedra, m. p. 186° (decomp.). When the latter is treated with moist ethereal diazomethane, methyl groups enter on both oxygen and nitrogen, giving 2 : 5-oxido-4-methoxy-6 : 8-diketo-3 : 7 : 9-trimethyl-3 : 4 : 5 : 6 : 8 : 9-hexahydropurine, small, four-sided prisms, m. p. 178—179° (decomp.). This compound is also formed by the methylation of 2 : 5-oxido-4-methoxy-6 : 8-diketo-3 : 7-dimethylhexahydropurine, prisms, m. p. 205—206° (decomp.), which is obtained by oxidising the 4-methoxy-3 : 7-dimethyl acid by means of 5% ferric chloride solution. The oxido-3 : 7-dimethyl compound undergoes isomerisation when boiled for a short time with water, the

product being 2 : 5-oxido-4 : 6-diketo-5-(α -methylcarbamido)-3-methyl-3 : 4 : 5 : 6-tetrahydropyrimidine (V), hard rhombohedra, m. p. 245° (decomp.). The production of this isomeride, by fission of the glyoxalone ring, is obviously dependent on the presence of the hydroxyl group in position 4. The reverse change is effected by dissolving in dilute sodium hydroxide solution, followed by acidification; it is also brought about by the agency of diazomethane, since on methylation the isomeride gives the same methoxytrimethylhexahydropurine derivative as the original oxido-compound. On boiling with water for a longer period, the oxido-compound gradually passes, with generation of carbon dioxide and ammonia, into the lactone of 5-hydroxy-1-methylglyoxalone-4-methylcarbamic acid, cf. formula (II), four-sided prisms, m. p. 263—264° (decomp.), which gives methylparabanic acid on oxidation by means of chromic acid, and therefore still contains the glyoxalone ring. The lactone passes on methylation, using diazomethane, into the lactone of 5-hydroxy-1 : 3-dimethylglyoxalone-4-methylcarbamic acid, short, four-sided prisms, m. p. 172—173° (slight decomp.). The conversion of the lactone, m. p. 263—264°, into the dioxin derivative proceeds with greater difficulty than in the other two series investigated. Neither boiling water nor boiling 10% sodium hydroxide solution suffices, but the change is brought about by boiling with 20% potassium hydroxide solution or with concentrated hydrochloric acid. *Bis-N-methylglyoxalonodioxin*,



short, flat, four-sided prisms, m. p. 327° (decomp.), gives methylparabanic acid on oxidation by means of chromic acid. It is acidic, owing to the presence of two $\text{-NH}\cdot\text{CO}\cdot$ groups. On treatment with moist ethereal diazomethane, two methyl groups enter, with production of bis-*N* : *N'*-dimethylglyoxalonodioxin (above). The latter is also formed by the action of boiling 10% sodium carbonate solution on the lactone of 5-hydroxy-1 : 3-dimethylglyoxalone-4-methylcarbamidic acid. W. S. N.

Mercaptans of the Purine Group. I. SIR PRAFULLA CHANDRA RÂY, GOPÂL CHANDRA CHAKRAVARTI, and PRAFULLA KUMÂR BOSE (T., 1923, 123, 1957—1962).

The Configuration of Naphthalene Azo-dyes possessing Affinity for Cellulose. II. N. N. VOROSHOV and K. A. GRIBOV (*Bull. Inst. Polytech. Ivanovo-Voznesensk*, 1923, 7, 102—109).—It has already been suggested (*ibid.*, 1921, 4, 95) that the substantivity of naphthalene azo-dyes to cotton is dependent on the presence of two or more nitrogenous substituents, one of these being an azo-group, in certain relative positions. A number of azo-compounds possessing a nitro-group in different positions have now been studied and 1 : 4-, 1 : 5-, 2 : 6-, and 2 : 8-nitroamino-compounds were found to give substantive cotton

dyes on diazotisation and coupling with various substances such as Cleve's acid, N and W acid, H acid, etc. [Cf. *J.S.C.I.*, 1923, 42, 822A]. G. A. R. K.

The Isosterism of Phenylcarbimide and Diazobenzene-imide. WALLACE H. CAROTHERS (*J. Amer. Chem. Soc.*, 1923, 45, 1734—1738).—Assuming the atoms of phenylcarbimide and of diazobenzeneimide to be arranged as indicated by the formulæ $\text{Ph}\cdot\text{N}\cdot\text{C}\cdot\text{O}$ and $\text{Ph}\cdot\text{N}\cdot\text{N}\cdot\text{N}$, application of the octet theory leads to the conclusion that they are isosteric. They should therefore be very similar in their physical properties. Measurements of their densities, vapour pressures, and viscosities at various temperatures have confirmed this prediction. The densities (g./c.c.) are expressed by the following equations: for phenylcarbimide, $d=1.1152-0.001044t$, and for diazobenzeneimide, $d=1.1152-0.001044t'$, where $t'=t-2.44^\circ$. The vapour pressures are given by the equation: for phenylcarbimide, $p=157-4.76t+0.042t^2$, and for diazobenzeneimide, $p=157-4.76t'+0.042(t')^2$, where $t'=t-1.7^\circ$. The viscosities (centipoises) are expressed as follows: for phenylcarbimide, $\eta=1.326-0.02163t+0.000174t^2$, and for diazobenzeneimide, $\eta=1.326-0.02163t'+0.000174(t')^2$, where $t'=t-4.8^\circ$.

W. S. N.

Halogenated Aromatic Hydrazines. I. The True 3:4-Dibromophenylhydrazine, and Meyer's so-called 3:4-Dibromophenylhydrazine. ÉMILE VOTOČEK and P. JIRŮ (*Bull. Soc. chim.*, 1923, [iv], 33, 918—934).—3:4-Dibromophenylhydrazine, prepared from 3:4-dibromoaniline, crystallises from light petroleum in yellow needles, m. p. 75° , and is not identical with the supposed 3:4-dibromophenylhydrazine, m. p. 104° , described by Meyer (*A.*, 1893, i, 155). Its *hydrochloride* decomposes at 215° , the normal *sulphate* at 180° , and the *acid sulphate* at 135° . The *oxalate* is soluble with difficulty and decomposes at $162-163^\circ$, the *picrate* forms yellow needles decomposing at $154-156^\circ$. The *acetyl* derivative forms pale red needles, m. p. $181-182^\circ$. 3:4-Dibromophenylhydrazine forms *hydrazones* with *benzaldehyde*, m. p. 128° ; *salicylaldehyde*, m. p. 190° ; *acetone*, an oil; *arabinose*, m. p. $82-83^\circ$; *rhamnose*, m. p. $153-154^\circ$, and *dextrose*, m. p. $165-167^\circ$. It forms an *osazone* with *dextrose* or *lævulose*, m. p. $225-226^\circ$ (decomp.). This brominated phenylhydrazine is not suitable for the characterisation of sugars because it yields derivatives which are difficult to purify.

Meyer's so-called 3:4-dibromophenylhydrazine is shown to be 4-bromophenylhydrazine, which is obtained by the bromination of acetonephenylhydrazone according to the following scheme. One atom of bromine enters the nucleus in the para-position, and the hydrogen bromide so formed combines with the acetone-*p*-bromophenylhydrazone to give the hydrobromide. This decomposes to form *p*-bromophenylhydrazine hydrobromide. Further addition of bromine causes the formation of an *N*-bromo-derivative, which undergoes transformation into 2:4-dibromophenylhydrazine, small quantities of which are formed in the preparation of 4-monobromophenylhydrazine by Meyer's method.

H. H.

Protein Coagulation by Drops. II. J. BEČKA and F. ŠINKORA (*Biochem. Z.*, 1923, **138**, 326—334).—From observations on drops of horse-serum arranged in successive rows on a glass plate (cf. this vol., i, 717), it is concluded that with increasing electrolyte concentration the coagulation by mercuric-ions falls off, whereas that by hydrogen-ions increases. The kations as a rule follow Hofmeister's series, but a reversal is observed in acid solution when the concentration of the kation is above $M/4$. The action of carbamide in increasing the precipitating action of mercuric-ions and hydrogen-ions is proportional to its concentration.
H. K.

Protein Coagulation by Drops. III. J. BEČKA and F. ŠINKORA (*Biochem. Z.*, 1923, **138**, 335—340).—The precipitating action on horse-serum of mercuric chloride, copper sulphate, phenol, resorcinol, and catechol was studied by the drop on plate method. Having determined the limits of coagulation, the authors determined the new limits for mixtures of two or more of these coagulants. The precipitating effect of mixtures is greater than that of either component.
H. K.

The Digestibility of Proteins in Vitro. IV. The Digestibility of the Cotton Seed Globulin and the Effects of Gossypol on the Peptic-Tryptic Digestion of Proteins. D. BREESE JONES and HENRY C. WATERMAN (*J. Biol. Chem.*, 1923, **56**, 501—511).—When treated successively with pepsin and trypsin in vitro, the globulin isolated from cotton seed is digested at practically the same rate as casein. The digestion of both proteins is, however, interfered with if gossypol is added to the mixture in approximately the same proportion as it is present in cotton seed. These results confirm the view of Alsberg and Schwartze (*J. Pharm. Expt. Ther.*, 1921, **17**, 344) that the incomplete digestion in vivo of the proteins in cotton seed flours is due to the presence in the latter of gossypol.
E. S.

Influence of Moisture on the Diminution in the Solubility of Casein by the Action of Lactic Acid. MARC FOUASSIER (*Bull. Soc. Chim. biol.*, 1923, **5**, 487—490).—Experiments are described which show that the diminution in solubility which occurs on keeping certain types of dried milk is due to the presence of moisture. In the presence of small amounts of moisture the lactic acid contained in the milk renders the casein insoluble. E. S.

Metallic Compounds of Proteins. A. J. J. VANDEVELDE (*Rec. trav. chim.*, 1923, **42**, 620—622).—The author has precipitated the proteins of milk with equivalent quantities of copper sulphate, chloride, nitrate, and acetate, and has analysed both the precipitate and the filtrate. It is found that the amount of copper in the precipitate increases with the amount of copper added. In the case of the sulphate, it is shown that a variable amount of the anion is precipitated, so that it is impossible to state that an equilibrium is set up between the protein and the copper sulphate, as has previously been done by Galeotti (A., 1904, i, 355). J. F. S.

Electrical Conductivity of Caseinates. FRIEDRICH PLATTNER (*Kolloid Z.*, 1923, **33**, 98—101).—The electrical conductivity of alkali caseinate solutions has been measured at 25° at various periods after preparation. It is shown that caseinate solutions preserved under toluene do not change. A 1.2% solution had a conductivity 6.78×10^{-4} ohms⁻¹ and eleven days later the solution had a conductivity 6.80×10^{-4} . More concentrated solutions showed a similar stability. J. F. S.

Reaction between Proteins and Nitrous Acid. The Tyrosine Content of Deaminised Casein. HOWARD B. LEWIS and HELEN UPDEGRAFF (*J. Biol. Chem.*, 1923, **56**, 405—414).—In the deamination of casein by nitrous acid the destruction of amino-acids other than lysine is probably due to secondary reactions. In the present paper, it is shown that the maximum amount of tyrosine is present in deaminised casein when deamination is carried out at low temperatures. If such deaminised casein is treated with acetic acid and sodium nitrite, the tyrosine content is diminished, the diminution being proportional to the time of action and the temperature. E. S.

A New Sulphur-containing Amino-acid isolated from Casein. J. H. MUELLER (*Proc. Soc. Expt. Biol. Med.*, 1921, **19**, 161—163).—Commercial casein (13,608 g.) was hydrolysed with sulphuric acid, neutralised with sodium carbonate, and precipitated with mercuric sulphate solution; from the washed precipitate freed from electrolytes a second precipitation occurred with mercuric sulphate solution; the sulphur compound remained in the filtrate. This was further purified by silver sulphate and barium hydroxide, and the compound obtained from the silver- and barium-free filtrate by fractional crystallisation. From dilute acetone the substance $C_{11}H_{23}O_4N_2S$ is obtained (10 g.) in white plates or rosettes of indefinite crystalline form. The nitrogen is present as an amino-group; the sulphur does not blacken lead. It was not definitely established that the sulphur was not introduced into the molecule during the preparation. CHEMICAL ABSTRACTS.

Separation of the Hexone Bases from certain Protein Hydrolysates by Electrolysis. G. L. FOSTER and CARL L. A. SCHMIDT (*J. Biol. Chem.*, 1923, **56**, 545—553).—When the hydrolytic products of casein, fibrin, or red blood-cells are electrolysed in a three-compartment cell, the basic amino-acids, together with about 20% of the non-basic nitrogen, pass into the cathode compartment. By re-electrolysis of the contents of the latter the basic amino-acids may be separated practically completely from the non-basic material. If the reaction of the centre compartment, which contains the protein hydrolysate, is maintained at P_H 5.5, arginine, lysine, and histidine migrate into the cathode compartment in approximately the ratio in which they are present in the hydrolysate. At P_H 7.5, however, only the two former amino-acids are transported, the histidine remaining in the centre compartment. It may be possible to utilise this method for the preparation of histidine. E. S.

The Blood Pigments. I. H. FISCHER and K. SCHNELLER (*Z. physiol. Chem.*, 1923, **128**, 230—239).—When ethyl 2:4-dimethylpyrrole-3-carboxylate is dissolved in pyridine and acetyl chloride is added, a compound, $2C_9H_{13}O_2N, C_5H_5N$, is formed, which crystallises from alcohol in colourless needles, m. p. 173—174°. From 3-acetyl-2:4-dimethylpyrrole, an analogous compound, colourless crystals, m. p. 185°, is obtained, but no satisfactory formula could be assigned to it. From quinoline and ethyl 2:4-dimethylpyrrole-3-carboxylate, colourless needles are obtained, which apparently consist of a mixture of two compounds, $2C_9H_{13}O_2N, C_9H_7N$ and $C_9H_{13}O_2N, C_9H_7N$. These results are considered in relation to the formation of hæmochromogen according to Takayama's method (*Münch. med. Woch.*, 1922, **69**, 116). If hæmochromogen is treated with boiling acetic acid containing sodium chloride and hydrochloric acid, hæmin is formed. If mesoporphyrin is treated with ferrous acetate in acetic acid in the absence of oxygen, mesohæmin is formed, although the iron in mesohæmin must be tervalent. A change of valency must take place.

W. O. K.

Adsorption and Hæmoglobin. W. E. L. BROWN (*Nature*, 1923, **111**, 881—882; cf. this vol., i, 869, 870).—An experiment on the readiness with which the constituents of a mixture of carbon monoxide and oxygen are taken up by hæmoglobin gave results indicating that the union is not due to adsorption. This view is also supported by the fact that the electrical conductivity of gas-free, dialysed hæmoglobin solution is increased by shaking with oxygen or carbon monoxide. The reactions of hæmoglobin with carbon monoxide or oxygen are regarded as being purely chemical.

A. A. E.

Natural Porphyrins. I. Porphyrin from *Eisenia foetida*. H. FISCHER and O. SCHAUMANN (*Z. physiol. Chem.*, 1923, **128**, 162—166).—A porphyrin has been extracted in very small quantities from earthworms. It crystallises from ether in very fine needles and appears to have the formula $C_{40}H_{48}O_8N_4$. Attempts to prepare the methyl ester resulted in a substance having a too small nitrogen content, and giving in acetoacetic acid a spectrum resembling that of acid porphyrin.

W. O. K.

Natural Porphyrins. II. Turacin. H. FISCHER and J. HILGER (*Z. physiol. Chem.*, 1923, **128**, 167—174).—Turacin, a dye isolated from the feathers of certain crested birds, appears from its chemical and spectroscopic properties to be identical with the copper salt of urinoporphyrin.

W. O. K.

Composition of Thymic Acid. R. FEULGEN (*Z. physiol. Chem.*, 1923, **128**, 154—161).—The question of the isolation of thymic acid (A., 1918, i, 413) is discussed with reference to the views of Thannhauser and Ottenstein (A., 1921, i, 521), and it is concluded that there is no evidence leading to the conclusion that thymic acid is a mixture.

W. O. K.

The Sugar contained in Tuberculinic Acid, the Nucleic Acid of Tubercle Bacilli. ELMER B. BROWN and TREAT B. JOHNSON (*J. Amer. Chem. Soc.*, 1923, **45**, 1823—1827).—It is shown that the products of hydrolysis by means of dilute sulphuric acid of tuberculinic acid, purified by the method already given (this vol., i, 160), contain lævulic acid and formic acid, and only a relatively small amount of furfuraldehyde. It is therefore evident that the sugar functioning in tuberculinic acid is a hexose. A new analysis for pyrimidines in tuberculinic acid has confirmed results previously reported (*loc. cit.*). W. S. N.

Evidences of a Structure in Gelatin Gels. R. A. GORTNER and W. F. HOFFMAN (*Proc. Soc. Expt. Biol. Med.*, 1922, **19**, 252—253, 257—264).—Gelatin gels of different concentrations, when dried, will again imbibe water according to their original water content and independently of the amount of surface exposed. A 10% gel dried to less than 3% of water content had imbibed at the end of seventy-two hours 6.45 g. of water per g. of dry gelatin, as contrasted with 4.3 g. of water for a 40% gel similarly treated. Gelatin gels have a structure fixed at the time of gelation, and not appreciably altered by drying at room temperature. A crystal structure in which the gelation temperature is actually the m. p. of the crystals would explain the phenomena.

CHEMICAL ABSTRACTS.

A Complement of the Amylases. HANS PRINGSHEIM and WALTER FUCHS (*Ber.*, 1923, **56**, [B], 1762—1768).—The term “complement” is applied to an activator of a ferment which differs from the usual co-enzyme in that it is not in nature associated with the ferment and also because it causes the ferment, which is itself active towards a substrate, to become active to a portion of the substrate. Thus the conversion of starch into maltose by means of activated malt extract is generally considered not to proceed beyond the point at which 78% of the starch has undergone saccharification (indications have been obtained during the present work that this limit is rather low). A residual substance is thereby obtained which, under optimal conditions, is only relatively slowly attacked by highly active malt amylase. Addition of yeast which has been treated with toluene, however, so activates the amylase that the “residual substance” is energetically saccharified. In this manner it is possible to obtain maltose in 100% yield from potato or soluble starch.

Two methods are used for the isolation of the “residual substance.” Potato starch is fermented by dialysed malt extract in the presence of toluene until about 75% of it has undergone amyolytic fission. The solution is concentrated and submitted to dialysis until the dialysate does not contain fermentable carbohydrate. The remaining solution is concentrated to a small volume and the “residual substance” is precipitated by means of alcohol. Alternatively, the solution obtained after the use of malt extract is heated at 80—90° to ensure destruction of the amylase and subsequently fermented by yeast. The solution is centrifuged

after addition of kieselguhr and dialysed to remove the bulk of the soluble salts. The proteins derived from the yeast are precipitated by addition of colloidal iron hydroxide. The resultant solution is concentrated and precipitated by alcohol. The residual substances obtained by the two methods differ somewhat in their properties, but these differences disappear to a considerable extent on further purification, which is effected by solution in water and reprecipitation by alcohol. The residual substance is a colourless, amorphous powder which is freely soluble in water, but insoluble in organic media. It has $[\alpha]_D^{25} +160-161^\circ$ in 1% solution, $[\alpha]_D^{25} +159^\circ$ in 10% solution. It does not give a coloration with iodine.

H. W.

Nomenclature of the Activity and Affinity of Enzymes. H. VON EULER and K. JOSEPHSON (*Ber.*, 1923, 56, [B], 1749—1758).—For reasons which are discussed in detail in the original communication, it appears most reasonable to express the activity of enzymic preparations in the manner which has been proposed previously for saccharase and the starch saccharifying enzyme. When $a \cdot k$ is constant, the expression takes the general form $Xf = k + g(\text{substrate})/g$ (enzyme preparation) or, in the theoretically simplest case in which k is independent of the concentration of the substrate, $Xf = k/g$ (enzyme preparation). In special cases, the limits and conditions of the validity of the relationships are to be indicated. The reaction constants are to be given invariably for optimum acidity and generally for optimal concentration of the activator, preferably at 18° , 20° , or 37° , so that Xf is valid for these temperatures. The expression Xf is chosen, in which f denotes the enzymic faculty of the corresponding enzymic component; for the special enzyme—apart from the terms If and Sf —the initial letter of the name of the enzyme is adopted if possible (thus, for example, Uf for urease, Lf for lipase) or the initial syllable if necessary to avoid confusion (thus $Katf$ instead of Kf for catalase).

Enzymes are to be characterised further by their affinity constants. The previously proposed expression, K_M (Michaelis constant), is preferably used as affinity constant and not as dissociation constant, thus $K_M = (\text{enzyme substrate})/(\text{enzyme}) \times (\text{substrate})$. K_M does not appear to vary very greatly with the temperature, but it is nevertheless recommended that the latter should be indicated and chosen in harmony with that adopted in the determination of Xf . For saccharase, the values of K_M vary between 25 and 60; for urease the value is about 90, for a lipase about 15.

H. W.

Activation of an Enzyme Poisoned by Heavy Metal Salts. R. A. KEHOE (*J. Lab. Clin. Med.*, 1922, 7, 736—742).—The enzyme in saliva coagulated and inactivated by mercuric chloride and silver nitrate may be reactivated by sufficiently high concentrations of neutral salts of the alkali or alkaline-earth metals; bromides, iodides, and thiocyanates of ammonium, potassium, sodium, strontium, barium, calcium, and magnesium are effective, but not the nitrates, sulphates, citrates, acetates, or carbonates. Re-dissolution of the

precipitate and return (to about 80%) of the starch-splitting activity occurred simultaneously. The enzyme probably consists of, or is intimately associated with, a protein which is soluble and active only when combined with certain salts or metals. Inactivation is ascribed to the formation of insoluble compounds.

CHEMICAL ABSTRACTS.

The Purification of Insulin and some of its Properties. HAROLD WARD DUDLEY (*Biochem. J.*, 1923, **17**, 376—390).—A potent preparation of equal activity to but only about 6% by weight of the crude insulin is prepared by precipitating it as the picrate and converting the insoluble picrate into a soluble hydrochloride by means of alcoholic hydrogen chloride. This preparation does not contain phosphorus and does not give Selivanov's reaction for lævulose, or the glyoxylic acid reaction for tryptophan and gives only a very faint and atypical Millon test. On the other hand, the biuret, the Pauly, and the organic sulphur tests are positive. The hydrochloride is precipitated by acids and alkali hydroxides, the former precipitate being more and the latter less potent than the original, and it is destroyed by trypsin and pepsin. Insulin is relatively stable to acid, but is easily decomposed by alkali hydroxides and is rapidly adsorbed in faintly acid solution. It can, however, be filtered without any significant loss through Berkfeld filters if the solution is made weakly alkaline. S. S. Z.

Effect of Plant Extracts on Blood-sugar. WILLIAM THALLINER and MARGARET C. PERRY (*Nature*, 1923, **112**, 164—165).—The tentative suggestion is put forward that insulin, which is apparently not itself an oxydase or a peroxydase, indirectly stimulates or activates oxidising ferments in the tissue-cells to action on dextrose, whereas vegetable extracts contain active oxidising ferments and act directly when injected into animals (cf. Winter and Smith, this vol., i, 513, 727; Collip, this vol., i, 728, with whom coincident priority is claimed). A. A. E.

Glucokinin. A New Hormone Present in Plant-tissue. J. B. COLLIP (*J. Biol. Chem.*, 1923, **56**, 513—543).—Extracts which have been found to contain a hormone analogous to insulin have been prepared from baker's and brewer's yeast, wheat leaves, onions, lettuce, and the vegetative tissues of other plants. The name *glucokinin* is suggested for this new hormone. Glucokinin has been administered subcutaneously to normal rabbits and to depancreatised dogs. With the former animals there was an initial hyperglycæmia which was followed by a marked hypoglycæmia. In the case of the dogs, the primary effect was an increased rate of excretion of sugar which was followed by a fall in the level of blood-sugar and a decrease in the rate of elimination of sugar. These effects develop more slowly and are maintained for a longer period than in the case of insulin. It is probable that glucokinin plays a rôle in the sugar metabolism of plants similar to that of insulin in animals. E. S.

A Product of Mild Acid Hydrolysis of Wheat Gliadin. HUBERT BRADFORD VICKERY (*J. Biol. Chem.*, 1923, **56**, 415—428; cf. A., 1922, ii, 754).—Using dilute hydrochloric acid, the author has been unable to obtain conditions whereby the amide groups in gliadin are alone hydrolysed. The hydrolysis of the amide and peptide bonds proceeds simultaneously, although the former are hydrolysed more rapidly. These results do not support the view that hemi- and anti-groups are present in the protein molecule. E. S.

Chemistry of Vitamin-A. I. Separation of the Active Constituent of Cod-liver Oil, and its Properties. KATSUMI TAKAHASHI and KOZO KAWAKAMI (*J. Chem. Soc. Japan*, 1923, **44**, 580—605).—The authors have attempted to isolate vitamin-A from cod-liver oil and succeeded in obtaining it nearly pure in a semi-crystalline state.

One kg. of cod-liver oil was saponified by warming with 2 litres of alcohol containing 20% potassium hydroxide at 80—90° for thirty minutes. Then 2 litres of 28% alcoholic solution of calcium chloride were gradually mixed with cooling and agitated for one hour. After separation from the calcium soap and potassium chloride, the solution was saturated with carbon dioxide, the solvent distilled off below 60° under reduced pressure, and the residue extracted with ether or light petroleum. The ethereal extract was treated with dilute hydrochloric acid and the fatty acids set free were separated by means of 50% alcohol containing dilute alkali. After drying with sodium sulphate, the solvent was expelled by a current of carbon dioxide, and to the residue about 50 c.c. of 80—90% methyl alcohol were added, and the whole was cooled at 0° for two to three hours, 3—5 g. of cholesterol then separating. More impurities were separated by adding digitonin, and concentrating to a red, viscous syrup, which was once more dissolved in a small quantity of 80—90% methyl alcohol and cooled to -20°, whereby the vitamin-A was separated in the semicrystalline state, the yield being about 0.1%. A mouse dying from lack of vitamin-A recovered completely on taking 0.08 mg. of the substance per day for ten days. The active constituent of butter or egg-yolk has also been isolated by this method.

The isolated constituent contains carbon, hydrogen, and oxygen, but does not contain nitrogen, and seems to be of aldehydic nature. It is very hygroscopic and reduces ammoniacal silver solution, Fehling's solution, and phosphotungstic acid. It is unstable to light and oxygen, and is changed by reduction with hydrogen in the presence of platinum black, but is stable in ether or alcohol, especially in fats. It is insoluble in water, but soluble in alcohol, ether, benzene, acetone, or other organic solvents. In chloroform or carbon tetrachloride solution, it gives the lipochrome reaction and a blue coloration with Japanese acid clay. K. K.

Observations on the Properties of Arsphenamine [Salvarsan.] WALTER G. CHRISTIANSEN (*J. Amer. Chem. Soc.*, 1923, **45**, 1807—1811).—Salvarsan (arsphenamine) forms additive compounds with methyl ketones in which the ketone is very firmly

bound (cf. Fargher and Pyman, T., 1920, **117**, 372). Neither drying at room temperature or 98° nor reprecipitation from ketone-free methyl alcohol by means of ether removes the ketone. When an aqueous solution containing salvarsan and sodium arsenite is treated with hydrochloric and hypophosphorus acids, a red *polyarsenide* of salvarsan is formed. The velocity of this reaction depends on the method of preparation of the salvarsan, and is apparently greater the less the salvarsan is polymerised. The quantity of hydrochloric acid necessary to precipitate (coagulate) salvarsan from a dilute aqueous solution is constant if the method of preparation does not vary, otherwise varying amounts of acid are necessary. Titration with hydrochloric acid therefore affords a means of determining how closely the routine method of preparation has been followed. In order to obtain a well-coagulated product, in converting salvarsan base into the dihydrochloride, it is advantageous to use a slight excess over the two molecules of hydrochloric acid required. W. S. N.

Preparation of New Aromatic Carbonyl Compounds containing Tervalent Arsenic. OTTO MARGULIES (Brit. Pat. 199091).—Aldehydo- or keto-arsinic acids of the type $R \cdot AsO_3H_2$ are reduced to the corresponding oxides, $R \cdot As_2O_3$, and arseno-compounds, $R \cdot As \cdot As \cdot R$, by means of agents (*e.g.*, sodium hyposulphite, phosphorus trichloride, sodium hydrogen sulphite) which reduce the quinquevalent arsenic without affecting the carbonyl groups. [Cf. *J.S.C.I.*, 1923, **42**, 861A.] W. T. K. B.

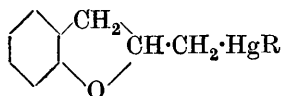
Preparation of New Derivatives of Organic Arsenic Compounds. OTTO MARGULIES (Brit. Pat. 199092).—Aromatic aldehydo- or mixed fatty-aromatic keto-arsinic acids, or the corresponding compounds containing tervalent arsenic (cf. preceding abstract), are treated with hydrazines containing one or more hydrazine groupings (*e.g.*, methylhydrazine, phenylmethylhydrazine, diaminoguanidine). The carbonyl groups are not reduced. The products are mostly well-characterised and crystalline, and possess valuable trypanocidal and spirillicidal properties. W. T. K. B.

Preparation of New Arsenoxides and Arsenobenzenes. OTTO MARGULIES (Brit. Pat. 199093).—New organic arsenoxides and arsenobenzenes are obtained from the hydrazones of aromatic aldehydo- or mixed fatty-aromatic keto-arsinic acids or arsenoxides by reduction as described above (preceding abstracts). W. T. K. B.

Magnesium Cumyl Chloride. L. BERT (*Compt. rend.*, 1923, **177**, 195—197).—Cumyl chloride, $C_6H_4Pr^a \cdot CH_2Cl$, reacts in ethereal solution with magnesium (previously activated with ethyl bromide) to give a pasty mass of Grignard reagent, and dicumyl (b. p. 350°), a little magnesium remaining undissolved. Decomposition with water affords *p*-cymene, dicumyl, cumyl chloride, and a small quantity of the hydrocarbon described by Errera (A., 1884, 300). The Grignard reagent absorbs oxygen and may thus be converted into cumyl alcohol, b. p. 246° (corr.). E. E. T.

Mercury Derivatives of Phenol Ethers. FRANK C. WHITMORE and EDMUND BURRUS MIDDLETON (*J. Amer. Chem. Soc.*, 1923, **45**, 1753—1755).—When boiled in alcoholic solution with potassium iodide or potassium thiocyanate, or when an aqueous solution containing sodium thiosulphate is allowed to remain, *o*-iodomercurianisole and *o*-iodomercuriphenetole give, respectively, *o*-mercury dianisyl and *o*-mercury diphenetyl. The resulting solution is always neutral, but contains inorganic mercury compounds. *o*-Mercury dianisyl and *o*-mercury diphenetyl react normally with alcoholic mercuric chloride, giving quantitative yields of *o*-chloromercurianisole and *o*-chloromercuriphenetole, respectively. *p*-Iodomercuriphenol ethers apparently react with potassium iodide or potassium thiocyanate similarly to the ortho-derivatives, but the product is difficult to purify. It is evident that the protection of the phenolic hydroxyl group prevents the fission of the carbon-mercury linking, with formation of alkali, which occurs with mercurated phenols. W. S. N.

Mercurated 1-Methyl-1 : 2-dihydrobenzofurans. LINDLEY E. MILLS and ROGER ADAMS (*J. Amer. Chem. Soc.*, 1923, **45**, 1842—1854).—The addition of mercuric salts to *o*-allylphenols, and the properties of the mercurated 1-methyl-1 : 2-dihydrobenzofurans (annexed formula) (A., 1922, i, 946), are shown to be general. Mercuric acetate and mercuric chloride react readily with *o*-allyl-*p*-methylphenol, *o*-allyl-*o*-methylphenol, *m*-hydroxy-*p*-allyltoluene, *p*-bromo-*o*-allylphenol, *p*-carboxy-*o*-allylphenol, *o*-carboxy-*o*-allylphenol, *o*-carbomethoxy-*o*-allylphenol, and *p*-hydroxy-*m*-allylcinnamic acid. The mercurated dihydrobenzofurans undergo the following reactions, in addition to those already reported (*loc. cit.*). The 1-acetoxymercuri- or 1-halogenomercuri-derivatives react with hot concentrated alcoholic potassium cyanide or potassium thiocyanate, to give, respectively, the corresponding 1-cyanomercuri- or 1-thiocyanatomercuri-compounds. The action of warm alcoholic sodium or potassium hydroxide on the 1-chloromercuri-derivatives causes replacement of the chlorine atom by the hydroxyl group; the 1-hydroxymercuri-compounds behave as salt-forming bases, and precipitate insoluble metallic hydroxides, such as cupric hydroxide, from neutral metallic salt solutions. The formation of hydroxymercuri-derivatives in this way is apparently a general reaction, since methylmercuric chloride is converted into methylmercurimethoxide by a similar procedure. The 1-halogenomercurimethyl-1 : 2-dihydrobenzofurans are converted into metallic mercury and the relevant *o*-allylphenol, by the action of alkaline sodium stannite solution, or of ammonium sulphide, potassium hydrogen sulphide, or hydrogen sulphide in dilute acid solution. By the action of hot, saturated, aqueous sodium thiosulphate solution, they are converted into 1-sodiumthiosulphatomercuri-derivatives, but these are unstable, and readily break down into mercuric sulphide and the *o*-allylphenol. The 1-halogenomercuri-



methyl derivatives do not react with methyl iodide or acetyl chloride.

The following compounds are described. 1-Acetoxymethyl-6-methyl-1:2-dihydrobenzofuran, m. p. 113°; 1-chloromethyl-6-methyl-1:2-dihydrobenzofuran, m. p. 91°; 1-acetoxymethyl-5-methyl-1:2-dihydrobenzofuran, an oil; 1-chloromethyl-5-methyl-1:2-dihydrobenzofuran, m. p. 127·5°; 1-acetoxymethyl-4-methyl-1:2-dihydrobenzofuran, an oil; 1-chloromethyl-4-methyl-1:2-dihydrobenzofuran, m. p. 99·5°; 4-bromo-1-acetoxymethyl-1:2-dihydrobenzofuran, an oil; 4-bromo-1-chloromethyl-1:2-dihydrobenzofuran, m. p. 108°; 1-chloromethyl-1:2-dihydrobenzofuran-6-carboxylic acid, m. p. 200° (decomp.), and its methyl ester, m. p. 107° (decomp.); 1-chloromethyl-1:2-dihydrobenzofuran-4-carboxylic acid, m. p. 212—213° (decomp.), and 1-chloromethyl-4-carboxyvinylene-1:2-dihydrobenzofuran, $\text{CO}_2\text{H}\cdot\text{CH}\cdot\text{CH}\cdot\text{C}_6\text{H}_3\left\langle\begin{smallmatrix}\text{O}\\\text{CH}_2\end{smallmatrix}\right\rangle\text{CH}\cdot\text{CH}_2\text{HgCl}$, m. p.

300° (decomp.), are white, crystalline solids, unless otherwise stated. 1-Iodomethyl-6-methyl-1:2-dihydrobenzofuran, m. p. 88°. 1-Iodomethyl-5-methyl-1:2-dihydrobenzofuran, m. p. 131·5°. 1-Iodomethyl-4-methyl-1:2-dihydrobenzofuran, m. p. 94°. 4-Bromo-1-bromomethyl-1:2-dihydrobenzofuran, m. p. 93°. 4-Bromo-1-iodomethyl-1:2-dihydrobenzofuran, m. p. 101°. 1-Hydroxymethyl-1:2-dihydrobenzofuran, m. p. 152°. 1-Hydroxymethyl-6-methyl-1:2-dihydrobenzofuran, a thick oil. 1-Hydroxymethyl-4-methyl-1:2-dihydrobenzofuran, m. p. 149°. 1-Tartrato-di-(methyl-1:2-dihydrobenzofuran), m. p. 192° (decomp.). 1-Oxalato-di-(methyl-1:2-dihydrobenzofuran), m. p. 175°. The following three *p*-nitrobenzoates are yellow. 1-*p*-Nitrobenzoatomethyl-1:2-dihydrobenzofuran, m. p. 148°. 1-*p*-Nitrobenzoatomethyl-6-methyl-1:2-dihydrobenzofuran, m. p. 162·5°. 1-*p*-Nitrobenzoatomethyl-4-methyl-1:2-dihydrobenzofuran, m. p. 136·5°. 1-Thiocyanatomethyl-1:2-dihydrobenzofuran, m. p. 112·5°. 1-Cyanomethyl-1:2-dihydrobenzofuran, m. p. 162°. 1-Thiocyanatomethyl-4-methyl-1:2-dihydrobenzofuran, m. p. 102·5°. 1-Cyanomethyl-4-methyl-1:2-dihydrobenzofuran, m. p. 148°. 1-Sodiumthiosulphatomethyl-1:2-dihydrobenzofuran forms glistening, white scales. 1-Sodiumthiosulphatomethyl-4-methyl-1:2-dihydrobenzofuran. 1:1-Mercuridimethylenebis-4-methyl-1:2-dihydrobenzofuran. Methyl *p*-allyloxycinnamate, $\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{Me}$, glistening, white plates, m. p. 65·5°, is prepared by boiling a mixture of *p*-coumaric acid, allyl bromide, anhydrous potassium carbonate, and acetone. When heated at 230—245°, it undergoes molecular rearrangement, with formation of methyl *p*-hydroxy-*m*-allylcinnamate, which is hydrolysed by means of aqueous sodium hydroxide solution, giving *p*-hydroxy-*m*-allylcinnamic acid,

$\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{H}$, white crystals, m. p. 169°, which is used in the preparation of 1-chloromethyl-4-carboxyvinylene-1:2-dihydrobenzofuran.

W. S. N.

New Organometallic Compounds. Cuprous Phenyl and Silver Phenyl. RENÉ REICH (*Compt. rend.*, 1923, 177, 322—324).—An ethereal solution of magnesium phenyl bromide dissolves cuprous iodide in the cold, in absence of air, cuprous phenyl, CuPh, being precipitated, after an interval, as a white powder, decomposing at 80°. On warming in benzene solution, diphenyl and a copper mirror result (quantitatively). Cuprous phenyl reacts with water to give benzene and cuprous oxide, with dilute nitric acid to give nitrobenzene, and explodes in presence of the concentrated acid. It decomposes, with blackening, within two days, even in a vacuum.

Cuprous iodide reacts with magnesium ethyl bromide, presumably to give cuprous ethyl, which, however, cannot be isolated, being unstable at temperatures above -18° .

Silver bromide reacts with ethereal magnesium phenyl bromide, the violet solution obtained depositing a yellow precipitate of silver phenyl, AgPh. The preparation is effected in darkness, and the product decomposes in ethereal suspension at -18° in a few hours, to give silver and diphenyl. It is highly explosive.

E. E. T.

Physiological Chemistry.

Effect of Insulin on the Respiratory Exchange. H. W. DUDLEY, P. P. LAIDLAW, J. W. TREVAN, and E. M. BOOCK (*Proc. Physiol. Soc., J. Physiol.* 1923, **57**, xlvii—xlix).—Two independent investigations, by the first two and last two authors, show that although sugar disappears from the blood, the injection of insulin does not produce its effect by directly increasing the rate of combustion of glucose. Experiments by the first-named author further show that the disappearance is not due to an increased glycogen storage in the liver. G. B.

The Distribution of Inorganic Phosphate of the Blood between Plasma and Cells. T. F. ZUCKER and M. B. GUTMAN (*Proc. Soc. Expt. Biol. Med.*, 1921, **19**, 169—171).—By working rapidly with the Bell and Doisy method, the inorganic phosphate found in the plasma is the same as that of whole blood. If the colorimetric reading is made within half an hour after the blood is drawn, the distribution is equal; if one hour elapses, the whole blood contains more than the plasma; after several hours the difference is still greater. Phosphate-ions freely permeate the cell-wall, and are stored as organic, acid-soluble phosphate; the latter in turn is readily hydrolysed when there is need of phosphate-ions in the plasma. CHEMICAL ABSTRACTS.

The Calcium Content of the Blood of Thyroidectomised Animals. MARIE PARHON (*Endocrinology*, 1923, **7**, 311—312).—The blood of thyroidectomised sheep contained a smaller amount

of calcium than normal, supporting the idea that one of the most important functions of the thyroid is the regulation of calcium metabolism.

CHEMICAL ABSTRACTS.

Distribution of Sugar in Whole Blood, Plasma, and Corpuscles; Permeability of Red-blood Corpuscles for Sugar in Diabetic and Non-diabetic Cases. H. J. JOHN (*Arch. Intern. Med.*, 1923, **31**, 555—566).—In the blood drawn from non-diabetic persons in the course of dextrose tolerance tests, the concentration of dextrose in plasma and corpuscles was nearly the same, whereas in diabetic blood obtained under the same conditions the concentration in the plasma was always greater. The difference was not due to relative impermeability of the diabetic corpuscles to dextrose, for when exposed for two hours to a 1% dextrose solution, these took up more dextrose than did non-diabetic corpuscles similarly exposed.

CHEMICAL ABSTRACTS.

The Nature of the Sugar in Blood. J. A. HEWITT (*Brit. Med. J.*, 1923, I, 590—591).—Objections are raised to the technique employed by Cooper and Walter and by Winter and Smith, and it is asserted that no evidence exists that γ -dextrose is a component of normal blood; neither are theories of diabetes mellitus which are dependent on the presence of γ -dextrose securely based. It is, however, admitted that γ -dextrose may have a transient existence, and may perhaps be regarded as an intermediate product in the katabolism of dextrose.

A. A. E.

The Blood Content in Various Animals of Sugar, Residual Nitrogen, Carbamide Nitrogen, Creatinine Compounds, and Uric Acid by Folin's Methods. ARTHUR SCHEUNERT and HERTHA VON PELCHRZIM (*Biochem. Z.*, 1923, **139**, 17—29).—A table is given summarising the values found for the constituents of blood mentioned in the title for a variety of vertebrates—dog, sheep, ox, horse, pig, birds, and fish. As a rule the physiological limits of variation of these constituents are the same in all the animals including man. Uric acid was, however, not found in the blood of dogs, sheep, oxen, horses, pigs, or fishes, but that found in birds agreed in content approximately with that of man.

H. K.

The Uric Acid Content of the Blood of Various Animals. CONSTANZE SCHMITT-KRAHMER (*Biochem. Z.*, 1923, **139**, 30—33).—In view of the results of Scheunert and von Pelchrzim (previous abstract) on the absence of uric acid from the blood of various animals and thus contrary to the results of some other workers, the method of Folin as modified by Pucher and with further slight modifications has again been applied to the blood of various animals containing added known amounts of sodium urate. In all cases, the uric acid found corresponded with that added except in birds, where the excess corresponded with the values found by Scheunert and von Pelchrzim.

H. K.

The Influence of the Normal Working Journey on the Composition of the Blood of the Horse. ARTHUR SCHEUNERT and M. BARTSCH (*Biochem. Z.*, 1923, **139**, 34—37).—The content of sugar, residual nitrogen, carbamide nitrogen, creatine, and creatinine of the blood of a horse performing its daily work was the same as during rest; the capacity for combining with carbon dioxide of the plasma was, however, as a rule depressed. H. K.

The Relation of the Individual Organs to Blood Clotting. KEIZO HIRUMA (*Biochem. Z.*, 1923, **139**, 152—187).—Ligature of the pancreatic ducts in rabbits leads to an enormous increase of fibrinogen in the blood whilst the thrombin content is unchanged. Parallel with this increase in fibrinogen there is a prolonged delay in blood clotting. Thrombin can be stored unimpaired in the frozen condition for some weeks. Its action is rapidly destroyed by shaking serum but is intensified by passage of carbon dioxide. H. K.

The Physico-chemical Bases of Vital Permeability. I and II. R. BRINKMAN and A. VON SZENT-GYÖRGYI (*Biochem. Z.*, 1923, **139**, 261—269, 270—273).—I. The normally observed impermeability of a collodion membrane for hæmoglobin is not due to the narrowness of the pores, because capillary-active substances such as sodium oleate, linolate, glycocholate, digitonin, and Witte peptone render the collodion permeable to hæmoglobin. This is a reversible condition of the pores. As a working hypothesis the view is adopted that only the positively adsorbed substances can enter the capillaries with the water and pass through. II. A collodion membrane impermeable to hæmoglobin is rendered permeable by treatment with atropine, pilocarpine, caffeine, strychnine, quinine, and morphine, but not by codeine. Cocaine and novocaine have no action. H. K.

The Swelling of Blood-corpuscles and Hæmolysis. KLOTHILDE GOLLWITZER-MEIER (*Biochem. Z.*, 1923, **139**, 86—113).—Washed blood-corpuscles of man, when suspended in various isosmotic salt solutions and submitted to increasing tensions of carbon dioxide, undergo swelling and hæmolysis. The swelling is favoured by anions in the order $\text{Cl} > \text{NO}_3 > \text{SO}_4$ and by kations in the order $\text{Ca} > \text{Mg} > \text{K} > \text{Na}$. For hæmolysis, however, a different order is observed, $\text{NO}_3 > \text{Cl} > \text{SO}_4$ and $\text{Ca} > \text{Mg} > \text{K} > \text{Na}$. Corpuscles washed with small quantities of isosmotic dextrose or sucrose solutions show little agglutination, but with increased carbon dioxide tension there is progressively increasing agglutination, sedimentation, and hæmolysis. Suspensions of corpuscles rotated in a tonometer undergo spontaneous hæmolysis attributable to electrokinetic processes. H. K.

Placental Transmission. I. The Calcium and Magnesium Content of Foetal and Maternal Blood-serum. L. JEAN BOGERT and E. D. PLASS (*J. Biol. Chem.*, 1923, **56**, 297—307).—At the time of birth, the calcium content of the serum of the foetus is

higher than that of the mother; the value for the former is usually higher, and that of the latter lower, than the normal value. No difference was observed in the magnesium content; in both cases, this showed a tendency to fall below the normal value. E. S.

Placental Transmission. II. The Various Phosphoric Acid Compounds in Maternal and Fœtal Serum. E. D. PLASS and EDNA H. TOMPKINS (*J. Biol. Chem.*, 1923, **56**, 309—317).—A comparison has been made between the distribution of phosphoric acid in maternal and fœtal serum at the time of birth. Lipoid phosphoric acid is present only in small quantities in fœtal blood, whilst its content is above the normal in the blood of the mother. The value for inorganic phosphoric acid is low in the serum of the mother and high in that of the fœtus. There is also a tendency for organic phosphoric acid to be higher in the serum of the fœtus than in that of the mother. The total phosphoric acid content is greater in maternal than in fœtal serum. E. S.

The Inhibitory Effect of Blood-serum on Hæmolysis. ERIC PONDER (*Proc. Roy. Soc.*, 1923, [B], **95**, 42—61).—Hæmolysis of red blood-cells by saponin or by sodium taurocholate is inhibited by serum protein. A quantitative study has been made of this effect. The degree of inhibition is measured in terms of the amount of hæmolysing agent used up by the protein. The inhibitory effect of serum is shown to be approximately constant for sera from different animals belonging to one species and to be constant from day to day, but to change if the serum be dried or exposed to air. The quantity of hæmolytic substance neutralised per unit of serum decreases with increase in the concentration of serum, and the general conclusion is drawn that the inhibition is due to the formation of a loose adsorption compound. Hæmoglobin inhibits in a way similar to that of serum protein. W. O. K.

Influence of Pyrimidone on Metabolism. HANS GESSLER (*Arch. expt. Path. Pharm.*, 1923, **98**, 257—287).—Administration of pyrimidone to patients with fever causes a reduction in heat production, a retention of water and of sodium chloride, and, apparently, a diminution in the destruction of body proteins. E. S.

The Calcium and Phosphoric Acid Metabolism of the Horse when Normally Fed. ARTHUR SCHEUNERT, ADOLF SCHATTKÉ, and MARTA WEISE (*Biochem. Z.*, 1923, **139**, 1—9).—For a horse receiving a daily ration of oats, hay, and chopped straw, the daily intake was 25.5 g. CaO and 53.2 g. P_2O_5 . Over an experimental period of thirteen days during which daily analyses were made of urine and fæces, the total unexcreted CaO for thirteen days was 26.0 g. and P_2O_5 148.5 g. In another horse, however, fed on oats and hay the daily intake was CaO 16.1 g., and P_2O_5 36.5 g. and over a ten-day period of observation the total unexcreted CaO over ten days was 3.5 g. whilst the P_2O_5 balanced. The conclusion is drawn that observations over too short periods are liable to lead to wrong conclusions. H. K.

The Influence of Exclusive Oat Feeding on the Calcium and Phosphoric Acid Metabolism of the Horse. ARTHUR SCHEUNERT, ADOLF SCHATKE, and MARTA WEISE (*Biochem. Z.*, 1923, **139**, 10—16).—Exclusive feeding of a horse on oats (a diet rich in phosphates but poor in calcium) over a period of ten days showed a surplus excretion of 83.9 g. of CaO, but an approximate P_2O_5 equilibrium. The same was observed in another horse fed initially on oats, hay, and chopped straw, when the hay was omitted. A rich phosphate diet poor in calcium can therefore extract calcium from the depots of the fully-grown horse. H. K.

The Calcium Balance. ADOLF SINDLER (*Pflüger's Archiv*, 1922, **197**, 386—403; from *Chem. Zentr.*, 1923, i, 859).—Two feeding experiments in three periods with growing individuals showed that the calcium balance depends on the supply of meat. The calcium balance is more favourably affected by a decrease in the meat ration than by addition of calcium chloride. In the latter case, the first retention of calcium is followed by its elimination by the kidneys and intestines. Loss in phosphorus consequent on administration of calcium was not observed, but rather an improvement of the phosphorus balance. Increased compensatory retention of potassium and increased excretion of sodium was also observed. The magnesium balance appears to depend on several factors. G. W. R.

The Influence of the Phosphate-ion on Carbohydrate Metabolism. I. H. ELIAS and A. LÖW (*Biochem. Z.*, 1923, **138**, 279—283).—Perfusion of surviving livers of frogs with Ringer solution containing phosphate and dextrose shows that glycogen is not stored, but is, on the contrary, mobilised. The fall of blood-sugar in cases of hyperglycæmia by administration of phosphates does not therefore appear to be due to storage of glycogen. H. K.

The Influence of the Phosphate-ion on Carbohydrate Metabolism. II. H. ELIAS, C. POPESCU-INOTESTI, and C. ST. RADOSLAV (*Biochem. Z.*, 1923, **138**, 284—293).—Intravenously administered hypertonic mono- or di-sodium phosphates depresses the blood-sugar content of dogs and rabbits in small doses. Larger doses lead to a hyperglycæmia in the rabbit, but in the dog to a protracted hypoglycæmia. H. K.

The Influence of the Phosphate-ion on Carbohydrate Metabolism. III. H. ELIAS, C. POPESCU-INOTESTI, and C. ST. RADOSLAV (*Biochem. Z.*, 1923, **138**, 294—298).—In dogs and rabbits the hyperglycæmia produced by adrenaline is depressed by phosphate injections. H. K.

The Influence of the Phosphate-ion on Carbohydrate Metabolism. IV. H. ELIAS, C. POPESCU-INOTESTI, and C. ST. RADOSLAV (*Biochem. Z.*, 1923, **138**, 299—306).—Intravenous doses of phosphate which are without action on the blood-sugar content of normal dogs depress the hyperglycæmia and glycosuria of dogs with extirpated pancreas. H. K.

Muscular Exercise, Lactic Acid, and the Supply and Utilisation of Oxygen. A. V. HILL and HARTLEY LUPTON (*Quart. J. Med.*, 1923, **16**, 135—170).—Oxygen is not used in the primary breakdown processes of rest or activity; it is used only in recovery processes. Large amounts of lactic acid, up to 1.5 g. per kg. body weight, may be produced. If exercise is too great the supply of oxygen cannot cope with the production of lactic acid and exhaustion results. The exhaustion following long continued moderate exercise is due to the diffusion of lactic acid out of the muscles where it is slowly oxidised and removed. Lactic acid in the body always appears as the lactate of sodium, potassium, or ammonium. The rate at which chemical processes of recovery occur starts at a low level, rises to a maximum, and slowly falls to zero. The greater the initial effort the greater is the relative rate of recovery.

CHEMICAL ABSTRACTS.

Carbamide as a Protein Substitute for Ruminants. F. HONCAMP and E. SCHNELLER (*Biochem. Z.*, 1923, **138**, 461—496).—Metabolism experiments were carried out on two wethers fed on a standard diet with and without the addition of carbamide. The nitrogen content of the faeces shows little change, but in one wether a protein sparing action of the carbamide was observed, and in the other almost all the carbamide was excreted in the urine. On a protein-deficient diet containing copious carbohydrate, carbamide promotes storage of protein. The substitution of casein for carbamide led to a greater storage of nitrogen. H. K.

The Life-supporting Action of the Leguminous Tribe. L. BERCZELLER and A. BILLIG (*Biochem. Z.*, 1923, **139**, 225—228).—White rats fed exclusively on the broad bean (*Vicia faba*) live fifteen to twenty times longer than when fed on the haricot bean. H. K.

The Nutritive Value of Fats and Lipoids. II. Nutritive Value of Fatty Acids and Glycerol in their Combined and Uncombined States. KATSUMI TAKAHASHI (*J. Chem. Soc. Japan*, 1923, **44**, 547—573).—The nutritive value of six pure fatty acids, stearic, palmitic, oleic, decolic, lauric, and myristic acids, and of the corresponding triglycerides in presence and absence of vitamin-A was investigated by means of feeding experiments on mice. Tables and curves of the results are given, and may be summarised as follows: (1) In like conditions, free fatty acids have a less nutritive value than the corresponding glycerides. (2) In the presence of a small quantity of vitamin-A, the nutritive value of the fatty acids increases as the molecular weight of the acids decreases and the same is the case with the corresponding glycerides. The higher acids, such as palmitic and stearic acids, are bad as food, but stearic is better than oleic acid. (3) By supplying a sufficient quantity of vitamin-A, mice grow normally with food in which fatty acids are present in the form of triglycerides but not if they are in the free state. The effect on the growth of each glyceride is almost the same. (4) Vitamin-A has no direct effect on the digestion and absorption of fats, (5) It is improbable that fats are

absorbed after complete decomposition into fatty acids and glycerol in the digestive organs. (5) Animals fed with a large quantity of free acids (stearic, palmitic, etc.) become less resistant to disease and are apt to develop diseases of the respiratory organs, especially pneumonia. K. K.

Nutritive Value of Fats and Lipoids. III. Are Carbohydrates and Fats Necessary as the Food of Animals? KATSUMI TAKAHASHI (*J. Chem. Soc. Japan*, 1923, **44**, 574—589).—As already stated by Funk ("The Vitamines," p. 346), vitamin-B has an intimate connexion with the metabolism of carbohydrates. When carbohydrates are ingested without vitamin-B, they have an injurious effect on the nutrition of animals. In general, unlike proteins, vitamins, and salts, fats and carbohydrates are not to be regarded as absolutely necessary elements of nutrition, but merely as auxiliary sources of energy. K. K.

The Phosphorus Metabolism of the Nervous System. I. ELISABETH HECKER and HANS WINTERSTEIN (*Z. physiol. Chem.*, 1923, **128**, 302—316).—Estimations made by Bloor's nephelometric method of the phosphorus content of the brain and of the cerebrospinal cord of the frog show that the latter contains twice as much phosphorus as the former and that the upper half of the spinal cord contains less than the lower. W. O. K.

The Content of the Normal Human Cerebrospinal Fluid in Phosphates and Sulphates. FELIX HAUROWITZ (*Z. physiol. Chem.*, 1923, **128**, 290—301).—The normal human cerebrospinal fluid contains on the average 0.0018% of phosphorus and 0.0011% of sulphur. These values are fairly constant for different cerebrospinal fluids and are less than the corresponding values for the blood. The phosphorus is almost completely inorganic, whilst about one-fifth of the sulphur is in combination in protein. W. O. K.

Metabolism of the Surviving Mammalian Heart. FELIX KLEWITZ (*Arch. expt. Path. Pharm.*, 1923, **98**, 91—105).—Perfusion experiments have been made with surviving hearts from normal dogs and rabbits and also from animals the glycogen supply of which had been depleted by hunger and injection of phloridzin. The results indicate that, in all probability, the surviving heart can utilise fats and nitrogenous substances, in addition to carbohydrates, as sources of energy. Further, when nitrogenous substances (amino-acids) are added to the perfusion fluid, these may be retained by the heart probably both as a reserve supply of energy and to replace wasted tissue. Creatine and creatinine are formed in varying quantities by surviving hearts. E. S.

The Effect of Insulin on the Glycogen in the Tissues of Normal Animals. HAROLD WARD DUDLEY and GUY FREDERIC MARRIAN (*Biochem. J.*, 1923, **17**, 435—438).—The sugar which disappears from the blood of normal animals under the influence of insulin is neither converted into nor stored as glycogen either in the liver or in the skeletal muscles. The glycogen in these two tissues

disappears almost completely when a dose of insulin which is sufficient to cause hypoglycæmic convulsions is administered. No evidence could be found that carbohydrate is converted into fat in normal animals on administration of insulin. S. S. Z.

Unsaponifiable Matters (Higher Alcohols) in Shark and Ray-liver Oils. II. YOSHIYUKI TOYAMA (*J. Chem. Ind. Japan*, 1923, 26, 37—48; cf. *ibid.*, 1922, 25, 1).—The unsaponifiable matter of the liver oil of *Chlamydoselachus anguineus*, Garman, is mainly composed of oleic alcohol. Small amounts of cetyl alcohol and of cholesterol were also found, but neither selachyl alcohol nor batyl alcohol could be detected. It also contains an appreciable amount of squalene and a minute quantity of a saturated hydrocarbon. The unsaponifiable matters of the liver oils of (1) *Scymnorhinus licha*, (2) *Centroscyllium ritteri*, (3) *Hyprtranchias deani*, (4) *Galeocерdo tigrinus*, and (5) two commercial shark-liver oils contained large amounts of selachyl alcohol, $C_{20}H_{40}O_3$, and of batyl alcohol, $C_{20}H_{42}O_3$. Squalene was found in those of (1), (2), and (5) K. K.

Presence of Sucrase in the Walls of the Ovarian Mucoid Cysts. P. LECÈNE and H. BIERRY (*Compt. rend.*, 1923, 177, 222—224).—By macerating the walls of ovarian mucoid cysts with water in presence of toluene and thymol, the authors obtained a solution which fermented sucrose, indicating the presence of a sucrase. Morphological analogy probably exists between the tissue examined and the lining of the foetal intestine, for which a sucrase is the characteristic enzyme. E. E. T.

The Function of the Parathyroids. HARALD A. SALVESEN (*J. Biol. Chem.*, 1923, 56, 443—456).—Parathyroidectomised dogs have been maintained alive for about two years by administration of calcium salts either intravenously in the form of calcium chloride, or orally in the form of milk or of soluble calcium salts. During this time, the animals were in a state of “latent tetany”; cessation of the administration of calcium salts always produced tetany. During latent tetany, the calcium content of the blood is below, and that of the inorganic phosphoric acid above, the normal. The appearance of tetany is always accompanied by a decrease, and its disappearance by an increase in the calcium content of the blood. During latent tetany, and more so during tetany, there is a lowered tolerance for sugar which is due to a functional disturbance of the glycogen-forming organs. These results are in agreement with the view put forward by MacCallum and Voegtlin (*J. Expt. Med.*, 1909, 11, 118), and subsequently abandoned, that the symptoms of parathyroid insufficiency are due to calcium deficiency. E. S.

Creatine Formation during Tonic Muscle Contraction. K. UYENO and T. MITSUDA (*J. Physiol.*, 1923, 57, 313—317).—In male toads and frogs, creatine was found to increase in the claspings muscles during coupling in the breeding season. Decerebrate rigidity in cats also increases the creatine in the rigid muscles in accordance with the results of Pekelharing and van Hoogenhuyze

(A., 1910, ii, 324), but contrary to those of Dusser de Barenne and Terveart (*Pflüger's Archiv*, 1922, 195, 370).

The carnosine content of muscle is, on the other hand, not influenced by rigidity. G. B.

Creatine Formation in Frog's Muscle Contracted by Nicotine. T. MITSUDA and K. UYENO (*J. Physiol.*, 1923, 57, 280—286).—The authors confirm the older results of Pekelharing (A., 1911, ii, 1115) that the contracted muscles contain more creatine than the normal; the increase is something like 5—10% of the total amount in the muscle. G. B.

The Pigment Question. B. BRAHN and M. SCHMIDTMANN (*Arch. path. Anat. Physiol.*, 1922, 239, 488—490; from *Physiol. Abstr.*, 1923, 8, 199).—The brown pigment which may be extracted from myocardium which has undergone brown atrophy cannot be distinguished from melanin. The wide variation in the published analysis of melanin indicates that this is not a single substance, but a group of substances with similar properties. The pigment of brown atrophy is, like melanin, iron-free and contains sulphur and phosphoric acid. Its rather sparing solubility in alcohol does not indicate a non-melanin nature, as melanin varies considerably in this respect, becoming decreasingly soluble with age. For the present, human endogenous pigments are to be divided into two classes, those derived from hæmoglobin, and the autochthonous pigments or melanins. W. O. K.

Pigment of Human Skin. G. O. E. LIGNAC (*Arch. path. Anat. Physiol.*, 1922, 240, 383—416; from *Physiol. Abstr.*, 1923, 8, 228).—Four stages in human skin pigmentation can be distinguished. First there is formed a parent substance, a prepigment sensitive to light, and reducing silver nitrate. From this is derived, by oxidation and polymerisation, a melanin which still reduces silver nitrate but is bleached only by active oxygen. It is possible that the prepigment is an *o*- or *p*-dihydrobenzene derivative and that melanin is produced by the oxidation of quinonoid substances. Strong oxidation of melanin brings about the third stage. A yellow pigment which will not reduce silver nitrate is formed. This pigment can be obtained by the action of hydrogen peroxide. In the body, it has been observed only in the skin lymph nodes. The fourth phase includes only the colourless decomposition products of melanin. There is no sufficient ground for assuming the presence of oxidising or other enzymes in the skin. Radiation with ultra-violet light leads to a primary pigmentation and secondary depigmentation, in which hydrogen peroxide may be concerned. W. O. K.

The Phosphorus Content of Pathological Melanin. O. SALKOWSKI (*Arch. path. Anat. Physiol.*, 1922, 240, 353—355; from *Physiol. Abstr.*, 1923, 8, 199).—Melanin from melanotic livers contained 0.99% and 0.71% of phosphorus in two cases. Phosphorus was found in the examination of another melanotic liver melanin. Brown pigment from a brown atrophied heart contained 0.18% of

phosphorus. The significance of this small amount with respect to the nature of the pigment of the brown heart is doubtful. Other investigators have found 0.50% of phosphorus in the pigment of the brown heart.

W. O. K.

Iron Reaction in Malarial Pigment. E. MAYER (*Arch. path. Anat. Physiol.*, 1922, **240**, 117—126; from *Physiol. Abstr.*, 1923, **8**, 199).—Although the usual microchemical reactions do not show the presence of iron in malaria pigment, iron can be demonstrated by certain modifications in which it is brought gradually into solution and made to react with reagents at the same time. This is achieved by staining with Berlin-blue in which aqueous hydrochloric acid is replaced by 2—5% alcoholic hydrochloric acid, in which the malaria pigment is slowly solidified, or with the Hueck modification of the Turnbull-blue reaction. In this method, the ammonium sulphide is allowed to act until the pigment begins to dissolve. The use of these methods confirms Seyfarth's finding of iron in malaria parasites. The finding of blue haloes indicates that the iron split from the pigment diffuses to the boundaries of the pigment containing cells. Occasionally blue or green globules of malaria pigment are seen with this technique. Formalin pigment does not give the iron reaction with this method, which can accordingly be used for differential diagnosis.

W. O. K.

The so-called Lipofuscin. O. LUBARSCH (*Arch. path. Anat. Physiol.*, 1922, **239**, 491—503; from *Physiol. Abstr.*, 1923, **8**, 199).—The evidence at hand indicates that lipofuscin is a mixture of pigment and fat. The designation "lipofuscin" and the distinction from melanin of the substance designated is not warranted. It is true that physiological melanin is formed in ectodermal cells. Lipofuscin is not limited to ectodermal cells, although it is found there chiefly. It is not known whether its rare occurrence in connective-tissue is to be attributed to its formation or to its deposition there. The author distinguishes three endogenous pigments: (1) the hæmoglobinogenous; (2) the proteinogenous, including "lipofuscin"; and (3) the lipoidogenous, including only the true lipochromes.

W. O. K.

Some Derivatives of "Saccharin." A. F. HOLLEMAN (*Rec. trav. chim.*, 1923, **42**, 839—845).—A discussion of the connexion between taste and constitution. A résumé of most of the work done on this subject is given. It is shown that benzene disulphimide has a very sweet taste, but much less than "saccharin," and in addition it has a bitter after-taste; "6-chlorosaccharin" is about half as sweet as "saccharin." The imide of quinoleinic acid is sour, whilst phthalimide is tasteless and quinoleic acid is acidic.

J. F. S.

The Formation of Lactose in the Lacteal Gland. The rôle of Leucine. ERICH HESSE (*Biochem. Z.*, 1923, **138**, 441—460).—The observation of Röhmann that addition of leucine greatly accelerates the formation of lactose in the sterile maceration juice of the lacteal gland of the cow has been followed up. By fraction-

ation of the osazones, maltosazone has been isolated. Attention is directed to Fischer's opinion that lactose could possibly arise out of maltose by a stereochemical change. H. K.

The Reduction of Methylene-blue by Iron Compounds. EDWARD JAMES MORGAN and JUDA HIRSCH QUASTEL (*Proc. Roy. Soc.*, 1923, [B], 95, 61—71).—Boiled milk to which ferrous sulphate has been added will reduce methylene-blue. The effect is shown to be due entirely to the mineral constituents of the milk, as methylene-blue is reduced by ferrous sulphate in the presence of sodium hydroxide, carbonate, hydrogen carbonate, or phosphate, and of the sodium salts of various organic acids such as acetic, tartaric, or citric, two molecules of ferrous sulphate being required to reduce one of methylene-blue. This effect seems to depend on the low ionisation of ferric hydroxide, that is, on the high affinity of the ferric-ion for the hydroxyl-ion. W. O. K.

Action of Alcoholic Extracts of Pancreas (Insulin) on the Critical Glycæmia. H. CHABANIER, C. LOBO-ONELL, and M. LEBERT (*Bull. Soc. Chim. biol.*, 1923, 5, 389—397).—Mainly a confirmation of results obtained by McLeod and his collaborators. E. S.

The Action of Insulin in Glycæmia and Acidosis. A. DESGREZ, H. BIERRY, and F. RATHERY (*Compt. rend.*, 1923, 176, 1833—1836).—Insulin in the form of powder, as prepared by a series of fractional precipitations, is to be preferred to the simple extracts of the active substance. The latter exert a characteristic toxicity in addition to their effect on glycæmia. Analyses are quoted showing the marked effect exerted by stated doses of insulin in diminishing the excretion of sugars, ketones, and β -hydroxybutyric acid. The suggestion is made that the metabolism of these substances is probably conditioned by certain tautomeric forms of dextrose. H. J. E.

Use of Yeast Extracts in Diabetes. L. B. WINTER and W. SMITH (*Nature*, 1923, 112, 205; cf. this vol., i, 513, 727).—The variability of the activity of the extract from different samples of yeast is confirmed, and it is noted that micro-organisms other than yeast can also yield substances which reduce the concentration of the blood-sugar. A. A. E.

Tetany. S. G. ROSS (*Can. Med. Assoc. J.*, 1923, 13, 97—103).—In four cases of tetany (three gastric, the fourth mercuric chloride poisoning), the sodium and chloride content of the blood were reduced, the hydrogen carbonate increased, the calcium normal, and the inorganic phosphorus increased in two cases. In a case of mercuric chloride poisoning with acute nephritis but no tetany, the sodium and chloride content were low, the hydrogen carbonate and calcium normal, and the phosphorus high.

CHEMICAL ABSTRACTS.

Derivatives of Phenylarsinic Acid (Quinquevalent Arsenic) in Treatment of Experimental Trypanosomiasis and Spirilliosis. Relation between the Therapeutic Action of the Aromatic Arsinic Acids and their Constitution. E. FOURNEAU, A. NAVARRO-MARTIN, and M. and MME. TRÉFOUEL (*Ann. Inst. Pasteur*, 1923, **37**, 551—617).—A very large number of previously known derivatives of phenylarsinic acid, $C_6H_5 \cdot AsO_3H_2$, have been prepared and examined with regard to their maximum tolerated dose, and their effective curative dose in animals infected with trypanosomes or spirochaetes. Brief accounts of the chemical methods used in preparing the compounds are given.

W. O. K.

The Analysis of the Pharmacological Action of Nitrous Oxide. HEINRICH BART (*Biochem. Z.*, 1923, **139**, 114—138).—Contrary to Wieland's results, the author finds that nitrous oxide acts as a true lipoid-soluble narcotic. Experiments were carried out on frogs at various temperatures between 3° and 25° with air, hydrogen, nitrogen, and nitrous oxide, and with various mixtures with oxygen, on tadpoles and worms and some anaërobes, as, for example, ascarids.

H. K.

The Pharmacology of Potassium- and Calcium-ions. M. ROSENMANN (*Z. ges. exp. Med.*, 1922, **29**, 334; from *Physiol. Abstr.*, 1923, **8**, 202).—Investigation of the action of adrenaline, pilocarpine, ergotoxin, etc., on various muscular processes in the presence and absence of calcium- and potassium-ions tends to show that the action of calcium is chiefly stimulant, whilst that of potassium is chiefly paralytic. Calcium in the presence of adrenaline shows an exaggerated paralytic action.

W. O. K.

Lævulose, Dextrose, and Galactose Tolerance in Dogs. MEYER BODANSKY (*J. Biol. Chem.*, 1923, **56**, 387—393).—The ingestion of lævulose is less effective than that of dextrose in producing a rise in blood-sugar. In agreement with the results of Foster (this vol., i, 503), and in opposition to those of Folin and Berglund (*A.*, 1922, i, 487), galactose has been found to produce a marked hyperglycæmia. This, however, is prevented if sufficient dextrose is present in the circulation. The reducing substances excreted in the urine following the ingestion of lævulose and galactose do not consist of these sugars.

E. S.

[Physiological] Action of Homologous Aliphatic Quaternary Ammonium Bases. FRITZ KÜLZ (*Arch. exp. Path. Pharm.*, 1923, **98**, 339—369).—A comparison has been made of the physiological actions of the quaternary salts comprised in the two general series trimethylalkylammonium iodide and triethylalkylammonium iodide. The curare action of the two series does not run parallel. In the trimethyl series, the activity decreases from the lowest member to that containing a propyl group; the butyl derivative

has ten times the activity of the propyl derivative; thereafter the activity increases slowly as the series is ascended. In the triethyl series, the first two members have approximately the same activity; succeeding members show a regular increase. The curve of activity of each series is, in general, the reciprocal of the curve of solubility of the corresponding perchlorates. The action of the various members of the two series on the vagus nerve and on skeletal muscle has also been determined. E. S.

The Relations between Constitution and [Physiological] Action in Alicyclic Tetrahydro- β -naphthylamine and its Derivatives. II. M. CLOETTA and E. WASER (*Arch. expt. Path. Pharm.*, 1923, **98**, 198—220).—The authors have previously shown (A., 1913, i, 1280) that the physiological action (dilation of the pupils and rise in body temperature and blood pressure) of tetrahydro- β -naphthylamine is not modified qualitatively by the introduction of one methyl group into the amino-group. When, however, two methyl groups are introduced, such a modification does occur. Thus, the dimethyl derivative causes a fall in blood pressure and dilation of the pupils, but is without action on the body temperature. The corresponding methochloride has an action intermediate between that of the mono- and di-methyl derivatives. It produces a rise in blood pressure, dilation of the pupil, and is without action on the body temperature; in addition, it has a curare-like action. This quaternary salt, like 2-amino-methyl-*ac*-tetrahydro- β -naphthalene, differs from the other derivatives which produce a rise in blood pressure in that successive injections are equally effective in their action. The observation made previously (*loc. cit.*), that the introduction of an acid group into the amino-group of tetrahydro- β -naphthylamine reverses the action of this substance, has been found to hold for other groups. Thus, injections of the carbamic ester and of the ethylthiocarbamido-, phenylcarbamido-, phenylthiocarbamido-, and even of the tetrahydro- β -naphthylthiocarbamido- derivatives of tetrahydro- β -naphthylamine cause none of the effects produced by the free base. When the distance of the amino-group from the aromatic nucleus is increased, as in aminomethyltetrahydro- β -naphthalene, no essential difference in the action is produced; when it is decreased, as in α -hydrindamine, the action is considerably diminished.

E. S.

Detoxication of Cyanides in Health and Disease. MEYER BODANSKY and MOISE D. LEVY (*Arch. Int. Med.*, 1923, **31**, 373—389).—A study of the excretion of thiocyanate in the saliva before and after the ingestion of potassium cyanide or thiocyanate by normal and diseased persons. The latter excreted less thiocyanate than the former, but the increases after ingestion of potassium cyanide and thiocyanate were somewhat greater. It appears that in certain diseases, such as pellagra, the cyanide detoxifying power remains unimpaired, provided the supply of cystine is adequate.

CHEMICAL ABSTRACTS.

Comparison of the [Physiological] Actions of *d*-, *l*-, and *i*-Camphor. V. Electrographical Investigation on Isolated Frog's Hearts. G. JOACHIMOGLU and E. MOSLER (*Arch. expt. Path. Pharm.*, 1923, **98**, 1—11).—The same physiological action was produced by the three enantiomorphs, thus confirming results obtained by other means (A., 1917, i, 528; 1921, i, 146). E. S.

Chemistry of Vegetable Physiology and Agriculture.

Protein Synthesis by *Azotobacter*. O. W. HUNTER (*J. Agric. Res.*, 1923, **24**, 263—274).—Dried *Azotobacter* cells containing 11·8% protein were obtained by culture on solid media, whereas those from an aërated liquid culture had a protein content of 30%. Within the limits of the experiment, the yield of cells increased with the amount of sugar in the medium, and the nitrogen fixed was generally of the order 16—17 mg. per g. of dextrose consumed. In media containing molasses, *Azotobacter* converted soluble nitrogenous substances into more complex proteins, and at the same time utilised the molasses as a source of energy for nitrogen fixation. The addition of straw to the media did not cause any appreciable increase in the quantity of nitrogen fixed.

A. G. P.

The Propionic Acid Fermentation of Lactose. J. M. SHERMAN and R. H. SHAW (*J. Biol. Chem.*, 1923, **56**, 695—700).—The accelerating effect which certain other organisms have on the production of propionic acid by *Bacterium acidii propionici* (d) (*J. Gen. Physiol.*, 1921, **3**, 657) is not due to the production of lactic acid from the lactose by these organisms.

E. S.

The Production of Tyrosine by a Putrefactive Anaërobe. S. C. HALL and F. FINNERUD (*Proc. Soc. Expt. Biol. Med.*, 1921, **19**, 48—50).—Certain anaërobes, as *Bacillus bifermentans*, *B. centrosporogenes*, and *B. histolyticus*, when grown in deep brain medium, ground meat, salmon, milk, or suspended casein, form tyrosine. The medium must not contain an excess of monosaccharides.

CHEMICAL ABSTRACTS.

Lactic Acid Fermentation of Dextrose by Peptone. CHR. BARTHEL and H. VON EULER (*Z. physiol. Chem.*, 1923, **128**, 257—283).—The experiments of Schlatter (A., 1922, i, 1096), who has claimed that he has demonstrated the lactic acid fermentation of dextrose by peptone, have been repeated with negative results, provided that the conditions were aseptic. Where fermentation with production of lactic acid set in, bacterial contamination could be shown.

W. O. K.

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Fat Metabolism of the Timothy Grass Bacillus. II. The Carbon Balance-sheet and Respiratory Quotient.

MARJORY STEPHENSON and MARGARET DAMPIER WHETHAM (*Proc. Roy. Soc.*, 1923, [B], 95, 200—206; cf. A., 1922, i, 500).—The carbon balance of timothy grass bacillus, grown in a culture medium containing dextrose as source of carbon, was studied. The carbon was completely accounted for by the carbon dioxide formed, the carbon in the organism, and the carbon remaining in the culture medium after filtration. The longer the duration of the experiment, the more carbon dioxide is produced from the reserve lipid of the bacillus. The respiratory quotient is greater than unity in the earlier part of the experiment when synthesis of lipid and protein is taking place. Afterwards, when the dextrose is consumed, the respiratory quotient sinks below unity. G. W. R.

Does the Introduction of an Ethoxyl Group into Aromatic Compounds Increase their Bactericidal Action on the *Pneumococcus* and the *Gonococcus*? A. D. HIRSCHFELDER and L. J. PANKOW (*Proc. Soc. Expt. Biol. Med.*, 1921, 19, 64—67).—The introduction of an ethyl group into substances like sodium phenol-sulphonate and sodium salicylate or *p*-aminophenol and *p*-nitrophenol does not cause increased bactericidal action.

CHEMICAL ABSTRACTS.

The Influence of the Medium on the Toxicity of certain Alkaloids towards Protozoa. T. A. HENRY and H. C. BROWN (*Trans. Roy. Soc. Trop. Med.*, 1923, 17, 61—71).—Quinine, emetine, and conessine are much more toxic to protozoa when in an alkaline medium. There would appear to be a specific toxic action of the alkaloid followed by some secondary action of the alkali. The uses of this observation in the alkaloidal treatment of protozoal diseases are noted. A. G. P.

Volutin and Nucleic Acid in Various Yeasts. M. GLAUBITZ (*Biochem. Z.*, 1923, 139, 77—85).—By staining the volutin granules in a variety of *Torula* and distillery yeasts with methylene-blue followed by dilute acid (Meyer) and the nucleic acid by methylene-blue followed by phosphine, an attempt has been made to determine whether volutin and nucleic acid are identical. The staining reactions were found insufficient to decide. In all cases, nucleic acid appeared to be present to a lesser extent than volutin. There is no relation between baking capacity and volutin content. For *Torula* yeasts the greater the reproductive capacity the greater the nucleic acid content. H. K.

Action of Yeast on Calcium Lactate: Production of Ethyl Alcohol. E. KAYSER (*Compt. rend.*, 1923, 176, 1662—1665).—The addition of various types of yeast to solutions of calcium lactate containing those inorganic substances which would be associated with the yeast under natural conditions results in the production of pyruvic, acetic, and valeric acids, together with aliphatic alcohols. The rate of action varies with the type of

yeast used, is more rapid at 28° than at 12°, and takes place to a greater extent at the surface than in the body of the solution. It increases with concentration of calcium lactate, and is most marked in the presence of potassium dihydrogen phosphate and of ammonium phosphate. The production of pyruvic acid is favoured by the addition of calcium carbonate. Small quantities of ethyl valerate and amyl acetate were also obtained in most of the experiments, the amount depending on the experimental conditions.

H. J. E.

Phytochemical Reductions. XVII. Partial Reduction of Dinitro-compounds. CARL NEUBERG and ELSA REINFURTH (*Biochem. Z.*, 1923, **138**, 561—568).—*m*-Dinitrobenzene, when added in alcoholic solution to an actively fermenting surface yeast in the presence of sucrose or starch syrup, becomes reduced to *m*-nitroaniline and *m*-dinitroazoxybenzene. An intermediate product in the formation of the latter is probably *m*-nitrophenylhydroxylamine as the solutions at an intermediate stage showed the methæmoglobin reaction.

H. K.

The Nitrogenous Bases in the Mycelium of *Aspergillus niger*. W. VORBRÖDT (*Bull. acad. polon. sci. let.; classe sci. math. nat.*, 1921, [B], 223—236; from *Physiol. Abstr.*, 1923, **8**, 208).—From 1400 g. of dry mycelium the following were obtained: adenine (0·7 g.), xanthine, guanine, cytosine (0·3 g.), choline (0·4 g.), lysine (0·6 g.); ammonia, arginine, and histidine were not found. It is thought that the relatively high content of free bases indicates that these are intermediate products in the synthesis of proteins and not catabolic products.

W. O. K.

Chemistry of the Higher Fungi. XVII. *Amanita muscaria*, L., *Inoloma alboviolaceum*, Pers., *Boletus Satanas*, Lenz., and *Hydnum versipelle*. LUCIE BARD and JULIUS ZELLNER (*Monatsh.*, 1923, **44**, 9—17).—*Amanita muscaria* contains a colloidal substance, viscosin (cf. A., 1918, i, 55), and a readily soluble substance, mycetid. The former, on hydrolysis, affords dextrose and methylpentoses, but no mannose or galactose; the latter affords dextrose and other sugars. Hydrolysis of the fungus membrane gives dextrose, pentoses, methylpentoses (the two latter being formed from the more readily hydrolysed portion of the parent polysaccharide) and glucosamine (produced with difficulty by the hydrolysis of a chitin-like parent substance).

Inoloma alboviolaceum contains oleic and palmitic acids (together with derived fats), lecithins (?), mycose, dextrose, choline (?), and a mixture of substances resembling ergosterol and cerebrin.

Boletus Satanas, known to contain mannitol and mycose, also contains palmitic acid and derived fats, unsaturated acids of the oleic and linoleic type (oxidation of the mixture of acids, with permanganate, affording a dihydroxystearic acid, m. p. 135°, and sativic acid, m. p. 173°), ergosterol, m. p. 164° (identical with that found in ergot and toadstools), a substance resembling cerebrin and one resembling a phlobaphen, mannitol, choline, muscarine, and potassium chloride.

Hydnum versipelle contains a resin [easily hydrolysed, giving amorphous acids and resembling one previously isolated (A., 1915, i, 1086)], a substance resembling ergosterol, mannitol, dextrose, and choline. The aqueous extract of the fungus contains carbohydrates, which, on hydrolysis, afford dextrose, pentoses, and methylpentoses. E. E. T.

Plant Respiration and Photosynthesis. H. A. SPOEHR and J. M. MCGEE (*Carnegie Inst. Pub.*, 1923, **325**, 1—98).—Interdependence may exist between photosynthesis and respiration. In the plant-cell, the carbohydrates and fats serve as the fundamental sources of energy in respiration; carbohydrates act as protein-sparers. The leaves of *Helianthus annuus* contain more amino-acid (which accumulates in the dark, the protein diminishing) and less carbohydrate than the stems. Amino-acids have stimulating effects on certain enzymes; they stimulate cells to metabolise more food material. An attempt to explain this on the basis of the isomerisation of dextrose to more rapidly metabolised isomerides gave negative results. Whilst lævulose metabolises more rapidly than dextrose, and shows relatively high respiratory activity, it depressed the activity of leaves when amino-acids were given. For the determination of the rate of respiration, an electrometric method was employed to estimate the carbon dioxide; the amino-acids were estimated by Van Slyke's micro-method, and the sugars by the author's method (A., 1921, ii, 715). Deleano's statement (*Jahrb. wiss. Bot.*, 1921, **51**, 552) that the nitrous acid method of estimating amino-groups is untrustworthy in the presence of carbohydrates and nitrates was not confirmed. A plant of *Helianthus annuus* showed a gradual increase in the rate of respiration during the first forty-eight hours, the amino-acids probably having a stimulating action, compensating for the diminishing carbohydrate content, whilst with excised leaves the rate decreases up to the forty-eighth hour, when there is a slight increase. There is a gradual depletion of carbohydrates and increase in amino-acid content, but the stem and roots show a slight decrease in amino-acid content. In excised leaves, the carbohydrate content decreases and that of the amino-acid increases. Excised leaves, when placed in the dark in a nitrogen-free nutrient solution containing 7% of dextrose, take up sugar and store it, and show an increased content of amino-nitrogen. Amino-acids are produced in the dark and accelerate the rate of carbohydrate consumption. Leaves fed on aminoacetic acid solution (for example) showed increased respiratory activity and rate of sugar consumption, whereas leaves fed on dextrose maintained an almost constant sugar content, but the amino-acid content increased three-fold, the rate of respiration decreasing for thirty hours, then increasing for fifty hours to a value slightly above the original. With leaves of the Canada Wonder bean, where the carbohydrate and amino-acid content increased during the experiment, the rate of respiration after falling to a minimum at the end of thirty-five hours rose to about the original value; the minimum marks the point

when the amino-acids have accumulated in a quantity sufficient to influence respiration. When the leaves are fed with amino-acids in addition to sugar the rise in the rate of respiration is continuous. The use of sucrose leads to similar results, but the influence of amino-acids was not observed with l  vulose. There was a great increase in amino-acid content and respiratory activity when it was fed to the leaf, but aminoacetic acid gave very little additional stimulation. A natural accumulation of amino-acids resulting when excised leaves are kept in the dark is as effective as artificial addition in stimulating respiratory activity. The rate of respiration has no direct relation to the carbohydrate supply. Light affects the carbohydrate and amino-acid content in opposite ways, decreasing the latter. Neither nitrate nor ammonia accumulates in leaves kept in the dark for ninety-five hours. The existence of an internal factor is postulated for cases in which the photosynthetic activity varies independently of external conditions. Whilst the chlorophyll content regulates the degree of photosynthetic activity in leaves poor in chlorophyll, the limiting factor in leaves rich in chlorophyll is this internal factor, which resembles an enzyme in its behaviour and is responsive to variation of temperature. The fact that reduced pressure and narcosis inhibit photosynthesis as well as respiration supports the view that a chemical or energetic relationship exists between the two processes. A molecular relation between photosynthesis and respiration depends on the activity of the intermediate products of sugar katabolism which act as "building blocks" with carbon dioxide or some of the primary products of its photochemical breakdown; this would account for asymmetric synthesis. Differential estimations of carbon dioxide showed, in the cases of leaves of the sunflower and Canadian Wonder bean, that the rate of photosynthesis of a leaf, the store of carbohydrates of which has been greatly depleted, is initially low and rises with continued exposure to light, the rate of respiration also increasing. Leaves previously kept in the dark show a continuous decrease in respiratory activity and a declining photosynthesis. This also holds for high concentrations of carbon dioxide, *i.e.*, respiration parallels carbon dioxide fixation. Photosynthesis may be a dual or coupled reaction.

CHEMICAL ABSTRACTS.

Influence of the Concentration of Organic Substances on the Formation of Starch in Vegetable Cells. A. MAIGE (*Compt. rend. Soc. Biol.*, 1922, **86**, 856—857; from *Physiol. Abstr.*, 1923, **8**, 209).—Increase of sugar and water in the cell leads to increased starch formation. W. O. K.

Influence of the Nature of Organic Substances of the Formation of Starch in Vegetable Cells. A. MAIGE (*Compt. rend. Soc. Biol.*, 1922, **87**, 303—304; from *Physiol. Abstr.*, 1923, **8**, 209).—Bean embryos without cotyledons were cultivated on 5 to 10% solutions of different sugars and the formation of starch observed. The amount of starch formed is held to depend on the penetrability

of the sugar except in cases where there is a definite toxic action, as with mannose and particularly with galactose. W. O. K.

Chemical Composition of Protoplasm of Plasmodium. W. W. LEPESCHKIN (*Ber. deut. bot. Ges.*, 1923, **41**, 179—187).—An examination of the protoplasm from plasmodia of *Fuligo varians* gave the following results. Dry matter 17.4%. In the dry matter, the water-soluble material, amounting to 40.7%, principally from the vacuoles, consists of monosaccharides, 14.2%; proteins, 2.2%, and amino-acids, purine bases, asparagine, etc., 24.3%. The material insoluble in water, 59.3%, forming the ground mass of the protoplasm, consists of nucleoproteins, 32.3%; nucleic acids, 2.5%; globulin, 0.5%; lipoproteins (plasmatin), 4.8%; neutral fats, 6.8%; phytosterol, 3.2%; phosphatides, 1.3%; other organic substances (polysaccharides, colouring matter, resin), 3.5%; ash constituents, 4.4%. G. W. R.

Comparative Plant Chemistry. V. *Alchemilla Alpina*, L. HANS VOGL (*Monatsh.*, 1923, **44**, 19—28).—The stems and leaves of this plant were found to contain an optically inactive hydrocarbon, $C_{28}H_{58}$, hexagonal plates, m. p. 70°, oleic and linoleic acids (in roughly equal amounts), a little combined phosphoric acid (lecithin?), and a dextrorotatory, white, amorphous substance, $C_{24}H_{42}O_3$, m. p. 268° (decomp.) (if not treated previously with alkali) or 253° (decomp.) (if alkali is used in its purification). This substance may be a resin-ester, which would account for the m. p. results. From the sample of m. p. 253°, no crystalline derivatives could be obtained. Short heating with acetic anhydride gave an *acetyl* derivative, m. p. 164°, prolonged heating, one melting at 138°. Nitric acid in glacial acetic acid solution gave a *nitro*-derivative, m. p. 206°. In addition to the above substances, the stems and leaves contain a phlobaphen and tannins (of two types), choline, phenolic compounds, dextrose, and lævulose (these two in the proportion of 4:1). Extraction with water revealed the presence of inorganic matter and of carbohydrates, which, on hydrolysis, gave a little galactose, considerable quantities of pentoses, but no dextrose or mannose. The total ash (from stem and leaf) was 7.03%.

A brief examination of *Alchemilla Alpina* root (mainly rhizomes) showed that alkaloids were absent. Very little of the above hydrocarbon was present, whereas the leaves, etc., contained 1—2%. A resin-substance, similar to that described above, was isolated, and was soluble in alkali. Tannins of the protocathechuic type were found in large quantities, and also dextrose and lævulose (in this case in the proportion 2:1). The total root extract was about 50% greater than the leaf extract (per cent.). What medicinal effect is possessed by the root can only be attributed to the tannins present. E. E. T.

Constituents of the Wax-like Coating on the Surface of the Apple. CHARLES E. SANDO (*J. Biol. Chem.*, 1923, **56**, 457—468).—Dried apple skins were extracted successively with light petroleum

and ether. Fractionation of the light petroleum extract yielded triacontane, $C_{30}H_{62}$, heptacosanol, $C_{27}H_{56}O$ (cf. Kipping, T., 1893, 63, 452), and a number of crystalline products which could not be identified owing to the small yield. Heptacosanol has not previously been isolated from natural sources. From the ether extract, a new *alcohol*, $C_{30}H_{48}O_3$, prismatic needles, m. p. 284—285°, was isolated. The name *malol* is suggested for this. Malol is dextrorotatory, exhibits mutarotation, and appears to be the lower homologue of the isomeric alcohols oleanol and prunol isolated by Power and Tutin (T., 1908, 93, 891) and by Power and Moore (T., 1910, 97, 1099), respectively. It gives the Liebermann-Salkowski reaction for cholesterol, forms a crystalline *sodium* salt, $C_{30}H_{47}O_3Na$, and a *diacetyl* derivative, $C_{30}H_{46}O_3Ac_2$, needles, m. p. 199—200° (decomp.), which, when dissolved in 70% alcohol and boiled for two hours, is converted into the *monoacetyl* derivative, $C_{30}H_{47}O_3Ac$, small needles, m. p. about 279—281° (decomp.). *Methylmalol*, $C_{30}H_{47}O_3Me$, m. p. 170·5—171·5° after sintering at 110°; and *acetylmethylmalol*, $C_{30}H_{46}O_3MeAc$, m. p. 243—244°, have also been prepared.

E. S.

The Chemical Contents of *Polygonum hydropiper*. JAN BIELECKI and DAWID LIBERMAN (*Zjazd Chemików Polskich*, 1923, 60—61). Whilst certain colour reactions seem to point to the presence of alkaloidal substances in *Polygonum hydropiper*, no alkaloid was isolated from the alcoholic or acid extracts, although the latter were found to contain certain organic acids, of which only gallic acid was identified. An extract of *P. hydropiper* made with lime water gave on distillation with steam and extraction with ether a small quantity of green oil, from which crystals of a characteristic odour separated, which gave many reactions for alkaloids.

R. T.

A New Essential Oil from the Seeds of *Sium latifolium*, L. G. V. PIGULEVSKI (*J. Russ. Phys. Chem. Soc.*, 1922, 54, 296—303).—The crushed seeds of the umbelliferous plant, *Sium latifolium*, L., yield about 6% of an essential oil, a typical sample of which has $d_4^{25.5}$ 0·8533, $[\alpha]_c + 77.24^\circ$, $[\alpha]_D + 98.40^\circ$, $[\alpha]_s + 127.24^\circ$, $[\alpha]_t 153.80^\circ$, $[\alpha]_t/[\alpha]_c 1.99$. Fractionation of the oil shows that it contains about 80% of *d*-limonene, which was identified by means of its tetrabromide. The higher boiling fraction appears to consist of a ketone, giving an *oxime*, m. p. 101—102°, $[\alpha]_D + 136.76^\circ$; the ketone, although having an odour reminiscent of carvone, is not identical with the latter. The oil prepared from unripe seeds has similar properties to the above.

In character, the oil is similar to oil of caraway, which is also composed of two main constituents, but contains a much higher proportion of ketone. The structure of the seeds was compared with that of caraway seeds, and it was found that the resin ducts of the former were much nearer the endosperm than those of caraway. It is thought possible that hydrocarbons are formed in the ducts lying nearer the endosperm, whilst oxygenated compounds

are produced in the outer portion of the seed; the difference of structure would thus account for the difference in character of the essential oils in the two plants. G. A. R. K.

Estimation of Adsorbed Bases in Soils and the Importance of these Bases in Soil Economy. D. J. HISSINK (*Soil Sci.*, 1923, 15, 269—276).—Twenty-five g. of soil (50 g. of sandy loams) are shaken in a beaker with 100 c.c. of a warm normal solution of sodium chloride and filtered into a litre flask. The soil on the filter is treated with successive portions of the sodium chloride solution until the flask is filled to the mark. Each portion of solution is allowed to pass through the filter before the addition of the next. The washing is repeated until a second litre of filtrate is obtained. The difference in calcium content of the two separate litres of filtrate corresponds with replaced calcium. For adsorbed potassium and magnesium, a similar method is employed, preferably using a 25 g. soil sample and normal ammonium chloride solution for leaching. Of the adsorbed ions calcium was the most preponderant, smaller proportions of the total potassium, magnesium, and sodium being adsorbed. A. G. P.

The Soil Solution and its Importance in the Growth of Plants. N. M. TULAIKOV (*Soil Sci.*, 1923, 15, 229—234).—The relationship between the osmotic pressure of the soil solution and plant growth is investigated. An increased osmotic pressure delayed the germination of seeds, weakened the seedlings, and arrested the growth of the plant in all its stages. There is an optimum osmotic pressure for plant growth. Increased osmotic pressure increased the total crop yield up to an optimum figure, after which there was a decline in yield. An increased osmotic pressure produced an increased nitrogen content in the crop, and greater hardness of grain. A. G. P.

The Question of Obtaining the Soil Solution. N. M. TULAIKOV and M. S. KUZMIN (*Soil Sci.*, 1923, 15, 235—239).—Soil is packed in the annular space between a metal cylinder and an inner cylinder of metallic net covered on the outward (soil) side with filtering muslin. Pressure is applied to the soil surface by an ordinary turn-screw press and the inner cylinder is evacuated. The soil solution can be extracted in about fifteen minutes. Consecutive samples of soil solution showed identical chemical constitution and osmotic pressures. Considerable amounts of soil solutions may be obtained in this way even when the moisture content is low. A. G. P.

Organic Chemistry.

Genesis of Hydrocarbons. R. D'ANDRIMONT (*J. Inst. Petr. Tech.*, 1923, 9, 287—291).—A brief general discussion on the genesis of hydrocarbons (petroleum) and their localisation in certain zones in the earth's crust. Whether from accumulations of vegetable and animal remains the processes of organic transformation give rise to coal or hydrocarbons depends on: (1) the proportion of cellulose to fatty matter; (2) the conditions of deposition; and (3) pressure, temperature, and time. The most favourable situation for the third of these conditions is in the fractured zones bordering mountain folding.
L. J. S.

Studies in Mutual Solubility. I. Introductory. The Mutual Solubility of Glycerol and Aliphatic and Aromatic Ketones. BASIL CHARLES McEWEN (*T.*, 1923, 123, 2279—2284).

Studies in Mutual Solubility. II. The Mutual Solubility of Glycerol and Alcohols, Aldehydes, Phenols, and their Derivatives. BASIL CHARLES McEWEN (*T.*, 1923, 123, 2284—2288).

The Alkylglycerols. R. DELABY (*Ann. Chim.*, 1923, [ix], 19, 275—326).—A more detailed description of work previously published (cf. this vol., i, 84, 85, 289, 531, 646; ii, 264).
H. J. E.

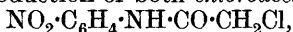
Ethylation with Ethyl Sulphate. A. R. CADE (*Chem. and Met. Eng.*, 1923, 29, 319—323).—Ethyl sulphate is a satisfactory general ethylating agent for the preparation of ethyl ethers, esters, amines, and imides. If the reagents employed be nearly dry both ethyl groups react; if there be a large amount of water present only one group reacts completely. A temperature of 100—150° is usually optimal, but reaction occurs even at room temperatures. Aromatic and aliphatic ethers are both prepared as with methyl sulphate in presence of an alkali. Amines are mono- and di-ethylated according to the conditions of reaction; both ethyl groups can be caused to react if an alkali be present. Imides and acids are best treated in the form of their alkali salts. Being non-inflammable, non-toxic, non-corrosive, and of low volatility, besides being available in large quantities and in a high degree of purity, ethyl sulphate should find a wide chemical use, especially as it reacts without application of pressure.
T. S. W.

The Colloidal Electrolyte extracted from Carrageen (*Chondrus Crispus*). FRANK COURTNEY HARWOOD (*T.*, 1923, 123, 2254—2258).

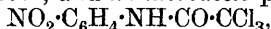
Bromination of Aliphatic Acids. BRIAN DUNCAN SHAW (*T.*, 1923, 123, 2233—2240).

Direct Conversion of Derivatives of Dichloroacetic Acid into Derivatives of Trichloroacetic Acid. ALVIN S. WHEELER and SAMUEL C. SMITH (*J. Amer. Chem. Soc.*, 1923, **45**, 1994—1998).

—*o*-Toluidine dichloroacetate, prisms, m. p. 140° , is formed when equimolecular proportions of *o*-toluidine and dichloroacetic acid react in ice-cold carbon tetrachloride solution; *p*-toluidine dichloroacetate is prepared similarly, and has m. p. 160° (Baralis, *Rev. chim. med. farm.*, **2**, 301, gives m. p. 140°). Aniline trichloroacetate, m. p. 163° (Beamer and Clarke, A., 1897, i, 785, give m. p. 145°), is obtained by the action of excess of dichloroacetic acid or trichloroacetic acid on aniline, without cooling, or by the interaction of aniline and trichloroacetic acid at -3° in carbon tetrachloride solution. *o*-Toluidine trichloroacetate, colourless plates, m. p. 167 — 168° (decomp.), *p*-toluidine trichloroacetate, m. p. 135° (Baralis, *loc. cit.*, gives m. p. 137°), α -naphthylamine trichloroacetate, pale violet plates, m. p. 173° (decomp.), and *m*-nitroaniline trichloroacetate, pale yellow plates, m. p. 147° , are prepared by similar methods. It is evident that the formation of these derivatives of trichloroacetic acid from dichloroacetic acid must be preceded by a rearrangement of 2 mols. of the latter, giving 1 mol. of chloroacetic acid and 1 mol. of trichloroacetic acid. This view is substantiated by the production of both chloroaceto-*p*-nitroanilide,



yellow prisms, m. p. 177° , and trichloroaceto-*p*-nitroanilide,



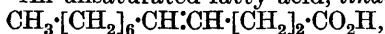
pale yellow, prismatic needles, m. p. 140° , when *p*-nitroaniline and dichloroacetic acid are warmed together, the product being then heated at 100° with phosphoric oxide. The identity of these anilides is confirmed by their direct synthesis from chloroacetic acid, or trichloroacetic acid, and *p*-nitroaniline. W. S. N.

The Oxidation of Stearic Acid and Related Compounds by Oxygen. ERNST ZERNER (*Naturprodukte*, 1923, 83—94).—

The higher fatty acids and related compounds are slowly oxidised by atmospheric oxygen in presence of a catalyst of the type of manganese stearate at 130° with formation of a variety of products. The oxidation is accompanied by a steady rise in the acid and saponification numbers and, in the case of unsaturated substances such as oleic acid, by a fall in the iodine number. A detailed study was made of the oxidation of stearic acid. The product obtained after oxidising for thirty-one hours formed a soap which lathered well but could not be salted out, indicating the presence of hydroxyl groups. It contained unsaponifiable matter which had the composition of an alcohol, $\text{C}_{14}\text{H}_{30}\text{O}$, and as identifiable products succinic, pimelic, and heptonic acids, and in the distillate carried forward with the oxygen current, the lower fatty acids down to formic acid and an alcohol, $\text{C}_{12}\text{H}_{26}\text{O}$. When ethyl stearate was oxidised in the same way, the rate of disappearance of the ethoxyl group did not indicate that one end of the chain was being attacked preferentially. Compounds containing as few as eight carbon atoms in a chain are not oxidised under the above conditions.

E. H. R.

Constitution and some Properties of an Unsaturated Fatty Acid, $C_{12}H_{22}O_2$, isolated from *Lindera obtusiloba*. YOSHITORA IWAMOTO (*J. Chem. Ind. Japan*, 1923, 26, 708—716; cf. *ibid.*, 1921, 24, 1114).—An unsaturated fatty acid, *linderic acid*,



a light yellow oil, was isolated from the oil obtained from *Lindera obtusiloba*, B.L. It has m. p. $1\cdot0$ — $1\cdot5^\circ$, d_4^{25} $0\cdot92461$, n_D^{20} $1\cdot44922$, n_D^{15} $1\cdot45113$, iodine value $126\cdot33$, neutralisation value $282\cdot26$. The methyl ester has b. p. 123 — 125° . Treated by Hazara's oxidation method, the acid gave *dihydroxylinderic acid*, $C_{12}H_{22}O_2(OH)_2$, slender needles, m. p. 102° . The original acid was ozonised and decomposed with hot water; from the decomposition products, succinic and *n*-octoic acids and *n*-octaldehyde were isolated. K. K.

Linoleic Acid and its Anhydride. D. HOLDE and S. WEILL (*Chem. Umschau*, 1923, 30, 205—206).—A sample of linoleic acid prepared by Grün and Schönfeld from poppy-seed oil (*Z. angew. Chem.*, 1910, 29, 47) was investigated and gave the following mean characters: iodine value (Hanus), $178\cdot6$; acid value, $196\cdot7$; d_4^{20} $0\cdot9025$; n_D^{20} $1\cdot4711$; m. p. -25° to -24° . The anhydride was prepared by boiling for seven hours with acetic anhydride and distilling off the excess of acetic anhydride and the acetic acid formed under reduced pressure. The residue was freed from unchanged linoleic acid by dissolving in light petroleum, treating with 5% sodium hydroxide solution, removing the soap with 50% alcohol and finally with water, and distilling off the light petroleum in a current of carbon dioxide under reduced pressure. The yield was 85—92% of the theoretical. When the light petroleum solution was cooled to -75° the anhydride was precipitated as a fine white precipitate, of which the melting point was, however, not sharp enough to be determined. H. C. R.

Hongay Oil [from the Seeds of *Pongamia glabra*, Vent.]. R. D. DESAI, J. J. SUDBOROUGH, and H. E. WATSON (*J. Ind. Inst. Sci.*, 1923, 6, 93—110).—The fatty acids present as glycerides include myristic (0·23%), palmitic (6·06%), stearic (2·19%), arachidic (4·30%), lignoceric (3·22%), dihydroxystearic (4·36%), linolenic (0·46%), linoleic (9·72%), and oleic (61·30%) acids. There is 3·56% of unsaponifiable matter, which contains brassicasterol and sitosterol together with an oil of high refractive index. [Cf. *J.S.C.I.*, 1923, Oct.] H. C. R.

Cashew Kernel Oil [from the Seeds of *Anacardium occidentale*, Linn.]. C. K. PATEL, J. J. SUDBOROUGH, and H. E. WATSON (*J. Ind. Inst. Sci.*, 1923, 6, 111—129).—The oil comprises glycerides of oleic (73·8%), linoleic (7·7%), palmitic (6·4%), stearic (11·2%), and lignoceric (0·5%) acids together with 0·42% of unsaponifiable matter consisting mainly of sitosterol. [Cf. *J.S.C.I.*, 1923, Oct.] H. C. R.

Preparation of Malono-*p*-ethoxyanilic Acid and its Esters. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 371692; from *Chem. Zentr.*, 1923, ii, 1089).—*p*-Phenetidine is treated with

a large excess of ethyl malonate. After removal of the excess of ethyl malonate, the product of reaction is treated with a dilute solution of an alkali hydroxide. The formation of the diphenetide, $\text{CH}_2(\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OEt})_2$, in large quantities is prevented by using large excess of ethyl malonate. Thus from ethyl malonate and *p*-phenetidine in the proportion of 7 : 1, four parts of *ethyl malono-p-ethoxyanilate*, $\text{CH}_2(\text{CO}_2\text{Et})\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OEt}$, are formed, together with one part of the diphenetide. After removal of excess of ethyl malonate and treatment with potassium hydroxide, *malono-p-ethoxyanilic acid*, $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, is obtained by treatment of the potassium salt with hydrochloric acid.

G. W. R.

Crystalline Structure of Anhydrous Racemic Acid. W. T. ASTBURY (*Proc. Roy. Soc.*, 1923, [A], **104**, 219—235).—From observations made with an X-ray spectrometer the crystalline structure of racemic acid has been deduced. The crystallographic cell is associated with only 1 mol. of tartaric acid ($\text{C}_4\text{H}_6\text{O}_6$) and is not the true fundamental cell. The fundamental cell is associated with 1 mol. of *d*-tartaric acid and 1 mol. of *l*-tartaric acid. There is no evidence from X-ray examination that racemic acid exists as an independent inactive doublet of molecular weight 300. The chemical molecule in racemic acid is substantially of the same shape and dimensions as the molecule in tartaric acid. A small contraction in the length of the molecule and the absence of a certain cleavage is associated with small changes in physical properties which accompany the formation of racemic acid from its active components. The disappearance of the distortion of the hydroxyl groups of tartaric acid is favourable to the hypothesis of the anomalous optical properties of the active acid. An explanation is given of the multiple twinning and irregular growth of anhydrous racemic acid.

J. F. S.

Dithioformic Acid. T. G. LEVI (*Atti R. Accad. Lincei*, 1923, [v], **32**, i, 569—572).—The author has prepared various derivatives of dithioformic acid from the potassium salt obtained by treating chloroform with potassium sulphide (cf. Cambi, A., 1909, i, 646) in alcoholic solution under definite conditions.

The *silver*, $\text{H}\cdot\text{CS}_2\text{Ag}$, and *lead* salts, $(\text{H}\cdot\text{CS}_2)_2\text{Pb}$, were obtained as orange-yellow precipitates, but could not be prepared quite pure owing to their insolubility in ordinary organic solvents; both are comparatively stable, the former blackening at 95—100° and the latter at 130—135°. The zinc salt is yellowish-white and the cobalt salt deep brownish-red.

The *disulphide*, $(\text{H}\cdot\text{CS}\cdot\text{S}\cdot\text{S}\cdot\text{CS}\cdot\text{H})_x$, obtained as a yellowish-red precipitate by cautious oxidation of the potassium salt in alcoholic solution by means of iodine, decomposes at above 200° into carbon disulphide, hydrogen sulphide, carbon, and sulphur. T. H. P.

Photochemical Production of Formaldehyde. E. C. C. BALY, I. M. HEILBRON, and W. F. BARKER (*Nature*, 1923, **112**, 323; cf. T., 1921, **119**, 1025, and Spoeher, this vol., ii, 452).—Further experiments confirm the previous observation that form-

aldehyde is formed by the action of ultra-violet light of short wave-length on aqueous solutions of carbon dioxide. Spoehr's failure to observe the formation of formaldehyde may be due to deterioration of the quartz mercury lamp employed. The method of procedure adopted by the authors is described in detail.

A. A. E.

The Action of Ozone on Hydrocarbons with Special Reference to the Production of Formaldehyde. II. The Action of Ozone on Ethylene. E. W. BLAIR and T. S. WHEELER (*J. Soc. Chem. Ind.*, 1923, **42**, 343—350T).—Experiments on the action of ozone on ethylene were made both by ozonising a mixture of ethylene and oxygen and by the direct action of ozonised oxygen or air on ethylene in presence and absence of water or ammonia. The resulting gas was then washed with water and the solution analysed for formic acid, dissolved ozone, hydrogen peroxide, and formaldehyde. The primary product of reaction of the gases at the ordinary temperature is the ozonide $C_2H_4O_3$, which may then decompose in various ways. When mixtures of dry oxygen and ethylene were ozonised there was much carbon monoxide formed, more hydrogen peroxide than would have been expected, and relatively little formaldehyde. Very dilute mixtures of ethylene and ozone were found to react rapidly and almost completely when well mixed. If no moisture is present, the ozonide decomposes into formic acid and formaldehyde or their decomposition products. In presence of water, more or less hydrolysis to formaldehyde and hydrogen peroxide occurs. If the ozone present is not sufficiently dilute, as compared with the ethylene, some oxidation of formaldehyde to formic acid takes place. Most of the hydrogen peroxide formed decomposes, but some may react with ozone or may oxidise formaldehyde. The rate of decomposition of the ozonide appears to be proportional to the concentration in which it is formed. The presence of ammonia during the reaction appears to increase the yield, probably by combining with the formaldehyde as it is formed, giving hexamethylenetetramine; no nitrate or nitrite was detected.

E. H. R.

The Condensation Products of Methyl Ethyl Ketone. JOHN B. EKELEY and W. WARREN HOWE (*J. Amer. Chem. Soc.*, 1923, **45**, 1917—1925).—The action of hydrogen chloride on cold methyl ethyl ketone gives γ -methyl- Δ^7 -hepten- ϵ -one, b. p. 156—160°/625 mm., d_4^{20} 0.8628, n_D^{20} 1.4453 (cf. Bodroux and Tabary, A., 1909, i, 766); the constitution of this is proved by the production of propionic acid when it is oxidised by means of cold dilute potassium permanganate solution (cf. Becker and Thorpe, T., 1922, **121**, 1303). It gives a liquid *oxime*, b. p. 132—137°/17 mm., and a *semicarbazide-semicarbazone*, microscopic prisms, m. p. 265—266° (decomp.). The semicarbazone, m. p. 114—115°, prepared by Bodroux and Tabary (*loc. cit.*) is a mixture. A second product of the above reaction is *homophorone*, $C_{12}H_{20}O$, a clear, slightly straw-coloured liquid with a camphor-like odour and taste, b. p.

206—210°/625 mm., d_4^{20} 0.8857, n_D^{20} 1.4792. When the condensation is effected by means of cold concentrated sulphuric acid, or of sodium ethoxide, there are formed, in addition to the above products, two ketones homologous with isophorone: (1) a clear, yellow liquid having a faint odour and taste of terpene, b. p. 256—260°/630 mm., d_4^{20} 0.9492, n_D^{20} 1.5045; (2) a golden-brown, somewhat viscous liquid, having a camphor-like odour and taste, b. p. 280—285°/630 mm., d_4^{20} 0.9693, n_D^{20} 1.5115. The same two compounds are formed when γ -methyl- Δ^7 -hepten- ϵ -one is condensed with methyl acetate by means of alcoholic sodium ethoxide solution. Hence one of these ketones, although it is not known which, is 1:2:3:4-tetramethyl-4-ethyl- Δ^1 -cyclohexen-6-one, the other being 1:2-dimethyl-1:5-diethyl- Δ^4 -cyclohexen-3-one. W. S. N.

Bromination of Compounds containing the Carbonyl Group. (a) Pyruvic Acid. (b) Acetophenone. CHARLES FREDERICK WARD (T., 1923, 123, 2207—2213).

Catalytic Hydrogenation and Steric Hindrance. Nonanones. G. VAVON and D. IVANOV (*Compt. rend.*, 1923, 177, 453—456).—Hydrogenation of four isomeric ketones of the formula $C_9H_{18}O$ (nonan- ϵ -one, γ -methyloctan- δ -one, γ -dimethylheptan- δ -one, and tetramethylpentan- γ -one) to the corresponding alcohols in presence of platinum black shows that the extent of the reduction follows the law of steric hindrance. A similar effect, but to a lesser extent, was observed in the formation of oximes and phenylhydrazones. The following compounds are described: *nonan- ϵ -ol* (*dibutylcarbinol*), b. p. 194°, d^{18} 0.823, n_D^{18} 1.4289; *γ -methyloctan- δ -ol*, b. p. 180°, d^{18} 0.834, n_D^{18} 1.4325; *γ -dimethylheptan- δ -ol*, b. p. 171°, d^{18} 0.836, n_D^{18} 1.4330. The corresponding *allophanates* melt at 158°, 160°, and 163° respectively. H. J. E.

The Methylation of Sugars. MARC BRIDEL (*Bull. Soc. chim.*, 1923, [iv], 33, 1005—1058).—A lecture delivered at the Collège de France on 17 March, 1923.

The Effect of Trichloroacetic Acid in Preventing Reduction by Reducing Sugars. B. M. MARGOSCHES and FRITZ STEINDLER (*Naturprodukte*, 1923, 67—72).—Chloroform is known to reduce Fehling's solution. It is therefore surprising to find that trichloroacetic acid not only does not reduce Fehling's solution but hinders its reduction by chloroform and formaldehyde. Further, it is found that comparatively small quantities of trichloroacetic acid retard the reduction of Fehling's solution by arabinose, dextrose, galactose, laevulose, maltose, and lactose, and larger quantities prevent reduction altogether. There appears to be a numerical relationship between the minimum quantities of trichloroacetic acid required to prevent reduction with different sugars, but the significance of this relationship is not clear. E. H. R.

Hemicellulose. III. Decomposition of Lichenin by Ferments. HANS PRINGSHEIM and KARL SEIFERT (*Z. physiol. Chem.*, 1923, 128, 284—289).—Lichenin, a polysaccharide obtained from

Iceland moss, *Cetraria islandica*, is fermented by the enzymes of malt yielding dextrose (isolated as glucosazone). This reaction has an optimum at P_H 5. Lichenin is hydrolysed also by acid but less rapidly than starch. W. O. K.

Structural Units of Starch determined by X-Ray Crystal Structure Method. O. L. SPONSLER (*J. Gen. Physiol.*, 1923, 5, 757—776).—Starch when submitted to X-ray analysis gives lines which are less intense and more diffuse than those produced, e.g. by sodium chloride, but nevertheless can be measured. Their position is satisfactorily explained on the supposition that there is in starch a lattice of the tetragonal system, the elementary cell of which is a square prism with dimensions $5.94 \times 5.94 \times 5.05$ Å. The volume of this cell corresponds with that of the unit group, $C_6H_{10}O_5$. A structure built up of concentric layers of such units would give reflections the intensity of which would be in general agreement with the experimental results. W. O. K.

Determination of the Viscosity of Cellulose (*Research Dept. Woolwich, Rept. No. 22, Part III*).—Most forms of cellulose have been found to be irregular in viscosity throughout their mass, when dissolved in cuprammonium solutions so that sampling must be on a large scale. To ensure the formation of clear solutions of uniform viscosity, thorough disintegration and teasing of the cellulose sample is essential. Drying at elevated temperatures or treatment of the cellulose with boiling water or dilute alkali solutions affects the viscosity and is inadmissible. Joyner's method for the preparation of cuprammonium solutions (T., 1922, 121, 1511, 2395) is satisfactory and to be recommended. An apparatus for preparing such solutions is described and also a method of filling viscosimeter tubes. The original specifications for the cuprammonium solvent have been found to be too wide; to obtain consistent results the narrower specifications outlined in the report must be adopted. T. S. W.

Qualitative and Quantitative Differences between some Wood and Straw Lignins. ERNST BECKMANN, OTTO LIESCHE, and FRITZ LEHMANN [with K. F. LINDNER] (*Biochem. Z.*, 1923, 139, 491—508).—A detailed investigation of the nature of wood and straw lignins isolated by alkali treatment at different temperatures. The straws investigated were those of rye, barley, oats, and rice, and the woods, maple, red beech, fir, and spruce. In each case the straw or wood was dried in air, ground to a meal, and after removal of the resins, fats, and waxes by exhaustive ethereal extraction, equal quantities of each meal were subjected to the action of 1.5% sodium hydroxide in a series of consecutive extractions as follows: (a) Forty-eight hours at room temperature, (b) six hours' boiling in a reflux apparatus, (c) six hours in an autoclave at 3 atm., (d) six hours at 6 atm., (e) six hours at 9 atm. Methods (d) and (e) were required only in the cases of the woods. The completion of the extraction was indicated by the destruction of the fibrous structure and the absence of red coloration with phloroglucinol hydrochloride. The

lignins extracted in each method were isolated by Beckmann's process (A., 1921, i, 546), and methoxyl estimations were made on each sample. In successive extraction methods, the straws gave diminishing yields of lignins, which became increasingly darker and less soluble in pyridine, acetic acid, or alcohol as the temperature of extraction rose. The methoxyl content was at a maximum in those isolated by method (b). The woods yielded increasing amounts of lignins in successive extractions up to method (d), at which the methoxyl content was also, in general, at a maximum. The two pine woods gave markedly uniform results, but more variation was encountered in the deciduous woods, and the latter contained less lignin of a higher methoxyl figure than did the former. As in the case of the straw lignins, increasing temperature of extraction gave products of a darker colour and of more restricted solubilities in basic, acid, or neutral solvents. In all cases the total lignin extracted was less than that estimated to be present in the original material by Willstätter's method, the difference being accounted for by experimental losses and the presence of silica in the straws (more especially in rice straw). A series of experiments on maple wood meal was carried out in which each method of extraction was continued until no further lignin was obtained before the next method in the series was employed. Methods (c), (d), and (e) were capable of removing all the extractable lignin but this was still found to be less than the total in the original material. Parallel extractions of maple wood meal with 1.5% and 3.0% sodium hydroxide showed that the more concentrated alkali gave higher yields of lignin, but the appearance and methoxyl content of corresponding fractions were the same. The lignins of winter rye straw at different periods of growth were investigated by these methods. The lignin content and methoxyl figure increases with the age of the plant, the increases being more marked in the earlier stages of growth. The results are given of various elementary analyses of the lignins isolated as above described, and in a chemical examination of their decomposition products the presence of protocatechuic acid, pyrocatechol, and pyrogallol was revealed. As a result of demethylation of a rye lignin by hydriodic acid, a dark brown, resinous *substance* was obtained to which the empirical formula $C_{36}H_{39}O_6I$ is provisionally ascribed. Maple and pine wood lignins on demethylation gave similar but more complex *substances* of empirical formulæ respectively, $C_{72}H_{85}O_{12}I$ and $C_{108}H_{98}O_{18}I$. No definite conclusion is drawn from the results of various experiments designed to elucidate the phloroglucinol reaction of native lignin. J. P.

Lignin Prepared by the Hydrochloric Acid Process. ERIK HÄGGLUND (*Naturprodukte*, 1923, 24—35, and *Cellulosechem.*, 1923, 4, 73—77).—Lignin prepared by Willstätter's process, by treating pine wood with highly concentrated (45%) hydrochloric acid, evolves furfuraldehyde when subsequently distilled with hydrochloric acid. Experiments now described indicate that the carbohydrate from which the furfuraldehyde is derived forms an integral

part of the lignin molecule. The carbohydrate can be removed by hydrolysing the lignin with hot 5% sulphuric acid or by the prolonged action of cold 45% hydrochloric acid. It was identified by its optical rotatory power and by its osazone as arabinose, and is present in pine wood lignin to the extent of 4.5%. Pyrocatechol and formic acid were found among the fusion products of lignin with alkali hydroxide. The methoxyl content of lignin is 14.68%, rising to 15.2% after complete removal of carbohydrate. E. H. R.

Characteristics of the Two Crystalline Forms of Glycine.

C. A. BRAUTLECHT and N. F. EBERMAN (*J. Amer. Chem. Soc.*, 1923, **45**, 1934—1941).—The action of hydrogen chloride, of bromine vapour, or of sulphur dioxide, with or without moisture, shows that moisture rapidly effects an equilibrium between the plate and needle forms of glycine, and that any difference in these forms will only appear if water is completely excluded. The dry crystals do not differ chemically or in m. p. when dried at 103° and ground to pass a 0.3 mm.-mesh sieve, or when air-dried and ground. Bromine does not form a compound with glycine, varying amounts being taken up temporarily, according to the amount of moisture present and time of contact, and lost again on exposure to the air. Neither phosphorus trichloride nor phosphorus pentachloride acts on glycine in carbon disulphide solution. In the formation of glycyl chloride by the action of acetyl chloride and phosphorus pentachloride (Fischer, A., 1905, i, 863), it is evidently the acetyl chloride which leads to the formation of glycyl chloride. Other compounds, some of which contain phosphorus, are also produced in this reaction. W. S. N.

Preparation of Homologues of Anilinolactic Acid. ÉTABLISSEMENTS POULENC FRÈRES (Fr. Pat. 532465; from *Chem. Zentr.*, 1923, ii, 1062).—Aniline or its homologues are allowed to react with halogenohydroxycarboxylic acids of the composition $\text{CH}_2\text{X}\cdot\text{CR}(\text{OH})\cdot\text{CO}_2\text{H}$ or $\text{R}\cdot\text{CH}(\text{OH})\cdot\text{CHX}\cdot\text{CO}_2\text{H}$, where R = alkyl or aryl. The amino-acids are converted by usual methods into ethers or salts. By the action of aniline on β -chloro- α -hydroxy- α -methylpropionic acid, β -anilino- α -hydroxy- α -methylpropionic acid, $\text{NHPh}\cdot\text{CH}_2\cdot\text{CMe}(\text{OH})\cdot\text{CO}_2\text{H}$, is obtained; it forms crystals, m. p. 60°. β -p-Ethoxyanilino- α -hydroxy- α -methylpropionic acid, $\text{EtO}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CMe}(\text{OH})\cdot\text{CO}_2\text{H}$, from *p*-phenetidine, has m. p. 180—181°. α -Bromo- β -hydroxy- β -phenylpropionic acid with aniline yields anilinophenyl-lactic acid, $\text{OH}\cdot\text{CHPh}\cdot\text{CH}(\text{NHPh})\cdot\text{CO}_2\text{H}$, m. p. 144°. G. W. R.

Alkyl Derivatives of Dicyanodiamide and of Dicyanodiamidine. G. PELLIZZARI (*Gazzetta*, 1923, **53**, i, 384—392; cf. A., 1919, i, 134; 1921, i, 363, 403, 620).—The action of nitrous acid on phenylmethyldiguanide and on piperidyldiguanide yields the corresponding substituted dicyanodiamides, the non-substituted guanidyl group being transformed into the cyano-amino-residue. In either case, however, a second compound is formed owing to
*n n**

the conversion of the substituted guanidyl group into the carbamide group, $\text{NR}_2\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot \rightarrow \text{NR}_2\cdot\text{CO}\cdot\text{NH}\cdot$. Thus, phenylmethyldiguanide gives cyanophenylmethylguanidine, which is neutral and has characteristics similar to those of dicyanodiamide, and guanylmethylphenylmethylcarbamide, which is a substituted dicyanodiamidine. Under similar conditions, piperidyldiguanide yields cyanopiperidyldiguanidine and guanylcarmylpiperidine.

Only a single product, cyanophenyleneguanidine, is obtained by the action of nitrous acid on *o*-phenylenediguanide, since the latter is substituted at two different nitrogen atoms and transformation of the guanidyl into the carbamide group is not possible; *o*-phenyleneguanidine, with which this possibility exists, is converted into phenylenecarbamide by nitrous acid. Phenyldiguanide, when treated with nitrous acid, yields only guanylmethylphenylcarbamide, without the corresponding dicyanodiamide.

The two substituted dicyanodiamides obtained resemble their parent compound in behaviour. When they are gently boiled with dilute acid, the cyanogen group undergoes hydration to the carbamide group with formation of the corresponding guanylcarmides, which have the substituent groups in the guanidyl residue, and are thus isomeric with the compounds obtained by means of nitrous acid. Thus, cyanophenylmethylguanidine,



gives phenylmethylguanylcarmide, $\text{NMePh}\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, which is isomeric with guanylmethylphenylmethylcarbamide,



and 1-cyanoguanidyldipiperidine, $\text{C}_5\text{H}_{10}\cdot\text{N}\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot\text{CN}$, gives 1-carbamylguanylpiperidine, $\text{C}_5\text{H}_{10}\cdot\text{N}\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, isomeric with 1-guanylcarmylpiperidine, $\text{C}_5\text{H}_{10}\cdot\text{N}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}(\text{NH})\cdot\text{NH}_2$. With nickel salts these dicyanodiamidines yield amorphous precipitates and not characteristic compounds such as that given by dicyanodiamidine.

Cyanophenylmethylguanidine crystallises in transparent, colourless laminae or slender needles, m. p. 143° , is neutral towards litmus, and forms a *hydrochloride* decomposing at about 165° .

Guanylmethylphenylmethylcarbamide forms isolated white, prismatic crystals or spherical aggregates, m. p. 175° , and gives an aqueous solution alkaline to litmus. Its *nitrate*, $\text{C}_9\text{H}_{12}\text{ON}_4\cdot\text{HNO}_3$, crystallises in long, transparent needles and decomposes at about 190° .

Phenylmethylguanylcarmide separates in white needles, m. p. 141° , and at 160 – 170° yields gas and a solid compound, which is probably a substituted biuret. In aqueous solution it is alkaline to litmus, and with copper sulphate and ammonia it forms a characteristic peach-blossom-coloured compound, whilst its isomeride gives a pale blue, flocculent precipitate under similar conditions.

1-*Cyanoguanidinopiperidine*, $\text{CH}_2\langle\begin{smallmatrix} \text{CH}_2\cdot\text{CH}_2 \\ \text{CH}_2\cdot\text{CH}_2 \end{smallmatrix}\rangle\text{N}\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot\text{CN}$, forms lustrous lamellae, m. p. 172 – 173° , resembling those of dicyanodiamide, and is neutral towards litmus.

1-*Guanylcarmylpiperidine* forms transparent, prismatic crystals or white masses of slender needles, m. p. 177 – 178° , and turns red

litmus paper blue. The *picrate*, $C_7H_{14}ON_4 \cdot C_6H_3O_7N_3$, crystallises in lustrous, yellow lamellæ, m. p. about 190° (decomp. and separation of a solid).

1-*Carbamylguanylpiperidine* is obtained as a syrup and yields a *picrate*, $C_7H_{14}ON_4 \cdot C_6H_3O_7N_3$, which forms lustrous, yellow needles, m. p. 245° with previous softening.

Guanylyphenylcarbamide, $NHPh \cdot CO \cdot NH \cdot C(NH) \cdot NH_2$, forms long, transparent, colourless crystals, m. p. $143-144^\circ$, yields an alkaline aqueous solution, and with copper sulphate and ammonia gives a brilliant green, pulverulent precipitate. Its *nitrate* ($+HNO_3$) separates in lustrous, colourless crystals and decomposes at $211-213^\circ$, and its *picrate* ($+C_6H_3O_7N_3$) forms slender, yellow needles and begins to decompose at about 230° . The constitution of guanylyphenylcarbamide is established by the fact that it yields aniline and guanidine and only traces of ammonia when hydrolysed by means of dilute nitric acid; the isomeric phenylguanylcaramide has m. p. $62-63^\circ$ (cf. Walther and Grieshammer, A., 1916, i, 173).

T. H. P.

The Isomorphism of the Amides and Substituted Amides of Dichloro- and Chlorobromo-acetic Acids. PHYLLIS V. MCKIE (T., 1923, 123, 2213-2217).

The Hydrates of Potassium and Lithium Platinocyanides and the System Potassium Platinocyanide-Lithium Platinocyanide-Water. HENRY TERREY and VICTOR GEORGE JOLLY (T., 1923, 123, 2217-2222).

The Action of the Grignard Reagent on Nitriles. Glutaronitrile. P. BRUYLANTS (*Bull. Soc. chim. Belg.*, 1923, 32, 307-310).—The reaction between two molecular proportions of magnesium phenyl bromide and one of glutaronitrile leads to the formation of the *hydrobromide* of γ -benzyliminobutyronitrile, m. p. 174° , which gives a *chloroplatinate*, m. p. 197° (decomp.), and a *picrate*, m. p. $200-202^\circ$. The hydrobromide of the base may be crystallised from warm water, and its aqueous solution, when treated with semicarbazide acetate, gives a precipitate of the *semicarbazone* of γ -benzoylbutyronitrile, m. p. $94-95^\circ$. γ -Benzyliminobutyronitrile, m. p. $88-90^\circ$, is obtained by the action of dry ammonia gas on a suspension of its hydrobromide in anhydrous ether. In aqueous solution, the action of ammonia on the hydrobromide is to give γ -benzoylbutyronitrile, m. p. $158-159^\circ$, which can be hydrolysed to the corresponding γ -benzoylbutyric acid of known constitution.

H. H.

Reactions of certain Aromatic Derivatives. A. ANGELI (*Atti R. Accad. Lincei*, 1923, [v], 32, i, 443-449).—The author quotes and co-ordinates further data which confirm the rule that two substituents, occupying ortho- or para-positions in an aromatic ring, behave in many reactions as though they were directly united one to the other (A., 1920, i, 665). Moreover, this rule, which holds with systems composed either of a single aromatic ring or of two aromatic rings joined by characteristic unsaturated chains,

appears to be applicable to certain derivatives of quinoline and, in all probability, to pyridine also. T. H. P.

The Solubility of Liquid Hydrocarbons in Superheated Water. A. JAEGER (*Brennstoff-Chem.*, 1923, 4, 259—260).—The apparatus described by Fischer (*ibid.*, 225) was used to determine the solubilities in water at temperatures from 100° to 300° of (a) benzene, (b) toluene, (c) xylene, (d) tetrahydronaphthalene, and various mixtures of hydrocarbons. The solubilities of the aromatic hydrocarbons are greater than those of the aliphatic; the higher the boiling point of a hydrocarbon the less is its solubility. The following results expressed in c.c. of hydrocarbon dissolved in 100 c.c. of water were obtained: at 100°, (a) 0.2; (b) <0.1; (c) trace; (d) trace; at 150°, (a) 0.6, (b) 0.2; (c) 0.1; (d) 0.02; at 200°, (a) 2.1; (b) 0.7; (c) 0.35; (d) 0.04; at 250°, (a) 7.3; (b) 2.8; (c) 1.1; (d) 0.4; at 285°, (a) 10.6; at 300°, (a) 14.6; (b) 13.0. The various solubilities increase very rapidly with temperature excepting benzene above 250°; that hydrocarbon is then near its critical temperature.

T. S. W.

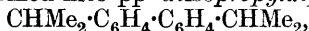
Chemical Composition of Lignite Tar. J. K. PFAFF and A. KREUTZER (*Z. angew. Chem.*, 1923, 36, 437—439).—A toluene fraction (b. p. 111.5—112.5°; S=4.4%), obtained from lignite tar, contained about 3% of α -thiotolene, which was identified by conversion into α -methyl- α -acetothienone. The ketone content of lignite tar oils, which was found to vary from 2.2—4.5%, was determined by warming the oil with excess of phenylhydrazine and estimating the unchanged base by oxidation with boiling Fehling's solution [cf. *J.S.C.I.*, 1923, 967A].

W. T. K. B.

Reactions of Strongly Electropositive Metals with Organic Substances in Liquid Ammonia Solution. III. The Reduction of Nitrobenzene by Sodium in Liquid Ammonia. GEORGE F. WHITE and KENNETH H. KNIGHT (*J. Amer. Chem. Soc.*, 1923, 45, 1780—1787).—Nitrobenzene and nitrosobenzene are reduced by means of sodium in liquid ammonia solution to the disodium derivative of phenylhydroxylamine (cf. Schmidt, A., 1900, i, 20), which probably has the structure $\text{NPhNa} \cdot \text{ONa}$. It is reconverted into nitrobenzene if air is passed into its solution in liquid ammonia, but the free base may be liberated by the action of ammonium chloride. By further reduction of this disodium derivative in liquid ammonia solution, disodioaniline is formed, from which aniline is liberated by the action of ammonium chloride or water. Phenylhydroxylamine itself is reduced directly to aniline in liquid ammonia solution. Azoxybenzene and azobenzene are not formed by direct reduction of nitrobenzene in liquid ammonia, but if the partly reduced mixture is poured into water, they are produced as secondary reaction products of phenylhydroxylamine in the alkaline, aqueous solution. Azoxybenzene is reduced to azobenzene, which is further reduced to a disodium derivative of hydrazobenzene. This gives hydrazobenzene when treated with ammonium

chloride, and is further reduced by sodium in ammonia solution to disodium anilide, whilst hydrazobenzene itself is reduced to monosodium anilide. Mono- and di-alkylanilines are formed in liquid ammonia solution by the action of alkyl halides on mono- and di-sodium anilides, respectively. W. S. N.

Preparation of the Magnesium Compound of *p*-Bromocumene and its Application to Organic Syntheses. L. BERT (*Compt. rend.*, 1923, **177**, 452—453).—Details of the action of magnesium on *p*-bromocumene are given; the resulting substance is stated to be as easy to prepare as the corresponding *p*-bromobenzene derivative. In the reaction, about 15% of the *p*-bromocumene was transformed into *pp'*-diisopropyldiphenyl,

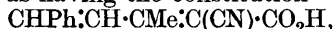


brilliant, colourless plates, m. p. 64—65°. Various syntheses have been effected by means of the magnesium compound. H. J. E.

Chlorosulphonyl Derivatives of Aromatic Amines. ROWLAND NICHOLAS JOHNSON and SAMUEL SMILES (*T.*, 1923, **123**, 2384—2388).

Preparation of Intermediate Compounds [*m*-Chloro-, *m*-Bromo-, and *m*-Iodo-phenol] for the Production of Colouring Matters. BRITISH DYESTUFFS CORPORATION, LTD., and HERBERT HENRY HODGSON (*Brit. Pat.* 200714).—A substantially quantitative yield of *m*-chlorophenol is obtained by diazotising *m*-chloroaniline and decomposing the diazo-solution, care being taken that the latter is free from nitrous acid and that the *m*-chlorophenol is removed from the reaction liquid by distillation in steam with such rapidity that combination cannot take place with further quantities of diazo-compounds. Diazotisation is effected in dilute sulphuric acid, addition of the nitrite solution to the paste of *m*-chloroaniline sulphate being stopped before all the crystals of the latter have disappeared. The filtered diazo-solution is dropped into boiling dilute sulphuric acid, through which a current of steam is blown. The liquid is simultaneously heated so as to maintain substantially the same volume. *m*-Bromo- and *m*-iodo-phenol are obtained in the same way from *m*-bromo- and *m*-iodo-aniline, respectively. W. T. K. B.

The Reaction between Cyanoacetic Esters and Styryl Methyl Ketone. E. P. KOHLER and PAUL ALLEN, jun. (*J. Amer. Chem. Soc.*, 1923, **45**, 1987—1990).—The compound described by Haworth (*T.*, 1909, **95**, 480) as having the constitution



m. p. 188°, is identical with cyanophenyldihydroresorcinol, m. p. 180° (Vorländer, A., 1897, i, 272), the constitution of which is confirmed by oxidising it to phenylsuccinic acid by means of cold alkaline potassium permanganate solution. The acid amide, and the monobasic acid, m. p. 190° (m. p. 187—188° according to Vorländer, *loc. cit.*), described by Haworth, must also be regarded as dihydroresorcinol derivatives. The primary product in the

formation of cyanophenyldihydroresorcinol from methyl cyanoacetate and styryl methyl ketone is *methyl α -cyano- γ -acetyl- β -phenylbutyrate*, a very pale yellow liquid, b. p. about $196^{\circ}/7$ mm. (*semicarbazone*, minute, white needles, m. p. 156 — 157°), or, if ethyl cyanoacetate is used, *ethyl α -cyano- γ -acetyl- β -phenylbutyrate*, a very viscous oil, b. p. $203^{\circ}/12$ mm. These can only be isolated if the condensation between the cyano-ester and the unsaturated ketone is conducted in the presence of a small quantity of sodium methoxide or ethoxide, since this causes ring formation with elimination of methyl or ethyl alcohol. *Methyl β -phenyl- γ -acetylmalonate*, $\text{COMe}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{CH}(\text{CO}_2\text{Me})_2$, a colourless solid, m. p. 64° , is formed by keeping a methyl-alcoholic solution of the above methyl cyano-ester after saturating with hydrogen chloride, or by the direct addition of methyl malonate to styryl methyl ketone in the presence of cold sodium methoxide. W. S. N.

Manufacture of Thymol. HOWARDS & SONS, LTD., and JOHN WILLIAM BLAGDEN (Brit. Pat. 200151).—*m*-Cresol is condensed with isopropyl alcohol in the presence of phosphoric acid at a temperature of 70 — 80° . If the reaction temperature is higher (e.g., 150°), a condensation product melting at 114° and possessing antiseptic properties is obtained. W. T. K. B.

The Humic Acid Problem. WALTER FUCHS (*Naturprodukte*, 1923, 98—107).—The author discusses current opinions on the constitution of humic acid, and compares experimentally the properties of the humic acid prepared from resorcinol by Stamberger (following abstract) with those of commercial humic acid from peat. The latter can be methylated in alkaline solution without being thrown out of solution; it must therefore contain both phenolic and carboxyl groups. By fusion with potassium hydroxide, it gives a product having acid properties and giving a chocolate coloration with ferric chloride. With ammonia, the humic acid forms a compound from which only part of the nitrogen can be removed by distillation with alkali. It is suggested that oxygen of a furan ring is displaced by nitrogen with formation of a pyrrole ring. The nitrogen-containing product is more resistant to oxidation than the original humic acid, and it reacts with nitrous acid as though it contained an imide group. It is concluded that humic acid contains both phenol and furan nuclei. The formation of such a complex compound from a variety of natural products is conceivable. E. H. R.

Synthetic Humic Acids. PAUL STAMBERGER (*Naturprodukte*, 1923, 108—112).—A synthetic humic acid is obtained when resorcinol is heated with sublimed ferric chloride in aniline or quinoline solution. The product is qualitatively similar to that obtained by Eller and Koch by oxidation of phenols capable of forming quinones (A., 1920, i, 733). It contains no nitrogen, but reacts with aqueous ammonia to form a "*N*-humic acid" containing 6.36% N. The humic acid can be methylated with methyl sulphate and benzoylated with benzoyl chloride. When fused with potassium

hydroxide, it gives an indistinctly crystalline product giving a chocolate coloration with ferric chloride, the coloration being intensified by hydrogen peroxide. The fusion product gives a *benzoyl* derivative, m. p. 100—101°, and a *bromo*-derivative, m. p. 120°. Humic acid prepared from starch is qualitatively similar to the above, but requires heating in ammonia gas at 110—120° to give a "*N*-humic acid." E. H. R.

Derivatives of *ortho*-Thiolphenols. DAVID TEMPLETON GIBSON and SAMUEL SMILES (T., 1923, 123, 2388—2393).

Preparation of Urethanes of Secondary Aliphatic-aromatic Alcohols. ÉTABLISSEMENTS POULENC FRÈRES (Fr. Pat. 532464; from *Chem. Zentr.*, 1923, ii, 1062).—Carbonyl chloride is allowed to react with phenylethylcarbinol, $\text{CHEtPh}\cdot\text{OH}$, or its homologues in the presence or absence of tertiary bases such as trimethylamine or dimethylaniline, and the chloroformates thereby obtained are treated with ammonia. The alcohols used are obtained by the action of magnesium alkyl halides on benzaldehyde. For example, phenylethylcarbinol obtained by the action of magnesium ethyl bromide on benzaldehyde is allowed to react with carbonyl chloride in benzene solution at 10° with addition of trimethylamine or dimethylaniline. After addition of ice, the benzene solution is dried and saturated with ammonia. After removal of ammonium chloride and dimethylaniline, *phenylethylcarbinol urethane*, $\text{CHEtPh}\cdot\text{O}\cdot\text{CO}\cdot\text{NH}_2$, is obtained; it has m. p. 89°. *Phenylpropylcarbinol urethane* has m. p. 80°; it is prepared from *phenylpropylcarbinol*, b. p. 119°/12 mm. *Phenylbutylcarbinol*, b. p. 132°/14 mm., yields a *urethane* having m. p. 75°. G. W. R.

Spontaneous Dissociation of Triphenylmethyl Disulphide with the Formation of Triphenylmethyl. The Potassium Derivative of Triphenylcarbinol and its Use as a Synthetic Agent. F. F. BLICKE (*J. Amer. Chem. Soc.*, 1923, 45, 1965—1969).—Triphenylmethyl disulphide dissociates spontaneously in benzene solution at the ordinary temperature with formation of triphenylmethyl, which is isolated as its peroxide (cf. this vol., i, 364). The *potassium* derivative of triphenylmethyl alcohol is prepared by the action of the alcohol on metallic potassium in boiling xylene solution. It forms colourless, transparent crystals containing approximately 1 mol. of xylene of crystallisation. It reacts in boiling benzene solution with methyl iodide, giving triphenylmethyl methyl ether, with ethyl iodide giving ethylene, triphenylmethyl alcohol, and potassium iodide, and with benzoyl chloride giving triphenylmethyl benzoate. The potassium compound reacts with triphenylmethyl sulphur chloride in cold benzene solution, with evolution of heat, to give a clear, reddish-brown solution from which triphenylcarbinol and triphenylmethyl peroxide are isolated. It is likely that triphenylmethyl thioperoxide is produced initially; the peroxide may be formed by interaction between the thioperoxide and unchanged potassium compound: $2\text{Ph}_3\text{C}\cdot\text{S}\cdot\text{O}\cdot\text{CPh}_3 + 4\text{Ph}_3\text{C}\cdot\text{OK} = 3\text{Ph}_3\text{C}\cdot\text{O}\cdot\text{O}\cdot\text{CPh}_3 + \text{Ph}_3\text{C}\cdot\text{CPh}_3 + 2\text{K}_2\text{S}$.

This explanation is supported by the observation of Vorländer and Mittag (A., 1913, i, 1335) that triphenylmethyl sulphur chloride reacts with sodium methoxide to give triphenylmethyl methyl thioperoxide. The opinion of those authors that the product of this reaction, when excess of sodium methoxide is used, is triphenylmethyl peroxide, has now been definitely proved to be correct. The potassium derivative of triphenylmethyl alcohol reacts with triphenylmethyl chloride in cold benzene solution, but does not give triphenylmethyl ether; the only product isolated is *p*-hydroxy-triphenylmethyl alcohol, which is probably present as its anhydride, diphenylquinomethane. The potassium compound reacts immediately with iodine, phosphorus trichloride, or other substances containing reactive halogen. W. S. N.

A Study of the Phytosterols of Corn [Maize] Oil, Cotton-seed Oil, and Linseed Oil. R. J. ANDERSON and M. G. MOORE (*J. Amer. Chem. Soc.*, 1923, **45**, 1944—1953).—Maize oil contains a relatively high percentage of unhydrolysable matter, as estimated by a modification of Bömer's method (*Z. Nahr. Genussm.*, 1898, **1**, 21), amounting in the crude oil to 2.01%, and in the refined edible oil to 1.68%. This unsaponifiable matter consists largely of phytosterol, which is identical with sitosterol. It has m. p. 137.5°, $[\alpha]_D^{20}$ -34.38°; its acetate has m. p. 127°. It does not contain any stigmasterol. These results are in agreement with those of Gill and Tufts (A., 1903, i, 417).

The observations of Wagner and Clement (*Z. Nahr. Genussm.*, 1909, **17**, 266) on cotton-seed oil are confirmed. It contains at least two phytosterols, which have, respectively, m. p. 138—139° and 134—135°, $[\alpha]_D^{20}$ -34.19° and -33.61°, the acetates having m. p. 124° and 119°, respectively. The separation of these two fractions by crystallisation is very difficult, and it is not thought that either of them is homogeneous.

Two phytosterols have been isolated from linseed oil, having, respectively, m. p. 138° and 134° (indefinite), $[\alpha]_D^{20}$ -34.22° and -31.16°, acetates, m. p. 129—130° and 124° (cf. Bömer and Winter, *Z. Nahr. Genussm.*, 1901, **4**, 865).

None of the phytosterols isolated contains as much as 1 mol. of water of crystallisation, the irregular loss observed on drying corresponding roughly with 0.5 molecule. W. S. N.

Japanese Birdlime. III. HIDEKICHI YANAGISAWA and NORIKAZU TAKASHIMA (*J. Pharm. Soc. Japan*, 1923, No. **494**, 251—258; cf. A., 1921, i, 760; 1922, i, 652).—Trochol, $C_{26}H_{44}O_2$, isolated from the saponification product of Japanese birdlime, *Trochodendron aralioides*, yields a *diphenylcarbamate*, $C_{26}H_{42}O_2(CO \cdot NPh)_2$, colourless prisms, m. p. 167°; *formate*, nacreous scales, m. p. 306°, and *phthalate*, a white, crystalline powder, m. p. 224—228°. On oxidation with hydrogen peroxide in glacial acetic acid, the alcohol gave a dihydroxymonoketone, *trocholone*, $C_{26}H_{42}O_3$, an amorphous powder, m. p. about 100°, *trochol peroxide*, $(C_{26}H_{42}O_5)_2$, colourless scales, m. p. 215°; (*semicarbazone*, fine, white needles, m. p. 290°; *acetyl* derivative, fine, white needles, m. p. 205°; *oxime*,

small, white needles, m. p. 217°), and *trocholic acid*, $C_{26}H_{42}O_4$, white granules, m. p. 282° (*diacetate*, white, crystalline powder, m. p. 145°). The authors conclude that trochol is a secondary-tertiary, but not a primary alcohol. When a mixture of trochol and chromic anhydride is treated with water, an odour of butyric acid is produced, and acetic acid can be isolated by the distillation of the mixture with steam. K. K.

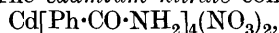
Esterification. I. Esterification of the *cyclo*Paraffin-monocarboxylic Acids. G. D. ADVANI and J. J. SUDBOROUGH (*J. Indian Inst. Sci.*, 1923, 6, 41—68; cf. T., 1912, 101, 237).—The investigation deals with the influence of ring-formation on rates of esterification (cf. Menshutkin, T., 1906, 89, 1532). The esterifications were carried out in absolute ethyl alcohol at 25° . The modified formula of Goldschmidt and Udby (A., 1907, ii, 852) for unimolecular reactions was found to give fairly good constants. The values of the constant, K , obtained were as follows (the figures in brackets are the corresponding dissociation constants $\times 10^5$): *cyclo*Butanecarboxylic acid, 0.544 (1.82). *cyclo*Pentanecarboxylic acid, 0.196. *iso*Butyric acid, 0.156 (1.62). *cyclo*-Hexanecarboxylic acid, 0.0812 (1.26). α -Methyl-*n*-butyric acid, 0.0384 (1.68). *cyclo*Propanecarboxylic acid, 0.0324 (1.44). α -Ethyl-*n*-butyric acid, 0.00313 (2.02). α -Ethyl-*n*-valeric acid, 0.00311. Goldschmidt and Udby's results were confirmed in that the values of K vary somewhat with the concentration of the catalyst. In the cases of the disubstituted acetic acids examined, *isobutyric* acid is most readily esterified, α -ethyl-*n*-butyric and α -ethyl-*n*-valeric acids least readily. The methyl group has the least inhibiting effect, whilst the ethyl and *n*-propyl groups have practically the same effect. By comparing the aliphatic and the corresponding cyclic acids, the following ratios for K are obtained: *isobutyric* acid: *cyclo*propanecarboxylic acid = 0.25 : 1; α -methyl-*n*-butyric acid: *cyclo*butanecarboxylic acid = 13.0 : 1; α -ethyl-*n*-butyric acid: *cyclo*pentanecarboxylic acid = 80.0 : 1; α -ethyl-*n*-valeric acid: *cyclo*hexanecarboxylic acid = 28.0 : 1. This agrees with Menshutkin's acetylation results (*loc. cit.*), in that the maximum occurs in the pentamethylene series. In the case of the cyclic acids alone, the ratios for K are: 3-ring = 1; 4-ring = 16; 5-ring = 7; 6-ring = 3. It is possible that the low values for the *cyclo*propanecarboxylic acid may be due to tautomeric change.

Improved methods were worked out for the preparation of several of the acids. *cyclo*Propanecarboxylic acid was made by a modification of Henry and Dalle's method (A., 1902, i, 525), using α - γ -dibromopropane in place of α -chloro- γ -bromopropane. *cyclo*Pentanecarboxylic acid was prepared from α - δ -dibromobutane, which was made by a modification of Braun and Beschke's method (A., 1907, i, 127). F. A. M.

Complexes of Benzamide with Metallic Salts. L. BELLADEN and R. ASTENGO (*Atti R. Accad. Lincei*, 1923, [v], 32, i, 491—493).—Compounds of benzamide with mercury and with silver

were obtained by Tafel and Enoch (A., 1890, 491, 973), and Curtius prepared sodiobenzamide (A., 1891, 58). The authors have now obtained the following complex benzamide compounds, all of which are decomposed by water, with separation of benzamide.

The *cadmium chloride* compound, $\text{Cd}[\text{Ph}\cdot\text{CO}\cdot\text{NH}_2]\text{Cl}_2$, and the analogous *cadmium bromide* compound both form slender needles, m. p. above 450° . The *cadmium nitrate* compound,



forms octahedral crystals, m. p. 194° . The *cupric chloride* compound, $\text{Cu}[\text{Ph}\cdot\text{CO}\cdot\text{NH}_2]\text{Cl}_2$, forms long, slender, pale green prisms, m. p. 230° (darkening), and dissolves in alcohol to a green solution. The *antimony trichloride* compound, $\text{SbCl}_3\cdot\text{HCl}[\text{Ph}\cdot\text{CO}\cdot\text{NH}_2]_2$, forms long prisms, begins to decompose at about 70° if heated slowly, and melts at 138° if heated rapidly. The analogous *bismuth trichloride* compound crystallises in large, colourless prisms, and, like the antimony compound, may be represented by a structural

formula of the type,
$$\begin{array}{c} \text{H} \quad \text{Cl} \\ \diagdown \quad \diagup \\ \text{M} \\ \diagup \quad \diagdown \\ \text{Cl} \quad \text{NH}(\text{HCl})\cdot\text{COPh} \\ \quad \quad \quad \text{NH}(\text{HCl})\cdot\text{COPh} \end{array}$$
 which is analogous

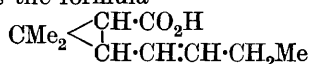
to that obtained by Bruni and Manuelli (A., 1905, ii, 689) from acetamide and antimony trichloride. T. H. P.

Lithium, Sodium, Potassium, and Ammonium Hippurates.

C. E. CORFIELD and B. W. MELHUISE (*Pharm. J.*, 1923, **111**, 97—98).—The lithium salt is readily obtained in crystalline form; the molecule contains $2\text{H}_2\text{O}$. Sodium hippurate is difficult to crystallise from its aqueous solution; the crystals obtained from an alcoholic solution contain $1\cdot5\text{H}_2\text{O}$ and $1\text{H}_2\text{O}$ after the salt has been dried over sulphuric acid. A sodium salt containing $0\cdot5\text{H}_2\text{O}$ could not be prepared. Potassium hippurate ($1\text{H}_2\text{O}$) is deliquescent. Ammonium hippurate is an anhydrous salt, whether crystallised from aqueous or alcoholic solution; it can be prepared most economically by keeping the solution saturated with ammonia during evaporation. When the salt is crystallised from alcoholic solution, it is necessary to treat the solution with twice its volume of ethyl ether in order to induce precipitation. Hippuric acid behaves as a monobasic acid and all attempts to prepare hydrogen salts were unsuccessful. W. P. S.

The Insecticidal Principle of *Chrysanthemum cinerariæ-folium*. II and III. Constitution of Pyrethronic Acid. RYO YAMAMOTO (*J. Chem. Soc. Japan*, 1923, **44**, 311—330; cf. A., 1919, i, 465).—Pyrethron, an effective constituent of *Chrysanthemum cinerariæ-folium*, is composed of higher alcohols, an oily substance and a solid and a liquid acid. The liquid acid has a weak effect on insects, but the oily substance none; when, however, the liquid acid was condensed with the oily substance, the ester had almost the same effect as pyrethron itself. The liquid, optically inactive *pyrethronic acid*, $\text{C}_{10}\text{H}_{16}\text{O}_2$, b. p. 110 — $115^\circ/1$ mm., d $0\cdot9685$, n_D^{20} $1\cdot4762$, was purified by way of its *ethyl* ester, b. p. 90 — $94^\circ/7$ mm. When reduced with hydrogen in the presence of

platinum black, a molecule of the acid absorbed two atoms of hydrogen, yielding the saturated acid, $C_{10}H_{18}O_2$, which did not crystallise at -15° . The saturated and unsaturated acids gave barium salts, needles, and the latter a lead salt. The results of analyses of the *amide*, needles, m. p. 128° , and *anilide*, needles, m. p. $106-107^\circ$, of pyrethronic acid, and *amide*, m. p. 133° , of the saturated acid showed considerable divergence from those expected from the above formulæ. On oxidising with 1% potassium permanganate solution in sodium carbonate solution at 0° , sodium pyrethronate gave a *dihydroxy-acid*, $C_9H_{15}(OH)_2 \cdot CO_2H$, needles, m. p. 146° , which gave barium and calcium salts. By treating with a mixture of potassium dichromate and sulphuric acid, dihydroxypyrethronic acid gave *trans*-caronic acid, $CMe_2 \begin{smallmatrix} \diagup CH \cdot CO_2H \\ \diagdown CH \cdot CO_2H \end{smallmatrix}$, needles, m. p. 212° , which gave terepinic acid by heating with acetic anhydride. When pyrethronic acid was ozonised in chloroform solution, caronic acid and its semi-aldehyde were produced; propionic acid and its aldehyde were also detected. The author ascribes the formula



to pyrethronic acid.

K. K.

Synthesis of Phenylanthranilic Acids. NEAL TUTTLE (*J. Amer. Chem. Soc.*, 1923, **45**, 1906—1916).—*p*-Dimethylaminodiphenylamine is formed by heating *p*'-dimethylaminodiphenylamine-*o*-carboxylic acid above its melting point. The latter is prepared by digesting *o*-chlorobenzoic acid, dimethyl-*p*-phenylenediamine, and potassium carbonate with copper powder in amyl-alcoholic solution; it forms pale green prisms or needles, m. p. 216° (decomp.). It is converted by the action of concentrated sulphuric acid at 100° into 2-dimethylaminoacridone, small, bright yellow clusters, m. p. $289-290^\circ$, which shows a green fluorescence in acetic acid solution, but blue in alcoholic sulphuric acid. Dimethyl-*p*-phenylenediamine and 2-chloro-5-nitrobenzoic acid react under similar conditions, or in the presence of copper and aqueous sodium acetate solution, to give *p*-nitro-*p*'-dimethylaminodiphenylamine-*o*-carboxylic acid, small, coppery needles, m. p. $234-235^\circ$. Dimethyl-*p*-phenylenediamine and 2-chloro-3:5-dinitrobenzoic acid react in the presence of cold aqueous sodium acetate solution, giving 2:4-dinitro-4'-dimethylaminodiphenylamine-6-carboxylic acid, a bright yellow, amorphous powder, m. p. 253° (decomp.), hydrochloride, reddish-brown plates, m. p. $240-260^\circ$. Dimethyl-*m*-phenylenediamine condenses with *o*-chlorobenzoic acid, giving *m*'-dimethylaminodiphenylamine-*o*-carboxylic acid, colourless needles, m. p. 155° . With 2-chloro-5-nitrobenzoic acid, the product is *p*-nitro-*m*'-dimethylaminodiphenylamine-*o*-carboxylic acid, small, greenish-brown needles, m. p. 247° (decomp.). The condensation of 2-chloro-3:5-dinitrobenzoic acid with dimethyl-*m*-phenylenediamine may be effected by boiling with alcohol, or with aqueous sodium acetate solution; copper need not be added. The product is 2:4-dinitro-

3'-dimethylaminodiphenylamine-6-carboxylic acid, slender, green needles of high melting-point, *hydrochloride*, green needles, which sinter at 320°. **p'-Diethylaminodiphenylamine-o-carboxylic acid** is obtained by the condensation of *o*-chlorobenzoic acid and diethyl-*p*-phenylenediamine; it is a blue solid, which becomes gummy on isolation from the reaction mixture. **p'-Diethylamino-p-nitrodiphenylamine-o-carboxylic acid** forms slender, brown needles, m. p. 239—240°. **4'-Diethylamino-2:4-dinitrodiphenylamine-6-carboxylic acid** is a bright yellow powder, m. p. 259°, *hydrochloride*, orange flakes, m. p. 252—253°; in its preparation, copper need not be employed. **m'-Diethylaminodiphenylamine-o-carboxylic acid** is a dark blue solid, which liquefies when separated from its mother-liquor. The condensation of diethyl-*m*-phenylenediamine with 2-chloro-5-nitrobenzoic acid gives *pp'*-dinitrodiphenyl-*oo'*-dicarboxylic acid. The use of 2-chloro-3:5-dinitrobenzoic acid gives **3'-diethylamino-2:4-dinitrodiphenylamine-6-carboxylic acid**, bright yellow needles, m. p. 220° (decomp.). The action of piperidine on *o*-chlorobenzoic acid in the presence of sodium carbonate, amyl alcohol, and copper powder gives salicylic acid, but the use of 2-chloro-5-nitrobenzoic acid leads to the formation of 5-*nitro-2-piperidinobenzoic acid*, very pale yellow, rhombic crystals, m. p. 200—202°. The action of piperidine on 2-chloro-3:5-dinitrobenzoic acid in aqueous sodium acetate solution in the presence of copper powder gives green needles of the *copper* salt of 3:5-dinitrosalicylic acid, which explode violently at about 320°. *o*-Chlorobenzoic acid is unchanged by boiling with 10% aqueous potassium hydroxide solution, and only partial conversion into salicylic acid occurs when amyl-alcoholic potassium hydroxide is used and sodium carbonate and copper powder are added. 5-Nitrosalicylic acid is formed when 2-chloro-5-nitrobenzoic acid is boiled with 10% aqueous potassium hydroxide solution. Aniline and potassium 2-chloro-3-nitrobenzoate condense when boiled in ethyl-alcoholic solution with copper powder, yielding **2-nitrodiphenylamine-6-carboxylic acid**, yellow clusters, m. p. 194°.

W. S. N.

Pharmacological and Clinical Examination of Benzyl Mandelate. DAVID I. MACHT (*J. Pharm. Expt. Ther.*, 1923, **21**, 443—455; cf. *J. Amer. Pharm. Assoc.*, 1923, **12**, 7).—Benzyl mandelate forms colourless crystals, m. p. 93°, soluble in the usual organic solvents. A pharmacological and toxicological study of this compound has been made. It shows low toxicity but marked pharmacological activity.

W. O. K.

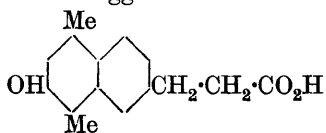
Attempted Absolute Asymmetric Syntheses. G. BREDIG [with P. MANGOLD and TH. G. WILLIAMS] (*Z. angew. Chem.*, 1923, **36**, 456—458).—A series of attempted syntheses of permanently optically active substances is described in which it was endeavoured to obtain these substances without any assistance whatsoever from other optically active materials, but entirely through the agency of asymmetrical exterior physical forces. The measurement of the dielectric constants and con-

ductivity of hydrocyanic acid and mandelonitrile is described. These measurements were undertaken because it appears there is no chance of the synthesis of an optically active mandelonitrile being effected by carrying out the reaction in an electric field unless the reaction itself is accompanied by a change in the dielectric constant of the material. The measurements indicated that such a change in the dielectric constant does actually take place.

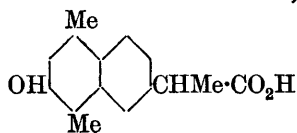
Several attempted asymmetrical syntheses and decompositions with the aid of circularly polarised light are described, the substances acted on being diazocamphor, lactic acid, and asymmetric cobaltamine salts, but in no case was the slightest asymmetry found in the decomposition product. It is considered possible that the effects of circularly polarised rays of a wave-length comparable with the dimensions of the atom might produce the desired results.

H. C. R.

Chemical Constitution of Artemisic Acid. P. BERTOLO (*Atti R. Accad. Lincei*, 1923, [v], **32**, i, 486—490; cf. A., 1920, i, 444, 445).—Two of the three oxygen atoms of the artemisic acid molecule occur in the carboxyl group of the propionic acid residue, whilst the third forms part of the phenolic hydroxyl. Since fusion of artemisic acid with potassium hydroxide yields 1:4-dimethyl- β -naphthol, this acid contains unchanged the fundamental nucleus of the artemisin, the ketonic oxygen of the latter being the phenolic oxygen of the acid. The oxygen atom lost as water in the formation of the acid from artemisin is the atom in virtue of which artemisin differs from santonin. Thus, the conversion of artemisin into artemisic acid by treatment with hydrochloric acid involves the elimination of a molecule of water, the rupture of the lactonic linking, and the transformation of the carboxylic oxygen into a phenolic hydroxyl group. On the basis of these considerations the author suggests for artemisic acid one of the two formulæ,



(I.)



(II.)

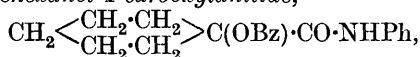
Owing to the optical activity of the acid, preference is accorded to formula (II), the analogy between this and the structure ascribed by Gucci and Grassi-Cristaldi to santinic acid (A., 1892, 869) being borne out by the similarity in the methods of formation of the two acids, as well as by physical resemblances.

T. H. P.

isoNitriles. VI. Reaction with Cyclic Ketones in Presence of Organic Acids. MARIO PASSERINI (*Gazzetta*, 1923, **53**, i, 410—417).—*cyclo*Hexanones behave like other ketones when treated with phenylcarbylamine in presence of benzoic acid (cf. A., 1921, i, 743, 895), yielding anilides of 1-benzoyl-*cyclo*hexanol-1-carboxylic acids: $C_5H_{10} \cdot CO + Ph \cdot NC + Ph \cdot CO_2H = C_5H_{10} \cdot C(OBz) \cdot CO \cdot NHPh$. Good yields of these anilides are readily obtained from *cyclo*hexanone and from the three isomeric methyl-

cyclohexanones. When heated above their melting points, the anilides of 1-benzoyl*cyclohexanol*-1-carboxylic acid and its 3-methyl derivative are converted into isomerides with higher melting points. With each of these two pairs of isomerides, removal of the benzoyl group by hydrolysis results in the formation of a single acid. Hydrolysis of the anilides of 1-benzoyl-2- and 4-methyl-*cyclohexanol*-1-carboxylic acids yields the anilides of the corresponding non-benzoylated hydroxy-acids, these giving aniline and the hydroxy-acids themselves when subjected to more energetic hydrolysis.

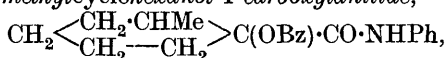
1-Benzoyl*cyclohexanol*-1-carboxylanilide,



forms colourless crystals, m. p. 134—135°, and, when heated above its melting point or boiled in benzene solution, is converted into an *isomeride*, which forms acicular crystals, m. p. 155—156°, and cannot be reconverted into the original compound by addition of the latter to its solutions.

cycloHexanol-1-carboxylanilide, $\text{C}_{13}\text{H}_{17}\text{O}_2\text{N}$, prepared from either of the above isomerides, forms lustrous, white crystals, m. p. 174—175°.

1-Benzoyl-2-methyl*cyclohexanol*-1-carboxylanilide,



forms minute, colourless crystals, m. p. 158—159°.

2-Methyl*cyclohexanol*-1-carboxylanilide, $\text{C}_{14}\text{H}_{19}\text{O}_2\text{N}$, crystallises in colourless needles, m. p. 144—146°.

1-Benzoyl-3-methyl*cyclohexanol*-1-carboxylanilide, $\text{C}_{21}\text{H}_{23}\text{O}_3\text{N}$, forms crystals, m. p. 65°, and, on prolonged heating at 80°, yields an *isomeride*, m. p. 172—174°, which crystallises unchanged from ethereal solution, but is reconverted into the form of lower melting point when crystallised from alcohol. Hydrolysis of either isomeride gives

3-Methyl*cyclohexanol*-1-carboxylanilide, $\text{C}_{14}\text{H}_{19}\text{O}_2\text{N}$, which crystallises in square plates, m. p. 142—143°. Markownikov and Smirnov (A., 1907, i, 418) prepared this anilide in its *cis*- and *trans*-modifications by the action of aniline on the mixture of the two 3-methyl*cyclohexanol*-1-carboxylic acids prepared from the cyanohydrin of 3-methyl*cyclohexanone*, but both modifications exhibited lower melting points than that now found. 3-Methyl*cyclohexanol*-1-carboxylic acid, described by Markownikov and Smirnov as a vitreous mass, composed of the *cis*- and *trans*-modifications, forms a crystalline mass, m. p. 25—27°.

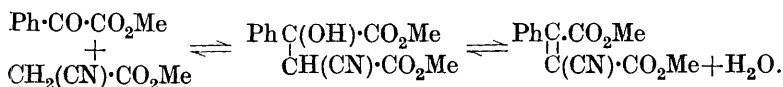
1-Benzoyl-4-methyl*cyclohexanol*-1-carboxylanilide, $\text{C}_{21}\text{H}_{23}\text{O}_3\text{N}$, crystallises in minute, colourless needles, m. p. 160—162°.

4-Methyl*cyclohexanol*-1-carboxylonitrile, $\text{C}_{14}\text{H}_{19}\text{O}_2\text{N}$, has m. p. 145—147°.

T. H. P.

The Mechanism Underlying the Reaction between Aldehydes or Ketones and Tautomeric Substances of the Keto-Enol Type. E. P. KOHLER and B. B. CORSON (*J. Amer. Chem. Soc.*, 1923, 45, 1975—1986).—When methyl benzoylformate and

methyl cyanoacetate, in equivalent proportions, are treated at 0° with a small quantity of ammonia, methylamine, piperidine, or methyl-alcoholic sodium methoxide solution, an equilibrium is rapidly established, with the formation of *methyl β -cyano- α -hydroxy- α -phenylsuccinate*, hexagonal plates, or hard, lustrous, tabular crystals, m. p. 155° , to the extent of 75–80%. This reverts to its components when dissolved in a solution containing any of the above catalysts, and also partly dissociates when distilled under a very low pressure. The action of dehydrating agents, such as boiling glacial acetic acid or phosphoric oxide in phosphorus oxychloride solution, leads, however, to the production of *methyl β -cyano- α -phenylethylene- $\alpha\beta$ -dicarboxylate*, large, transparent prisms, m. p. 79 – 80° , which is also formed if the initial condensation is conducted at the ordinary temperature, or in the presence of a larger quantity of catalyst. It is evident that the effect of the basic condensing agents generally employed in such reactions is dual; they cause condensation, and also bring about elimination of water. These relations are plausibly expressed by the scheme :



There is, however, no proof that the hydroxy-ester is an intermediate product in the formation of the unsaturated ester, because under those conditions which lead to the elimination of water, dissociation can also occur into the components, from which the unsaturated ester may be derived by direct elimination of water. Inasmuch as methyl benzoylformate, which cannot enolise, condenses with methyl cyanoacetate, there is no ground for the assumption that reactions between aldehydes or ketones, and substances containing a mobile hydrogen atom, proceed in general through the enol form of the aldehyde or ketone (Ingold, T., 1921, **119**, 329).

The structure of the unsaturated ester is proved as follows. When it is hydrolysed by means of cold, concentrated, methyl-alcoholic potassium hydroxide solution, the product is *α -cyano- β -phenylmaleic acid*, very pale yellow needles, m. p. about 142° (decomp.), *potassium hydrogen salt*, colourless needles, m. p. 193 – 195° , *anhydride*, yellow needles, m. p. 145 – 146° . Hydrolysis by boiling with concentrated sulphuric acid and glacial acetic acid gives *α -cyano- β -phenylfumaric acid*, pale yellow crystals, $+2\text{H}_2\text{O}$ (lost below 100°), m. p. 158 – 160° , which sublimes unchanged when heated under reduced pressure. The reduction of the dipotassium salt of this acid in aqueous solution by means of sodium amalgam gives an *amino-acid*, $\text{CO}_2\text{H}\cdot\text{CHPh}\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{NH}_2$, m. p. 168 – 169° , and phenylsuccinic acid. *Methyl α -phenylethane- $\alpha\beta$ -tricarboxylate*, needles, m. p. 107 – 108° , is formed by esterifying the reduction product of the dipotassium salt formed from the unsaturated cyano-ester.

Similar reactions have been conducted using dimethyl malonate. When condensed with methyl benzoylformate, it gives *trimethyl*

β-hydroxy-β-phenylethane-αα-tricarboxylate, lustrous prisms, m. p. 109—111°. The corresponding unsaturated ester, *trimethyl β-phenylethylene-αα-tricarboxylate*, is a liquid, b. p. 180—190°/10 mm. The structure of this is proved by hydrolysing it by means of cold, concentrated, alcoholic potassium hydroxide solution, and reducing the resulting potassium salt by means of sodium amalgam to phenylethanetricarboxylic acid, which loses carbon dioxide when heated, and gives phenylsuccinic acid. W. S. N.

The Structure of Phenolphthaleinoxime. W. R. ORNDORFF and S. T. YANG (*J. Amer. Chem. Soc.*, 1923, 45, 1926—1933).—Phenolphthaleinoxime undergoes the Beckmann rearrangement when acetylated or benzoyleated, giving the triacetate or dibenzoate of the intermediate product, the *p-hydroxyanilide* of *o-4'-hydroxybenzoylbenzoic acid* (I), $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{OH})\langle\text{N}(\text{C}_6\text{H}_4\cdot\text{OH})\rangle\text{CO}$, +1.5H₂O, small, colourless, flaky crystals, m. p. 135° (decomp.). The latter is obtained from the triacetate by hydrolysis by means of cold concentrated sulphuric acid or of cold 4% sodium hydroxide solution. It has a different m. p. when crystallised from different solvents: from acetone, 94—95°; from methyl alcohol, 125°; from ethyl alcohol, 130°; and from ethyl acetate (apparently +0.5MeCO₂Et), 195—198°. It loses 2.5 molecules of water when heated at 95° in an atmosphere of carbon dioxide, giving a red glass, probably having the structure $\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{C}\langle\text{N}(\text{C}_6\text{H}_4\cdot\text{OH})\rangle\text{CO}$. The glassy substance dissolves in dilute aqueous alkali solutions, giving a dark green solution from which a yellow, amorphous precipitate separates on acidification. It is assumed that the compound (I) is formed intermediately when phenolphthaleinoxime is hydrolysed by means of dilute sulphuric acid, since when similarly treated it gives the same products, *p*-aminophenol and *o-4'*-hydroxybenzoylbenzoic acid. It gives the same reduction product as the oxime when treated with zinc dust and dilute sulphuric acid; also, like the oxime, it is converted into phenol and *p*-hydroxyphthalanil when heated with a solution of hydroxylamine hydrochloride. The oxime and the intermediate product give the same triacetate when acetylated, and the same dibenzoate when benzoyleated; the tribenzoate of the oxime described by R. Meyer and Kissin (A., 1909, i, 651) could not be obtained. When methylated in 30% aqueous sodium hydroxide solution by means of methyl sulphate, the intermediate product gives a colourless *trimethyl ether*, m. p. 131—133°, isomeric with the yellow trimethyl ether formed, by similar treatment, from the oxime. In an attempt to synthesise the intermediate product by fusing *p*-aminophenol with *o-4'*-hydroxybenzoylbenzoic acid, a dark purple solid was obtained. This is probably a mixed phthalein; it dissolves in alkali solutions with formation of a deep purple solution, from which it is reprecipitated by acids. The above results are only explained by means of the formula for phenolphthaleinoxime advanced in an earlier paper (A., 1917, i, 339). W. S. N.

4 : 4'-Dihydroxy-1 : 1'-dinaphthyl-ketone-3 : 3'-dicarboxylic Acid. G. DE MONTMOLLIN, J. SPIELER, and G. BONHOTE (U.S. Pat. 1453659; cf. *ibid.*, 1387596).—The action of tetrahalogenomethane derivatives on α -naphthol-2-carboxylic acid yields, besides a dye, 4 : 4'-*dihydroxy-1 : 1'-dinaphthyl-ketone-3 : 3'-dicarboxylic acid*, a white powder, decomp. about 259°, and α -naphthol-2 : 4-dicarboxylic acid.

CHEMICAL ABSTRACTS.

Chemical and Optical Behaviour of some *dicyclo*Pentane and *cyclo*Pentene Derivatives. N. J. TOIVONEN (*Acta Sci. Fennicæ*, I, 1922, 26, 1—33; from *Chem. Zentr.*, 1923, i, 1356—1358).—The constitution of the compounds described as *cyclopentane* derivatives by Perkin and Thorpe (T., 1901, 79, 729) is discussed with reference to the more recent work of the author (*Annalen*, 1919, 419, 176) and of Farmer, Ingold, and Thorpe (T., 1920, 117, 1362; 1922, 121, 128). Their chemical reactions and optical behaviour are considered to be more in accord with the monocyclic (*cyclopentene*) constitution. It is pointed out that in view of the strain necessitated by the *dicyclopentane* structure, as high a degree of unsaturation is indicated as by the *cyclopentene* structure. The following data are given for the compounds in question: Ethyl dicarboxydimethyl*cyclo*propanemalonate, prepared by the method of Perkin and Thorpe (*loc. cit.*), b. p. 203—205°/14 mm.; d_4^{20} 1.1135; n_D^{20} 1.45753; R_D 91.13; $M \times n_D^{20}$ (Eisenlohr, A., 1921, ii, 1) 542.63. The yellow sodium compound of ethyl 5 : 5-dimethyld*cyclopentane*-3-one-1 : 2 : 4-tricarboxylate, prepared from methyl dibromodimethylglutarate (1 mol.), ethyl malonate (2 mols.), and sodium ethoxide (4 mols.), has m. p. 208°; the free ester (?) prepared from the last compound by the action on it of dilute sulphuric acid, a viscid liquid, has b. p. 200—212°/14 mm.; d_4^{20} 1.1465; n_D^{20} 1.48742; R_D 81.91; $M \times n_D^{20}$ 485.29. Ethyl 5 : 5-dimethyl*cyclopentan*-3-one-1 : 2 : 4-tricarboxylate, from the reduction of the above-mentioned yellow sodium compound, is a liquid having b. p. 170—195°/16 mm.; d_4^{20} 1.1202; n_D^{20} 1.46203; R_D 80.56; $M \times n_D^{20}$ 479.94. 1 : 2-Diethyl 5 : 5-dimethyld*cyclopentan*-3-one-1 : 2 : 4-tricarboxylate, $\text{Me}_2\text{C} < \begin{array}{c} \text{C}(\text{CO}_2\text{Et}) \\ \text{C}(\text{CO}_2\text{H})-\text{CO} \end{array} \begin{array}{c} \text{CH} \cdot \text{CO}_2\text{Et} \\ \text{CO} \end{array}$ or $\text{Me}_2\text{C} < \begin{array}{c} \text{C}(\text{CO}_2\text{Et}) \\ \text{CH}(\text{CO}_2\text{H}) \cdot \text{CO} \end{array} \begin{array}{c} \text{C} \cdot \text{CO}_2\text{Et} \\ \text{CO} \end{array}$ has m. p. 75°; n_D^{20} 1.49999; $M \times n_D^{20}$ 447.31. Ethyl 2 : 5 : 5-trimethyld*cyclopentan*-3-one-1 : 2 : 4-tricarboxylate has b. p. 205—208°/14 mm.; d_4^{20} 1.1250; n_D^{20} 1.47458; R_D 85.09; $M \times n_D^{20}$ 501.77. Ethyl 4 : 5 : 5-trimethyld*cyclopentan*-3-one-1 : 2 : 4-tricarboxylate, obtained by reduction of the last compound, is a liquid, d_4^{20} 1.1189; n_D^{20} 1.46155; R_D 84.03; $M \times n_D^{20}$ 500.15. Ethyl 5 : 5-dimethyld*cyclopentan*-3-one-1 : 2-dicarboxylate, obtained by distillation in a vacuum of the 1 : 2-diethyl ester of 5 : 5-dimethyld*cyclopentan*-3-one-1 : 2 : 4-tricarboxylic acid, has d_4^{20} 1.1132; n_D^{20} 1.47853; R_D 64.66; $M \times n_D^{20}$ 375.86. Ethyl 5 : 5-dimethyl*cyclopentan*-3-one-1 : 2-dicarboxylate has d_4^{20} 1.0960; n_D^{20} 1.45867; R_D 63.87; $M \times n_D^{20}$ 373.76; the acid corresponding with

the last compound has m. p. 143° (decomp.). The 2-ethyl ester of 5:5-dimethyldicyclopentan-3-one-1:2:4-tricarboxylic acid has m. p. $161\text{--}162^{\circ}$. Ethyl 5:5-dimethyldicyclopentan-3-one-1-carboxylate is a liquid having b. p. $90^{\circ}/20$ mm.; d_4^{20} 1.0411; n_D^{20} 1.47204; R_D 48.99; $M \times n_D^{20}$ 268.14. G. W. R.

Derivatives of Phthalonic Acid, 4:5-Dimethoxyphthalonic Acid, and 4:5-Dimethoxy-*o*-tolylglyoxylic Acid. (MISS) CHIKA KURODA and WILLIAM HENRY PERKIN, jun. (T., 1923, 123, 2094—2111).

Preparation of Aromatic Aldehydes. THE BARRETT CO. (Brit. Pat. 189107).—Monoaldehydes are produced by catalytic oxidation of aromatic hydrocarbons containing a benzene nucleus in which at least two hydrogen atoms have been substituted, one at least of the substituents being an alkyl group. The vapour of the hydrocarbon, mixed with an oxygen-containing gas (*e.g.*, air) is passed over a metallic oxide, other than vanadium oxide, of the fifth or sixth periodic group. The reaction temperature is between 300° and dull redness, and the time of contact in the neighbourhood of 0.3 seconds. Acid formation is negligible. Vanadium oxide differs from the other oxides specified in oxidising the aliphatic side-chain to the acid stage and even causing disruption of the aromatic nucleus itself. The production of monoaldehydes from *o*-, *m*-, and *p*-xylene, ψ -cumene, mesitylene, *p*-cymene, and of *o*-chlorobenzaldehyde from *o*-chlorotoluene, is described, the yields varying from 17% (ψ -cumene) to 63% (*o*-chlorotoluene). W. T. K. B.

The Isomerism of the Oximes. XIII. Phenylethyl-, Diethyl-, and α -Naphthyl-carbamyl Derivatives. OSCAR LISLE BRADY and DUDLEY RIDGE (T., 1923, 123, 2163—2174).

4-Methoxyresorcylaldehyde [2-Hydroxy-4-methoxybenzaldehyde] from the Roots of *Decalepis Hamiltonii*. M. G. SRINIVASA RAO and M. SESA IYENGAR (*Perf. Essent. Oil Rec.*, 1923, 14, 300—301).—When the crushed roots of *Decalepis Hamiltonii* are distilled in steam with a little animal charcoal, there is obtained a white, crystalline solid, m. p. 41° , which possesses an odour resembling that of vanillin. This compound is shown to be 2-hydroxy-4-methoxybenzaldehyde. H. H.

New Isomeride of Wieland's Dibenzenyloxoazoxime. E. PARISI (*Atti R. Accad. Lincei*, 1923, [v], 32, i, 572—575).—Two compounds of the formula $C_{14}H_{10}O_2N_2$ have been obtained by oxidation of benzaldoxime, namely, so-called diphenylglyoxime peroxide (*cf.* Scholl, A., 1891, 316), and dibenzenyloxoazoxime (*cf.* Wieland and Bauer, A., 1906, i, 412; 1907, i, 527). The author finds that oxidation of benzaldoxime by means of iodine and alkali (*cf.* Robin, A., 1919, i, 592) yields dibenzenyloxoazoxime, m. p. 135° , together with a third isomeride, $C_{14}H_{10}O_2N_2$, which crystallises in stellate groups of laminae, m. p. 63° ; either of these isomerides yields dibenzenylazoxime when reduced by means of zinc and

acetic acid. With iodine the two isomerides, m. p. 135° and 63°, respectively, form additive *compounds*, m. p. 140° and 151°, respectively.

Diphenylglyoxime peroxide, however, yields no additive compound with iodine, and, when reduced by means of zinc and acetic acid, gives diphenylfurazan, $\text{O} \begin{array}{c} \text{N:CPh} \\ \text{N:CPh} \end{array}$, which may be regarded as a product of anhydride formation with benzildioxime. It is therefore probable that the peroxide has the formula $\text{O} \begin{array}{c} \text{N—CPh} \\ \diagup \quad \diagdown \\ \text{O} \\ \diagdown \quad \diagup \\ \text{N—CPh} \end{array}$ or $\begin{array}{c} \text{O} \cdot \text{N:CPh} \\ \text{O} \cdot \text{N:CPh} \end{array}$. The other two isomerides contain the nucleus $\text{O} \begin{array}{c} \text{N:C} \\ \text{C:N} \end{array}$, and the constitution proposed by Wieland for the compound, m. p. 135°, $\text{O} \begin{array}{c} \text{N:CPh} \\ \text{CPh} \cdot \text{O} \end{array} \text{N}$, is supported by its sensitiveness towards the influence of light. The isomeride, m. p. 63°, has probably the structure $\text{O} \begin{array}{c} \text{NO=CPh} \\ \text{CPh:N} \end{array}$. T. H. P.

Ring Formation from γ -Ketonic Esters. CLAUDE LE PELETIER DE ROSANBO (*Ann. Chim.*, 1923, [ix], **19**, 327—355).—The formation of a cyclic compound from a γ -ketonic ester was effected by using the ethyl ester of $\beta\beta$ -trimethyl-lævulic acid, in which the two hydrogen atoms in the β -position are substituted and reaction of the enolic form of the ester is thus obviated. The action of sodium ethoxide on this substance yields 1 : 1 : 3-trimethyl-cyclopentane-2 : 4-dione, $\text{C}_8\text{H}_{12}\text{O}_2$, white needles, m. p. 163°, b. p. 130°/10 mm., d_{25}^{25} 0.83901, n_{25}^{25} 1.38949, *monoacetyl* derivative, b. p. 124°/21 mm., *phenylhydrazone*, white needles, m. p. 229°. A mixture of two isomeric methyl derivatives was obtained, but neither was separated in the pure condition. It was not found possible to prepare cyclic compounds from the ethyl esters of lævulic, β -methyl-lævulic, or $\alpha\alpha\delta$ -trimethyl-lævulic acids.

H. J. E.

Dioximes. XI. G. PONZIO (*Gazzetta*, 1923, **53**, i, 379—384).—If the compound obtained by the action of nitrogen tetroxide on phenylglyoxime (cf. this vol., i, 472) possesses the phenylfuroxan structure attributed to it by Wieland and Semper (A., 1908, i, 108) it should, in accordance with the results of Forster and Barker (T., 1913, **103**, 1918), Green and Rowe (T., 1913, **103**, 897, 2023), and Angeli (A., 1916, i, 655) and in virtue of its unsymmetrical ring, be capable of existing in two modifications. That the latter actually exist is stated by Wieland (A., 1921, i, 605), who describes an unstable form of phenylfuroxan, m. p. 106—108°, the ordinary, stable form having m. p. 96—97°.

The author finds that only one compound of the formula $\text{C}_2\text{HPhO}_2\text{N}_2$ exists, that it melts at either 95° or 96—97° or 108°, according to its degree of purity, and that its behaviour towards hydrochloric acid, acetic anhydride, and nascent hydrogen indicates

it to be neither phenylglyoxime peroxide nor phenylfuroxan, but the oxide of benzoyl cyanide oxime (oximinobenzyl cyanide oxide),

$\text{NOH:CPh}\cdot\text{C}\begin{smallmatrix} \text{O} \\ \diagup \\ \text{N} \end{smallmatrix}$. In the pure state, this compound has m. p.

108° and exhibits the normal molecular weight in acetic acid. It is converted completely into benzonitrile, benzoic acid, and hydroxylamine when subjected to prolonged boiling with concentrated hydrochloric acid, and it yields an *acetyl* derivative,

$\text{NOAc:CPh}\cdot\text{C}\begin{smallmatrix} \text{O} \\ \diagup \\ \text{N} \end{smallmatrix}$, crystallising in white needles, m. p. $115\text{--}116^\circ$.

When reduced with zinc dust and acetic acid, it yields benzoyl cyanide oxime.

This structure for the compound explains the formation of aminophenylglyoxime when it is treated with aqueous ammonia (this vol., i, 472), and that of anilinophenylglyoxime when treated with aniline (this vol., i, 855). As regards the mechanism of its formation, it has been shown that the two oximino-groups of the α -forms of the glyoximes are not equivalent, and it is assumed that α -phenylglyoxime reacts with nitrogen tetroxide as its tautomeride, α -oximino- β -nitroso- α -phenylethane, $\text{NOH:CPh}\cdot\text{CH}_2\cdot\text{NO}$, giving α -oximino- β -nitrolephenylethane, $\text{NOH:CPh}\cdot\text{CH}(\text{NO})\cdot\text{NO}_2$. The latter, being unstable, would then yield the oxide of benzoyl cyanide oxime by loss of nitrous acid.

T. H. P.

Piperitone. V. The Characterisation and Racemisation of *l*-Piperitone. JOHN READ and HENRY GEORGE SMITH (T., 1923, 123, 2267—2272).

Hydroxynaphthaquinone. VI. The Chlorination of Juglone. ALVIN S. WHEELER, P. R. DAWSON, and JOSEPH L. McEWEN (J. Amer. Chem. Soc., 1923, 45, 1970—1975).—The best conditions are described for the preparation of dichlorojuglone (A., 1919, i, 490) by the chlorination of juglone in glacial acetic acid solution at 100° . Attempts to prepare a trichloro-derivative have only led to the formation of the same dichlorojuglone. It forms an indigo-blue *sodium* salt, which gives a deep violet, aqueous solution from which silk and wool may be dyed buff and brown shades. 2:3-Di-chloro-5-benzoxo-1:4-naphthaquinone, pale yellow needles, m. p. 225° , is prepared by boiling dichlorojuglone with benzoyl chloride. Dichlorojuglone is converted by the action of boiling alcoholic sodium hydroxide solution into 3-chloro-2:5-dihydroxy-1:4-naphthaquinone, golden-brown needles, m. p. 191° , which gives a deep red, aqueous solution changing to yellow on addition of acid (*diacetate*, slender, yellow needles, m. p. 147°). This chlorodihydroxy-derivative is also produced by the action of sodium ethoxide on dichlorojuglone in benzene solution. Dichlorojuglone reacts in boiling alcoholic solution with aniline, *p*-chloroaniline, or *p*-toluidine, but not with 2:4-dichloroaniline, to give, respectively, 3-chloro-2-anilino-5-hydroxy-1:4-naphthaquinone, very small, short, flat, lustrous, violet-carmine needles, m. p. 222° ; {3-chloro-2-*p*-chloro-anilino-5-hydroxy-1:4-naphthaquinone, flat, dark reddish-purple

needles, m. p. 243°, or 3-chloro-2-p-toluidino-5-hydroxy-1 : 4-naphthaquinone, flat, lustrous, dark reddish-purple needles, m. p. 234°. Reduction of dichlorojuglone by treating its ethereal solution with dilute sulphuric acid and zinc dust gives 2 : 3-dichloro-1 : 4 : 5-trihydroxynaphthalene, very small, short, lustrous, grey prisms, m. p. 157° (decomp.), triacetate, pale yellow, transparent needles, m. p. 182°. An oxime of dichlorojuglone has not been obtained.

W. S. N.

Preparation of 1- and 2-Nitro-derivatives of Anthraquinone and its Substitution Products. EDUARD KOPETSCHNI (D.R.-P. 363930; from *Chem. Zentr.*, 1923, ii, 1029—1030).—Aminoanthraquinones are treated with per-acids and the products are also submitted to oxidation with another oxidising agent. By the oxidation of 2-aminoanthraquinone with persulphuric acid, 2-nitroanthraquinone may be obtained directly. The reaction is also applicable to substitution products of aminoanthraquinone. By the action of persulphuric acid or Caro's acid on 1-aminoanthraquinone or its 4-chloro-substitution product, nitroso-compounds are first formed which may be oxidised to nitroanthraquinones by means of chromium trioxide. For example, 2-aminoanthraquinone, dissolved in strong sulphuric acid is added to an aqueous solution of ammonium persulphate and the mixture finally heated at 100°. Addition of acetic acid facilitates the reaction through formation of peracetic acid. The 2-nitroanthraquinone is obtained as yellow needles, m. p. 181—182°. 1-Chloro-2-nitroanthraquinone, similarly obtained, forms yellow needles, m. p. 257—258°. On being heated with copper powder in nitrobenzene solution, it gives 2 : 2'-dinitro-1 : 1'-dianthraquinonyl, yellow prisms, m. p. 342° (decomp.). Reduction with sodium hyposulphite in alkaline solution gives flavanthren. By treating 4-chloro-1-aminoanthraquinone, dissolved in strong sulphuric acid, with ammonium persulphate, 4-chloro-1-nitrosoanthraquinone is first obtained; it forms golden-yellow leaflets, m. p. 240° (decomp.). This, by oxidation with chromium trioxide in boiling acetic acid, yields 4-chloro-1-nitroanthraquinone, sulphur-yellow needles, m. p. 260—261°. By successive oxidation of 1-aminoanthraquinone with Caro's acid and chromium trioxide, 1-nitroanthraquinone, m. p. 227—228°, is obtained. G. W. R.

Preparation of 1 : 1'-Dianthraquinonyl and its Derivatives. EDUARD KOPETSCHNI (D.R.-PP. 360419 and 362984; from *Chem. Zentr.*, 1923, ii, 1030).—Dianthraquinonyl 1 : 1'-disulphide, 1-anthraquinone thiocyanate, or their substitution products, are heated with metals, such as copper or iron, which combine with sulphur. For example, by heating dianthraquinonyl disulphide or anthraquinone 1-thiocyanate with copper and anthracene at 220—240°, 1 : 1'-dianthraquinonyl is obtained as brownish-yellow crystals, m. p. 430°. From 2 : 2'-dimethyldianthraquinonyl 1 : 1'-disulphide, 2 : 2'-dimethyl-1 : 1'-dianthraquinonyl is obtained; it forms yellow crystals and, when heated with alcoholic potassium hydroxide, gives pyranthrene. 2 : 2'-Dihydroxy-1 : 1'-dianthraquinonyl, to-

gether with 2-hydroxyanthraquinone, is obtained by a similar reaction. G. W. R.

Camphor Series. III. Catalytic Action of Reduced Copper on *d*-Camphoroxime. SHIGERU KOMATSU and SHOZO YAMAGUCHI (*Mem. Coll. Sci. Kyoto*, 1923, **6**, 245—250; cf. this vol., i, 234).—When *d*-camphoroxime is reduced by means of hydrogen and reduced nickel, bornylamine is formed (Aloy and Brustier, A., 1911, i, 730). With reduced copper at 200°, however, a molecular rearrangement occurs, and the products are levorotatory *d*- α -campholenamide, α -campholenic acid, *d*-camphor, α -campholenonitrile, and only a trace of bornylamine. The authors therefore conclude that the oxime is converted into the *isooxime* by the rupture of a *cyclopentane* ring, and that this is followed by the decomposition of the *isooxime* to give campholenamide. H. H.

The Reaction between α -Pinene and Acids. I. α -Pinene and Sulphuric Acid. KASHICHI ONO (*Mem. Coll. Sci. Kyoto*, 1923, **6**, 305—311).—The influence of time, temperature, and concentration of acid on the reaction between pinene and sulphuric acid was studied. The optimum conditions for the formation of terpin hydrate are attained when pinene and three times its weight of 45% sulphuric acid are allowed to react at a temperature in the neighbourhood of 0°. A scheme is proposed to represent the catalytic hydration of pinene. H. H.

New Syntheses from Hydrocyanic Acid by Means of the Silent Electric Discharge. Behaviour of Pinene. LUIGI FRANCESCONI and ADOLFO CIURLO (*Atti R. Accad. Lincei*, 1923, [v], **32**, i, 566—569; *Gazzetta*, 1923, **53**, 470—472; cf. this vol., i, 764).—Under the influence of the silent discharge, pinene vapour and hydrogen cyanide interact at 50°, yielding a nitrile and an *isonitrile*, the latter in predominating proportion. At lower temperatures the hydrogen cyanide condenses in the ozoniser and undergoes change under the influence of the discharge, whilst at higher temperatures the pinene gives a dense, resinous product and the amount of *isonitrile* formed diminishes, to vanish at 120°. T. H. P.

The Essential Oil in the Leaves of *Dacrydium biforme*. BASIL HUGHSON GOUDIE (*J. Soc. Chem. Ind.*, 1923, **42**, 357—358t).—Leaves of the conifer, *D. biforme*, when extracted by treatment with superheated steam, yield 0.25% of a pale green oil, *d* 0.8876, *n* 1.5, α -11.96°, together with a small quantity of a crystalline compound. The oil was separated into three fractions by distillation. The first, b. p. 130—140°/13 mm., had *d* 0.916, *n*_D 1.505, α _D -54.9°, and was probably cadinene. The second, b. p. 140—185°/13 mm., consisted mainly of an oxygenated compound. The third, highest boiling fraction, solidified on cooling. It crystallises from benzene in colourless plates, m. p. 91°, and is a diterpene with one ethylene linking, C₂₀H₃₂, for which the name *dacrene* is suggested. It has α +14.9° and forms a *dibromide*, m. p. 110°. H. H.

The Essential Oils in the Leaves of *Librocedrus Bidwillii*.

BASIL HUGHSON GOUDIE (*J. Soc. Chem. Ind.*, 1923, **42**, 350—351r).—The leaves of *Librocedrus Bidwillii* when distilled with superheated steam give a greenish-yellow oil, d 0.8754, n_D 1.845, having the composition C_5H_8 . The yield varies from 0.62% from older, to 0.42% from younger trees. The oil consists of about 30% of terpenes, of which d -pinene is the chief constituent, and 70% of sesquiterpenes. The original oil was laevorotatory, but when fractionated at the ordinary pressure the fractions were dextro-rotatory. Fractionation at low pressure, however, gave a sesquiterpene fraction, b. p. 120—130°/12 mm., d 0.887; n_D 1.50, α_D -74.6°. This could not be identified with either of the known laevorotatory sesquiterpenes, cadinene and cedrene. E. H. R.

Thevetia neriifolia*, Juss. R. WEITZ and A. BOULAY (*Bull.

Sci. Pharmacol., 1923, **30**, 81—88; from *Chem. Zentr.*, 1923, i, 1328).—The glucoside extracted from *Thevetia neriifolia*, Juss., has a bitter taste. It gives with sulphuric acid an ochre-yellow coloration, becoming pink after twelve hours. A yellow coloration is given with nitric acid. When heated with resorcinol and hydrochloric acid a pink coloration is obtained. G. W. R.

New Sources of Santonin. ARNO VIEHOEVER and RUTH

G. CAPEN (*J. Amer. Chem. Soc.*, 1923, **45**, 1941—1944).—Of fifty-six species of *Artemisia* indigenous to America, pronounced tests for santonin were obtained from *A. mexicana*, Willd., from *A. neomexicana*, Wooton, and probably from *A. Wrightii*, all of which grow in the region of New Mexico and Mexico. W. S. N.

The Action of Organomagnesium Compounds on Cyano-hydrins. I. A New Method for the Preparation of Substituted Benzoin.

YASUHIKO ASAHINA and MASANOBU TERASAKA (*J. Pharm. Soc. Japan*, 1923, No. **494**, 219—228).—Aromatic organomagnesium compounds combine fairly smoothly with aromatic aldehyde cyanohydrins in ethereal solution; from the products, substituted benzoin is obtained by decomposition with water and dilute sulphuric acid: $R \cdot CH(OH) \cdot CN + 2R \cdot MgX \rightarrow R \cdot CH(OMgX) \cdot CR \cdot NMgX \rightarrow R \cdot CH(OH) \cdot COR$. Benzoin was thus prepared from benzaldehyde cyanohydrin and magnesium-phenyl bromide, the yield being 32.7% of the theoretical. *iso*Benzofuroin, $C_4H_4O \cdot CH(OH) \cdot CPh$ (1 g.), colourless prisms, m. p. 119°, was prepared from furfuraldehyde cyanohydrin and magnesium phenyl bromide. It is an isomeride of Fischer's benzofuroin (*Annalen*, 1882, **211**, 288), and its oxidation with Fehling's solution produced benzfural, $CO \cdot Ph \cdot CO \cdot C_4H_4O$, m. p. 41°, identical with that of Fischer. *p*-Methoxybenzoin, $OMe \cdot C_6H_4 \cdot CH(OH) \cdot CPh$, (3 g.), was prepared from anisaldehyde cyanohydrin (5 g., m. p. about 62°) and magnesium phenyl bromide as colourless prisms, m. p. 89°. *o*-Hydroxybenzoin, $OH \cdot C_6H_4 \cdot CH(OH) \cdot CPh$, prepared from magnesium phenyl bromide and salicylaldehyde cyanohydrin, forms colourless plates from alcohol and has m. p. 148°. *o*-Methoxy-

benzoin (5 g.), $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OH})\cdot\text{COPh}$, was obtained from magnesium phenyl bromide and *o*-methoxysalicylaldehyde cyanohydrin (8.2 g.), as colourless prisms, m. p. 58° . On oxidation with Fehling's solution, the benzoin gave *o*-methoxybenzil, slightly yellow prisms, m. p. 71.5° , which was changed by warming with alkali into *o*-methoxybenzilic acid, colourless needles (+2EtOH), m. p. $100-101^\circ$, and giving a dark red colour with concentrated sulphuric acid. *op'*-Dimethoxybenzoin, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OH})\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$, (3.8 g.), was prepared from magnesium *p*-methoxyphenyl bromide and *o*-methoxysalicylaldehyde cyanohydrin (8 g.), as colourless prisms, m. p. $92-93^\circ$. By oxidising with Fehling's solution, the benzoin gave *op'*-dimethoxybenzil, fine, colourless prisms, m. p. $104-105^\circ$, which was converted by alkali into *op'*-dimethoxybenzilic acid, m. p. 162° . K. K.

Triethylene Tri- and Tetra-sulphides. III. The Sulphones, Sulphinic, and Sulphonic Acids of the Series. Extension of Stuffer's Law. (SIR) PRAFULLA CHANDRA RAY (T., 1923, 123, 2174—2178).

The Preparation of *N*-Derivatives in the Carbazole Series. THOMAS STEVENS STEVENS and STANLEY HORWOOD TUCKER (T., 1923, 123, 2140—2147).

Derivatives of Tetrahydrocarbazole. III. Amino-compounds. GEORGE F. ALFRED EDWARDS and SYDNEY GLENN PRESTON PLANT (T., 1923, 123, 2393—2399).

Oxidation of Benzylidenemethylisooxazolone. MARIO BETTI and NATALIA VIANSINO (*Atti R. Accad. Lincei*, 1923, [v], 32, i, 494—498).—It has been shown (A., 1922, i, 52) that oxidation by means of atmospheric oxygen of 4-benzylidene-3-methylisooxazolone, dissolved in alcoholic ammonia containing benzaldehyde, gives an amide which yields an unstable acid, $\text{C}_{11}\text{H}_9\text{O}_3\text{N}$, or an isomeric stable acid, according as it is hydrolysed by dilute or by concentrated sodium hydroxide solution. When, however, the oxidation is effected in ammoniacal alcoholic solution by means of hydrogen peroxide, the product is the ammonium salt of an acid, $\text{C}_{11}\text{H}_{11}\text{O}_4\text{N}$, whereas in aqueous ammonia a different compound, m. p. 120° , is obtained.

The free acid, $\text{C}_{11}\text{H}_{11}\text{O}_4\text{N}$, forms minute, lustrous crystals, m. p. 131° (decomp.), and the ammonium salt, $\text{C}_{11}\text{H}_{10}\text{O}_4\text{N}\cdot\text{NH}_4+\text{O}\cdot5\text{H}_2\text{O}$, massive, lustrous crystals, m. p. 157° (decomp.); the silver salt was analysed.

Oxidation of 4-*p*-chlorobenzylidene-3-methylisooxazolone in alcoholic ammonia solution by means of hydrogen peroxide gives the ammonium salt, $\text{C}_{11}\text{H}_9\text{O}_4\text{NCl}\cdot\text{NH}_4\cdot2\text{H}_2\text{O}$, which forms small, white crystals, m. p. 165° . T. H. P.

Oxidation of isooxazolone Compounds. MARIO BETTI and NATALIA VIANSINO (*Atti R. Accad. Lincei*, 1923, [v], 32, i, 563—565; cf. preceding abstract).—Oxidation of 3-phenyl-4-benzylideneisooxazolone in alcoholic ammonia solution by means of hydrogen

peroxide proceeds similarly to that of 4-benzylidene-3-methylisoxazalone under the same conditions, the only difference being that the amide and not the ammonium salt is obtained in the present case.

This *amide*, $\text{NO}_2 \cdot \text{CHPh} \cdot \text{C}(\text{CHPh}) \cdot \text{CO} \cdot \text{NH}_2$ (?), forms lustrous, white, acicular crystals, m. p. 232° . The corresponding *acid*, $\text{C}_{16}\text{H}_{13}\text{O}_4\text{N}$, forms white, acicular crystals, m. p. 118° , and exhibits the normal molecular weight in freezing benzene. T. H. P.

Studies in the Benzothiazole Series. I. The Pseudo-bases of the Benzothiazole Quaternary Salts. WILLIAM HOBSON MILLS, LESLIE MARSHALL CLARK, and JOHN ALFRED AESCHLI-MANN (T., 1923, 123, 2353—2362).

Studies in the Benzothiazole Series. II. Thio-2-methylbenzothiazolone and its Oxidation Products. WILLIAM HOBSON MILLS, LESLIE MARSHALL CLARK, and JOHN ALFRED AESCHLI-MANN (T., 1923, 123, 2362—2370).

Dyestuffs Derived from Heterocyclic Bases containing Reactive Methyl Groups. JAMES LEONARD BRIERLEY SMITH (T., 1923, 123, 2288—2296).

Condensation of Amidines with Ethoxymethylene Derivatives of β -Ketonic Esters and of β -Diketones. PRAFULLA CHANDRA MITTER and JOGENDRA CHANDRA BARDHAN (T., 1923, 123, 2179—2184).

Compounds of Diketopiperazines and Amino-acids or Polypeptides. EMIL ABDERHALDEN and EMIL KLARMANN (Z. physiol. Chem., 1923, 129, 320—324).—By the action of chloroacetyl chloride on glycine anhydride in nitrobenzene solution, 1:4-di(chloroacetyl)-2:5-diketopiperazine is obtained, white scales, m. p. 168.5° . On treatment with alcoholic ammonia, 1:4-diglycylglycine anhydride is obtained, colourless leaflets, decomp. above 220° . This substance gives the biuret reaction, and its solution becomes cloudy on the addition of phosphotungstic acid.

W. O. K.

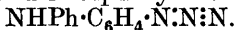
Benzbisthiazoles. IV. STEPHEN RATHBONE HOLDEN EDGE (T., 1923, 123, 2330—2333).

Studies in Phototropy. The Reversed Phototropy of Cinnamaldehydesemicarbazone and its Methoxy-derivatives. ISIDOR MORRIS HEILBRON, HERBERT EDWARD HUDSON, and DORIS MABEL HUISSH (T., 1923, 123, 2273—2279).

Triazole Compounds. I. Some Substituted Hydroxybenzotriazoles and their Methylation Products. OSCAR LISLE BRADY and JAMES NELSON EDMUND DAY (T., 1923, 123, 2258—2267).

6:6'-Diacetylamino-1:1'-diethylcarbocyanine Iodide. FRANCES MARY HAMER (T., 1923, 123, 2333—2336).

Formation of certain Azides. A. ANGELI and ANTONIO PIERONI (*Atti R. Accad. Lincei*, 1923, [v], **32**, i, 450—455).—The formula $\text{NH}\cdot\text{NPh}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}$ is improbable for the compound, m. p. 71° (this vol., i, 612), since the latter readily yields derivatives of triazole, the ring of which contains a direct chain of three nitrogen atoms. This reaction has been shown by Dimroth (A., 1902, i, 403) to be characteristic of the azides, and the conclusion is drawn that the above compound is diphenylamine-4-azide,



As regards the mode of formation of this compound, true nitroso-derivatives react with hydroxylamine to furnish diazo-hydroxides, $\text{C}_6\text{H}_5\cdot\text{NO} \rightarrow \text{C}_6\text{H}_5\cdot\text{N}_2\cdot\text{OH}$, but in alkaline solution *p*-nitrosodiphenylamine may be regarded as containing the oximino-group, $\text{NPh}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NOH}$. It must therefore be assumed that the hydroxylamine is first added to the double quinonoid linking to give a diazo-compound possibly identical with that described by Hantzsch, $\text{NPh}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}$ (A., 1902, i, 324). This product would then react with a second molecule of hydroxylamine to give the azoimide derivative. No reaction analogous to this has, however, been observed.

Diphenylamine-4-azide forms pale yellow or reddish-yellow crystals and in most of its reactions decomposes with formation of intensely coloured or resinous products. When poured into concentrated sulphuric acid, it reacts violently with evolution of much gas; with concentrated nitric acid, it explodes with emission of flame. An acetic acid solution of nitric acid converts it into a reddish-brown *product*, m. p. 84° (decomp.), as yet not investigated further. It is extremely sensitive to the action of light, and yields an almost colourless, crystalline hydrochloride. Nitrous acid converts it into the *nitroεoamine*, $\text{C}_{12}\text{H}_{10}\text{ON}_5$, which crystallises in lustrous, yellow laminæ, m. p. 55° , explodes when heated on platinum, yields an intense Liebermann's reaction, and gives the original azide when treated with hydroxylamine hydrochloride in acetic acid solution.

The compound, $\text{NHR}\cdot\text{C}_6\text{H}_4\cdot\text{N} < \begin{smallmatrix} \text{CMe}\cdot\text{C}\cdot\text{CO}_2\text{Et} \\ \text{N}=\text{N} \end{smallmatrix}$, obtained by the

action of ethyl acetoacetate on diphenylamine-4-azide, crystallises in colourless prisms, m. p. 170° . The free acid, $\text{C}_{16}\text{H}_{14}\text{O}_2\text{N}_4$, forms colourless crystals, m. p. 208° , the compound losing carbon dioxide at this temperature with formation of the triazole, which separates in colourless crystals, m. p. 123° . T. H. P.

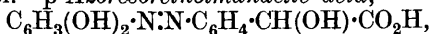
Bromination of 2-Amino-*p*-xylene and certain New Azo-dyes. ALVIN S. WHEELER and E. W. CONSTABLE (*J. Amer. Chem. Soc.*, 1923, **45**, 1999—2001).—The bromination of 2-amido-*p*-xylene in cold glacial acetic acid solution gives 5-bromo-2-acetamido-*p*-xylene, rosettes of colourless needles, m. p. 187° , which, when hydrolysed by means of concentrated hydrobromic acid, *d* 1.3, is converted into the *hydrobromide*, flat needles, m. p. 255° (decomp.), of 5-bromo-2-amino-*p*-xylene (Fischer and Windhaus, A., 1900, i, 484). The constitution of the latter is fixed by

its conversion into the known 2 : 5-dibromo-*p*-xylene, by diazotisation, followed by treatment with copper powder and potassium bromide. This proof is extended by the oxidation of 2 : 5-dibromo-*p*-xylene, by heating at 300° with nitric acid, *d* 1.15, to 2 : 5-dibromoterephthalic acid.

Azo-dyes have been prepared by diazotising 5-bromo-2-amino-*p*-xylene, and coupling with phenols. When phenol, resorcinol, or α -naphthol is used, a bis-compound is formed, but not with β -naphthol. Owing to difficulty in making the sodium salts, the tinctorial properties on silk and wool are found by employing the development method of application. 2 : 4-Bis(5'-bromo-2'-*p*-xylylazo)phenol forms small, dark brown scales with a metallic lustre, which appear pale green under the microscope, m. p. 233—234°. Silk is coloured *écru*, and wool, orange-brown. 2 : 4-Bis(5'-bromo-2'-*p*-xylylazo)resorcinol, a microcrystalline, claret-brown mass, m. p. 263°, dyes silk *écru* and wool Brazil-red. 2 : 4-Bis(5'-bromo-2'-*p*-xylylazo) α -naphthol, a dark brown or black mass, m. p. 222—223°, dyes silk a Mars-orange and wool a claret-brown. 1 : 5'-Bromo-2'-*p*-xylylazo- β -naphthol forms long, scarlet-red needles in felted masses, and colours silk a light red and wool a Nopal-red.

W. S. N.

Asymmetric Dyes. C. W. PORTER and HARRY K. IHRIG (*J. Amer. Chem. Soc.*, 1923, **45**, 1990—1993).—Two new series of asymmetric dyes are described. The members of the first group are made by producing asymmetric amines through the condensation of bromo-acid bromides with acetanilide, then diazotising these products and coupling with aromatic amines or phenols. Those of the second class are prepared by diazotising aminomandelic acid, and coupling with aromatic amines or phenols. *p*-Azo- β -naphtholmandelic acid, $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{N}:\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$, is a bright red dye, m. p. 118°, from diazotised *p*-aminomandelic acid and β -naphthol. *p*-Azoresorcinolmandelic acid,

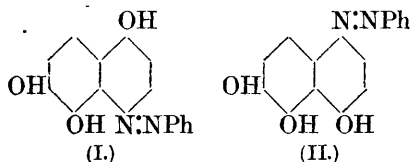


m. p. 154° (decomp.), is a red dye. *p*-Azodimethylanilinomandelic acid, $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}:\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$, m. p. 125—129° (decomp.), is brown, but bright red in acid solution. *m*-Azoresorcinolmandelic acid, m. p. above 280°, is a red dye. *m*-Azodimethylanilinomandelic acid, m. p. 158°, is reddish-purple. *m*-Azophenolmandelic acid, m. p. 119°, is a bright yellow compound. β -Naphtholazo- α -hydroxypropionophenone, $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{N}:\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}(\text{OH})\cdot\text{CH}_3$, m. p. 132°, is a red dye made by condensing α -bromopropionyl bromide with acetanilide, hydrolysing the product, diazotising the resulting *p*-aminopropionophenone, and coupling with β -naphthol. β -Naphtholazo- α -hydroxybutyrophenone, m. p. 72°, is a red dye, made from *p*-aminobutyrophenone and β -naphthol. β -Naphtholazo- α -hydroxyisovalerophenone is a red dye, m. p. above 265°, derived from the condensation product of α -bromoisovaleryl bromide and acetanilide, by hydrolysis, diazotisation, and coupling with β -naphthol.

The cinchonine salt of *m*-aminomandelic acid has m. p. 156.5°,

By fractional crystallisation of this salt, and subsequent treatment with hydrochloric acid, *d-m*-aminomandelic acid, m. p. 130° (decomp.), $[\alpha]_D +33.80^{\circ}$ and *l-m*-aminomandelic acid, m. p. 130° (decomp.), $[\alpha]_D -33.65^{\circ}$, are obtained. By diazotising these acids at 0° , and coupling in alkaline solution with β -naphthol, *d-m-azo- β -naphtholmandelic acid* and *l-m-azo- β -naphtholmandelic acid* are prepared. Each is a red dye, m. p. 210° , $[\alpha]_D \pm 49^{\circ}$ ($\pm 5^{\circ}$). These dyes do not attach themselves equally readily to wool or silk; the dextro-form is more rapidly removed from solution. Hence if dyeing is conducted from a solution of the racemic mixture of the dyes, the unused dye is optically active. By using an excess of wool and extending the time of contact to seventy-two hours, the residual dye is almost a pure levorotatory compound. Thus selective absorption by wool of an optically active dye is definitely established (cf. Porter and Hirst, A., 1919, i, 558). W. S. N.

Naphthazarin (5 : 6-Dihydroxy-1 : 4-naphthaquinone). G. CHARRIER and G. Tocco (*Gazzetta*, 1923, **53**, i, 431—436).—Like 1 : 4-naphthaquinone (cf. Zincke and Bindewald, A., 1885, 391), naphthazarin reacts with phenylhydrazine (1 mol.) in presence of



acetic acid, giving rise to the benzeneazo-derivative of a trihydroxynaphthalene of the annexed formula I or II. No decision between these structures is yet possible, since the two corresponding tri-

hydroxy- α -naphthylamines, as well as the trihydroxynaphthalenes obtained from these by replacement of the amino-groups by hydrogen, are unknown.

Benzeneazotrihydroxynaphthalene, $C_{16}H_{12}O_3N_2$, forms slender, golden-brown crystals, m. p. $186-188^{\circ}$, dissolves in alkali hydroxide solution giving a deep blue, and in concentrated sulphuric acid giving an intense violet, coloration, and is not decomposed when boiled with dilute sulphuric acid for some hours. Its *trimethyl* ether, $C_{10}H_4(OMe)_3 \cdot N_2Ph$, forms slender, chestnut-coloured needles, m. p. $145-146^{\circ}$, and yields a *hydrochloride* and a *nitrate* crystallising in minute needles showing green, metallic reflection.

T. H. P.

Azo-dyes from 5- and 8-Nitro- α -naphthylamines. GILBERT T. MORGAN and FRANK RAYMOND JONES (*J. Soc. Chem. Ind.*, 1923, **42**, 341—343T).—The formation of tarry impurities in the nitration of α -naphthylamine to a mixture of 5- and 8-nitro- α -naphthylamines can be avoided by nitrating at a low temperature, between -9° and -1° , in concentrated sulphuric acid, and maintaining very vigorous stirring during addition of the nitrating acid to the sulphuric acid solution of α -naphthylamine. A separation of the two products is effected through the sparing solubility of 5-nitro- α -naphthylamine sulphate in *N*- to 3*N*-sulphuric acid. Both 5- and 8-nitro- α -naphthylamines can be employed as primary, middle, and end components in the production of azo-dyes, and

the shades of colour obtained differ appreciably from those obtained with α -naphthylamine.

3'-Sulphobenzene-4-azo-8-nitro- α -naphthylamine, obtained by coupling diazotised metanilic acid with 8-nitro- α -naphthylamine, forms a dark, brownish-red sodium salt and gives a dark crimson coloration with concentrated sulphuric acid. This dye and also *6' : 8'-disulphonaphthalene-2'-(4)-azo-5-nitro- α -naphthylamine* dye wool brownish-red. *Toluene-p-4-azo-5-nitro- α -naphthylamine* forms coppery brown four-sided prisms, m. p. 174—176°, giving an orange-red sulphuric acid coloration; its *hydrochloride* forms green, microscopic rhombohedra, m. p. 231°. It can be diazotised and coupled with resorcinol to give a diazo-dye. Diazotised 5-nitro- α -naphthylamine couples with chromotrope acid to form *5'-nitronaphthalene-1'-(2)-azo-1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid*, which dyes wool dark violet-red, changing to purple-black with chromium fluoride or copper sulphate; the sulphuric acid coloration is deep Prussian blue. The corresponding dye from 8-nitro- α -naphthylamine is similar but more soluble. The dye from diazotised 8-nitro- α -naphthylamine and acetyl-J acid (2-acetyl-amino-5-hydroxynaphthalene-7-sulphonic acid), coupled in alkaline solution, is sparingly soluble in the form of the free acid; it dyes wool brownish-scarlet and gives a brilliant blue coloration with sulphuric acid. The corresponding dye from 5-nitro- α -naphthylamine is almost insoluble in the form of the free acid; the sulphuric acid coloration is crimson-violet. Benzoyl-J acid appears to give two distinct products when coupled with 5- or 8-nitrodiazonaphthalene. The two diazo-compounds can also be coupled with β -naphthol on cotton fibre.

E. H. R.

Diazo-ethers. A. ANGELI (*Atti R. Accad. Lincei*, 1923, [v], 32, i, 539—543).—The views of Hantzsch and Reddelien ("Die Diazoverbindungen," 1921, 57) on the constitution of the few known diazo-ethers are discussed. The results obtained by the author during recent years show that azoxy-compounds contain, not the ring suggested by Kekulé, $\begin{smallmatrix} \text{N} & \text{---} & \text{N} \\ & \diagdown & / \\ & \text{O} & \end{smallmatrix}$, but the chain, NO:N , and that, in the form of salts, nitroamines exhibit the structure NR:N(OH):O , and *isonitroamines*, $\text{O:NR:N}\cdot\text{OH}$. Moreover, the results of Angeli, Alessandri, and Aiazzi-Mancini (A., 1911, i, 544) show that the *N*-alkyl ethers of the oximes contain the grouping :C:NR:O , which agrees fully with their mode of formation and with their behaviour, and also justifies the physical analogies between these compounds and the azoxy-compounds.

The possible structural isomerides of an aromatic diazo-hydroxide are (1) $\text{NR:N}\cdot\text{OH}$, (2) O:NR:NH , (3) NR:NH:O , and (4) $\text{NHR}\cdot\text{NO}$. Replacement of the hydrogen atom may thus lead to ethers of four different types, compounds corresponding with each of these being known.

T. H. P.

The Partial Decomposition of Proteins. EMIL ABDERHALDEN (*Z. physiol. Chem.*, 1923, 129, 106—110; cf. this vol., i, 718).—Goose feathers when hydrolysed with sulphuric acid in

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the cold yield in addition to the substance previously described containing proline (3 mols.) and glycine (1 mol.), a substance, $C_{17}H_{24}O_5N_4$, m. p. 251° (decomp.), $[\alpha]_D^{25} -136.0^\circ$ (5% solution in 5% sodium hydroxide solution). When this is hydrolysed, glycine, proline, and hydroxyproline are obtained, and it is concluded that this product consists of 1 mol. of glycine, 2 mols. of proline, and 1 mol. of hydroxyproline. W. O. K.

The so-called Artificial Globulin. G. FANCONI (*Biochem. Z.*, 1923, **139**, 321—335).—Albumin solutions from horse-serum were treated by two methods similar to those employed by Moll (A., 1904, i, 356) and Ruppel, by which they claimed to convert the albumin into globulin. The solutions developed the ammonium sulphate precipitation reactions of a globulin, but neither of the "artificial globulin" preparations agreed in all their physical properties with the natural globulin obtained from the same serum. The two preparations were not identical, and they did not show the antigen properties of natural serum-globulin. Moll's preparation in this respect resembled the parent albumin, whilst the other was inactive and behaved like a racemised protein. It is concluded that no evidence exists for the transformation of albumin into globulin in vitro. J. P.

The Purification and Precipitation of Casein. JOHN H. NORTROP (*J. Gen. Physiol.*, 1923, **5**, 749—750).—Purified casein is conveniently prepared by precipitating the casein from milk as described by L. Van Slyke and Baker (A., 1918, i, 413), and then washing thoroughly to remove salts. Ten g. are then suspended in 1 litre of water, and the suspension brought to a p_H of from 2.5 to 3 by the addition of hydrochloric acid. The cloudy solution is filtered and a solution of sodium hydroxide added until the p_H is 4.7. The precipitate is then washed with distilled water. This method avoids the denaturation by acid, which very easily occurs if the casein is dissolved in alkali and reprecipitated by acid. W. O. K.

The Constitution of Proteins. The Structure of Silk Fibroin. EMIL ABDERHALDEN and WALTER STIX (*Z. physiol. Chem.*, 1923, **129**, 143—156).—Chlorodinitrobenzene in presence of sodium hydrogen carbonate reacts with a free amino-group of an amino-acid to yield dinitrophenylamino-derivatives. It will not react with the $-NHCO-$ grouping in a simple straight chain but reacts with a diketopiperazine ring. More chlorodinitrobenzene is found to combine with silk fibroin than corresponds with the number of free amino-groups. This may be explained by the existence in the protein molecule of diketopiperazine groups.

The following new compounds have been prepared. *Ethyl α -dinitrophenylaminopropionate*, yellow crystals, m. p. 60° . *Dinitrophenyltyrosine*, m. p. 57° . *Dinitrophenyltyrosine ethyl ester*, a yellow, amorphous compound, m. p. 46° . *Dinitrophenylacetyl tyrosine*, m. p. 106° . *α -Dinitrophenylamino- β -dinitrophenyloxyphenylpropionic acid*, from 1 mol. of tyrosine and 2 mols. of chlorodinitrobenzene, m. p. 84° . *Dinitrophenyl-leucylglycine*, yellow crystals,

m. p. 120°. *Di(chloromononitrobenzyl)leucylglycine anhydride*, m. p. 75—76°, from the condensation of dinitrochlorobenzene and leucylglycine anhydride. Apparently, a loss of nitro-groups occurs.

W. O. K.

Formoxyhæmin. WILLIAM KÜSTER and ERHARD WILLIG (*Z. physiol. Chem.*, 1923, **129**, 130—142).—If washed coagulated blood is extracted with methyl alcohol containing sulphuric acid, and the extract boiled with the addition of formic acid, β -formoxymonomethylhæmin is obtained. Extraction with methyl alcohol containing formic acid yields α -formoxymethylhæmin, described by Partos (cf. A., 1922, i, 596). β -Formoxymethylhæmin is distinguished from the α -form by its solubility in hot sodium carbonate solution. It forms a bluish-black powder, leaflets, prisms, and rhombs, with the formula $C_{35}H_{34}O_4N_4FeO \cdot CHO$. Two forms of formoxyhæmin have also been obtained. By extracting coagulated blood with acetone containing formic acid, the α -form is obtained, needles, insoluble in sodium hydrogen carbonate solution, of the formula $C_{34}H_{32}O_4N_4FeO \cdot CHO$. This is methylated with difficulty with diazomethane to yield a monomethyl derivative which could not be obtained crystalline, but may be identical with Partos's compound. If the coagulated blood is extracted with acetone containing sulphuric acid and the filtrate heated with formic acid and sodium formate, a β -formoxyhæmin, fine needles, is obtained soluble in sodium carbonate solution and easily methylated with diazomethane to yield a monomethyl derivative. If in the preparation of β -formoxyhæmin, acetone containing methyl alcohol is used, a β -formoxymonomethylhæmin is obtained. It is suggested that the α -form of the hæmin group is present in hæmoglobin, and that if a strong mineral acid (sulphuric acid) is used in the extraction the attachment of one of the carboxyl groups to the iron atom is loosened, and a derivative of the β -type is obtained.

W. O. K.

Thiocyanohæmins. WILLIAM KÜSTER (*Z. physiol. Chem.*, 1923, **129**, 157—187).—Thiocyanohæmin may be obtained in two forms analogous to the α - and β -forms of chlorohæmin or of formoxyhæmin. α -Thiocyanohæmin, $C_{34}H_{32}O_4N_4Fe \cdot SCN$, is formed when defibrinated blood is added to acetic acid containing thiocyanic acid. It may be recrystallised as dark brown prisms or rods, or six-sided leaflets, from a mixture of pyridine and chloroform if it is not allowed to remain too long in contact with the solvent. It is insoluble in 5% sodium hydrogen carbonate solution, is methylated by diazomethane only with difficulty and incompletely, and shows a rather low conductivity in benzonitrile solution. If the crude α -thiocyanohæmin is allowed to remain in contact with the chloroform-pyridine mixture for two days, a *pseudo- β -thiocyanohæmin*, six-sided leaflets, is formed. This is soluble in 5% sodium hydrogen carbonate solution, and in methyl alcohol containing sulphuric acid, but not in pure methyl alcohol, and its solution in benzonitrile possesses a higher conductivity than that of α -thiocyanohæmin. One carboxyl group may be

completely methylated and the other partly. If α -thiocyanohæmin is allowed to remain in contact with the chloroform-pyridine mixture for two hours, the product consists chiefly of β -thiocyanohæmin. This compound may be conveniently prepared following Zaleski's method. The blood-coagulum is extracted with acetone containing sulphuric acid, and to the extract is added ammonium thiocyanate. Crystals of (acetone)- β -thiocyanohæmin separate, and when recrystallised from a mixture of acetone and pyridine this compound forms deep bluish-black prisms with a metallic lustre, of the formula $C_{34}H_{32}O_4N_4FeSCN$. It is slowly soluble in 5% sodium hydrogen carbonate solution at room temperature. Thiocyanic acid is split off only with difficulty by alkali, and only very slightly by pyridine, whereas β -chlorohæmin is very easily decomposed by these reagents. Diazomethane forms from β -thiocyanohæmin a mixture of (acetone)-dimethyl- β -thiocyanohæmin, obtusely pointed prisms stable towards 5% sodium carbonate solution even on heating, and (acetone)monomethyl- β -thiocyanohæmin. Monomethyl- β -thiocyanohæmin may be prepared, following Mörner, by extracting blood coagulum with methyl alcohol containing sulphuric acid, and precipitating the extract with ammonium thiocyanate. It forms needles, $C_{35}H_{34}O_4N_4FeSCN$, soluble in hot sodium carbonate. If blood coagulum be extracted with acetone containing sulphuric acid, a 5% solution of thiocyanic acid saturated with ammonium thiocyanate added, and the mixture boiled for thirty minutes, a pseudo- β -(acetone)thiocyanohæmin is obtained, forming prisms, soluble in sodium hydrogen carbonate solution and in acid methyl alcohol, which may be partly methylated by diazomethane. Chlorohæmin may be converted into a pseudo- β -thiocyanohæmin by dissolving in a mixture of chloroform and acetone and treating the solution with 5% thiocyanic acid saturated with ammonium thiocyanate. Measurements of the conductivity of various hæmin derivatives in pyridine and benzonitrile are given.

W. O. K.

The Isolation of Nucleic Acid from Tissues. WALTER JONES and CASPAR FOLKOFF (*Bull. Johns Hopkins Hosp.*, 1922, **33**, 443—444).—The method of isolation of the additive product of yeast-nucleic acid with ammonium acetate is described in detail. The crude acid, after having been separated, is ground with ammonium hydroxide solution, the excess of which is not neutralised until after the addition of alcohol. Subsequent addition of alcohol yields a pure product. The procedure described cannot be employed in the case of animal glands. CHEMICAL ABSTRACTS.

The Course of Enzyme Reactions. SVANTE ARRHENIUS (*Z. angew. Chem.*, 1923, **36**, 455—456).—The most completely investigated enzyme reactions are non-molecular, *i.e.*, the quantity of substrate converted is proportional to the time. Exceptions to this simple law, which depends on the substrate being in large excess of the enzyme, occur when this condition is not realised, when the enzyme becomes decomposed, and when the reaction products enter into the reaction.

H. C. R.

The Inactivation of Trypsin. IV. The Adsorption of Trypsin by Charcoal. JOHN H. NORTHROP (*J. Gen. Physiol.*, 1923, 5, 751—755).—The removal of trypsin from solution by charcoal is not reversible, and is independent of the p_H over a wide range (p_H 3 to p_H 9). Charcoal previously treated with gelatin does not remove trypsin from solution. These facts demonstrate that the inactivation of trypsin by charcoal is essentially different from the inactivation by serum, which is a homogeneous reaction (cf. this vol., i, 261). W. O. K.

The Specificity of Enzymes. V. Comparison of Yeast- and Taka-saccharase. RICHARD KUHN (*Z. physiol. Chem.*, 1923, 129, 57—63).—The inversion of saccharose by yeast-saccharase is not inhibited by α -glucose, whilst it is strongly inhibited by β -glucose or by lævulose. On the other hand, the action of taka-saccharase is retarded strongly by α -glucose and not by β -glucose or by lævulose. Inversion by fresh yeast-cells in presence of toluene is also not inhibited by α -glucose. W. O. K.

The Action of Halogens on Diastases. L. BERCZELLER and J. FREUD (*Biochem. Z.*, 1923, 139, 476—481).—As in the case of ptyalin (this vol., i, 404), it is now shown that the action of malt diastase on starch is also decreased by iodine. The presence of starch has a protective effect on the enzyme against iodine inactivation. Bromine and chlorine also inactivate both ptyalin and malt diastase, and again the presence of starch protects these from the halogens. Bromine and chlorine do not inhibit the acid hydrolysis of starch as does iodine. J. P.

Effect of Amino-acids in Retarding the Hydrolytic Decomposition of an Enzyme (Pancreatic Amylase). H. C. SHERMAN and FLORENCE WALKER (*J. Amer. Chem. Soc.*, 1923, 45, 1960—1964).—Highly purified preparations of pancreatic amylase, which deteriorate more rapidly in aqueous solution than the other amylases studied (A., 1920, i, 101; 1922, i, 283) are also more affected by the presence of amino-acids (*loc. cit.*). In the following experiments, the activity of the amylase is measured by the amount of reducing sugar (chiefly maltose) formed when the quantity of enzyme necessary to saccharify about one-fifth of the substrate acts for thirty minutes at 40° on 100 c.c. of a 10% dispersion of Lintner "soluble" starch, the reducing sugar being subsequently estimated by means of Fehling's solution. Solutions of pancreatic amylase containing optimum concentrations of sodium chloride and disodium hydrogen phosphate which have been kept for one hour at 40° show considerably greater activity when alanine has been added to the solution previously. Amylase solutions to which the salts have not been added deteriorate more rapidly, and with these the protective action of the amino-acid may be demonstrated at 22°. There is a striking increase, between 30° and 60°, in the apparent activation by means of glycine or phenylalanine with increasing temperature of digestion, but above about 60° coagulation of the enzyme occurs, this not being prevented by the presence of the amino-acids. At the same temperatures, using

half the amount of enzyme solution but allowing the reaction to proceed twice as long, the apparent activation is even greater.

All these facts indicate that the favourable influence of amino-acids on the enzymic hydrolysis of starch is due largely, or perhaps even entirely, to a protection of the enzyme from deterioration (probably gradual hydrolytic decomposition) in the aqueous dispersion in which it acts. This is thought to support the view that the enzyme itself is of protein nature, or contains protein as an essential constituent.

W. S. N.

The Specificity of Enzymes. IV. The Simple Nature of the β -Glucosidase of Emulsin. RICHARD WILLSTÄTTER, RICHARD KUHN, and HARRY SOBOTKA (*Z. physiol. Chem.*, 1923, **129**, 33—56).—It has been found that the ratios of the time-values for β -glucosidase acting on helicin, salicin, β -phenylglucoside, arbutin, and β -methylglucoside do not remain constant (cf. A., 1922, i, 390). It does not, however, follow that the different glucosides are hydrolysed by different enzymes. The affinity constant $K = (\text{Free Enzyme}) \times (\text{Substrate}) / (\text{Enzyme-Substrate})$ varies with different preparations. When correction is made for this varying affinity it is found that the ratio of the activities of the enzyme preparations acting, for example, on salicin and β -methylglucoside, remains approximately constant. The variations, therefore of the time-value ratios are not to be referred to variations in the active groups, but rather to the variations in the affinities, no doubt depending on the colloids present in the different preparations.

W. O. K.

The Influence of Glycine on the Fermentative Action of a Soja-bean Urease. II. The Stable Constituent of Soja-bean Urease. NAOSABURO KATÔ (*Biochem. Z.*, 1923, **139**, 352—365).—In a previous communication (this vol., i, 622) the author postulated the presence of two constituents in urease. This has now been confirmed. The urease system consists of a thermolabile constituent which possesses fermentative properties, and a thermo-stable constituent with no fermentation action, which the author calls "Stable Component X." This last, at carbamide concentrations above the "equivalent carbamide concentration" (*loc. cit.*), increases the activity of the urease, but has no influence at substrate concentrations below this value, thus resembling in its action the effect of the addition of glycine to urease. The action of "Stable Component X" is not due to a p_H effect or to the presence of mineral salts.

J. P.

Researches on Antimony. I. Tri-*m*-xylylstibine and its Derivatives. ARCHIBALD EDWIN GODDARD (*T.*, 1923, **123**, 2315—2323).

Preparation of Alkyl Compounds of Boron. ERICH KRAUSE (D.R.-P. 371467; from *Chem. Zentr.*, 1923, ii, 1089; cf. A., 1922, i, 22, 694).—Boron trifluoride is allowed to react with organo-magnesium halides. The following compounds are mentioned: boron phenyl difluoride, $BPhF_2$, an oil, b. p. 70—75°; boron *p*-tolyl

difluoride, an oil, b. p. 95—97°; *phenylboric acid*, needles, m. p. 216°; *p-tolylboric acid*, needles, m. p. 240°; *p-chlorophenylboric acid* (from magnesium *p*-chlorophenyl bromide and boron trifluoride), sheafs of needles, m. p. 275°; *p-bromophenylboric acid*, needles, m. p. 191°; *benzylboric acid*, crystals, m. p. 161°.

G. W. R.

Physiological Chemistry.

Influence of the Medium of the Respiration of Living Cells.

W. RYFFEL (*Z. physiol. Chem.*, 1923, **129**, 223—247).—The respiratory activity of the living cell measured by the reduction of *m*-dinitrobenzene to *m*-nitrophenylhydroxylamine is greatest at a concentration of PO_4''' of 0.08—0.09 M., at p_{H} 9—10, and at a temperature, in the case of guinea-pigs and pigeons, of about 40°, and of frogs of between 20° and 35°.

W. O. K.

The Effects on the Circulation and Respiration of an Increase in the Carbon Dioxide Content of the Blood in Man.

E. C. SCHNEIDER and DOROTHY TRUESDELL (*Amer. J. Physiol.*, 1922, **63**, 155—175).—Among the physiological effects observed on gradual increase of the amount of carbon dioxide in inspired air were an increased pulse rate; increased arterial, capillary, and venous blood pressures; increased minimum volume and frequency of breathing.

CHEMICAL ABSTRACTS.

The Respiratory Exchange and Blood-sugar Curves of Normal and Diabetic Subjects after Epinephrine [Adrenaline] and Insulin.

RICHARD S. LYMAN, ELIZABETH NICHOLLS, and WM. S. McCANN (*J. Pharm. Expt. Ther.*, 1923, **21**, 343—365).—Investigations are described on the effect of administration of adrenaline and of insulin on the respiratory quotient, heat production, blood-sugar, pulse rate, and blood pressure of normal and of diabetic patients. Adrenaline was found as usual to increase the respiratory quotient, heat production and the blood-sugar, whilst insulin increased the respiratory quotient and the heat production but diminished the blood-sugar. Insulin and adrenaline, when injected together, have, generally speaking, an additive effect.

W. O. K.

The Effect of Parasympathetic Stimulation, especially by Means of Choline, on the Blood-sugar.

K. DRESEL and H. ZEMMIN (*Biochem. Z.*, 1923, **139**, 463—469).—The subcutaneous and oral administration of choline to normal and diabetic subjects produced a diminution in blood-sugar, minimal values being reached in from one-half to two hours in the former, and in from two to four hours in the latter method of administration. This is ascribed to parasympathetic stimulation. The results of Bornstein and Vogel (*A.*, 1922, **i**, 80), who observed an increase of blood-

sugar on parasympathetic stimulation using pilocarpine and physostygmine, are ascribed to the unsuitability of the stimulants.

J. P.

The Reversibility of Fibrin Coagulation. II. G. BARKAN and ADALBERT GASPAR (*Biochem. Z.*, 1923, **139**, 291—301).—Fibrin obtained from untreated blood plasma, in contrast to that obtained from oxalated or fluoride plasma, has no tendency to dissolve in 0.02% sodium hydroxide. If the insoluble fibrin be subsequently treated with 0.2% sodium oxalate or 0.75% sodium fluoride, it becomes, in part, soluble in dilute alkali. These results, in conjunction with the authors' previous work (*Biochem. Z.*, 1923, **136**, 411), are regarded as opposing the view that fibrin coagulation is reversible.

J. P.

Effect of Coagulation on the Amino-nitrogen Content of Blood. F. PETITJEAN (*Compt. rend. Soc. Biol.*, 1923, **87**, 1001—1004; from *Chem. Zentr.*, 1923, i, 1464—1465).—In the coagulation of blood a small initial decrease in the amino-nitrogen content is followed by an increase. The content after complete coagulation almost approximates to the original amino-nitrogen content. In certain cases, an increase is observed.

G. W. R.

Amino-acids of the Blood. I. Behaviour during Digestion. II. On Prolonged Fasting. S. MARINO (*Arch. Farm. speriment. Sci. aff.*, 1923, **36**, 20—32, 56—64).—I. The defibrinated blood of a fasting dog is found to contain from 3.3 to 6.6 mg. of amino-acids per 100 c.c. When proteins are undergoing digestion, the blood sometimes contains less than the normal proportion of amino-acids, but in other cases shows almost double the proportion present during fasting. In general the content tends to resume its normal value after the digestion of protein has proceeded for six hours.

II. If fasting is prolonged to the death of the animal, the blood exhibits a considerable increase in amino-acid content, although different animals show marked variations in this respect. Such increase, which is manifested almost exclusively after the twelfth day of fasting, is subsequently progressive until death ensues. In the latter stage, the proteins are probably hydrolysed so rapidly that the resulting amino-acids cannot be utilised and consequently accumulate in the blood; this effect may be aggravated by the pronounced autolytic changes and by the inefficiency of the regulating mechanism.

T. H. P.

The Blood of Mother and Foetus. M. G. HOWE and M. H. GIVENS (*Amer. J. Diseases Children*, 1923, **25**, 63—75).—The non-protein nitrogen and urea-nitrogen in maternal blood at parturition are normal. The values vary but there is no consistent preponderance in either blood. Differences are attributed to maternal or foetal renal insufficiency or impairment of placenta. The concentration of blood uric acid of parturient women tends to be higher than normal. The concentration of blood-sugar is temporarily increased at parturition, maternal values being greater

than foetal. This is due to the anæsthetic, to muscular contractions, and possibly to a psychic factor.

CHEMICAL ABSTRACTS.

The Distribution of Urea in Human Blood and in Secretions.

J. BERNARD COHEN (*Biochem. Z.*, 1923, **139**, 516—526).—Using the urease method and estimating the evolved ammonia in a micro-Kjeldahl apparatus, urea determinations were made on whole human blood and on plasma. In twelve recorded normal cases only three showed an equilibrium distribution of urea between corpuscles and plasma. In the other cases, the ratio corpuscle urea : plasma urea varied from 0.5 to 2.1. Similar results were obtained in eight cases of uræmia, and these were confirmed in dogs with high blood ureas produced by ligation of the pancreatic duct. Human bile, duodenal juice, and cerebrospinal fluid all contain less urea than the corresponding blood, and in the case of bile the urea content is higher during fasting than when food is being taken.

J. P.

The Origin of the Lipase in Blood.

KEIZO HIRUMA (*Biochem. Z.*, 1923, **139**, 336—341).—Ligation of the pancreatic duct in dogs caused an increase of lipase in the blood, the maximum increase being reached after four days. In eight to nine days the lipase content had returned to normal, due to the lessened activity of the secreting cells following on the ligation. No lipase appeared in the urine. Blood-serum collected from the pancreatico-duodenal vein contained more lipase than that from the portal vein, which in turn showed a higher content than that from the femoral artery and vein. These observations are taken to indicate the pancreas and intestine as the seat of origin of blood lipase, but this view does not accord with the results of Rona and Pavlović (this vol., i, 403) on the action of quinine and atoxyl on various lipases.

J. P.

Antihæmolytic Effect of Antithrombin.

NICOLAS L. COSMOVICI (*Compt. rend. Soc. Biol.*, 1923, **88**, 538—540; from *Chem. Zentr.*, 1923, i, 1520).—Antithrombin from the serum of rabbits was found to exert an antihæmolytic effect on a mixture composed of sheep blood-corpuscles and guinea-pig complement in sodium chloride solution. The effect is intensified by the alkalinity of the liquid containing the antithrombin.

G. W. R.

The Cholesterol Balance.

S. J. THANNHAUSER (*Deut. arch. Klin. Med.*, 1923, **141**, 290—311; from *Chem. Zentr.*, 1923, i, 1403—1404).—[With W. FLEISCHMANN.]—An enzyme which hydrolyses cholesterol esters was shown to be present in duodenal juice, pancreatic solution, and bile.

[With E. ANDERSEN.]—Cholesterol is estimated in total blood and in serum by the gravimetric method of Windaus after addition of anhydrous calcium sulphate and ether.

[With ECARIUS.]—The equilibrium between free cholesterol and cholesterol in the form of esters is held to be due to the function

of organs, in particular the liver, and not to a specific enzyme in the blood.

[With PAUL VON MILLER, H. SCHABER, and C. MONCORPS.]—Experiments are described on the cholesterol balance with diets low in cholesterol and fat.
G. W. R.

Tetany. I. The Effect of Calcium Chloride Ingestion on the Acid-Base Metabolism of Infants. J. L. GAMBLE, G. S. ROSS, and F. F. TISDALL (*Amer. J. Diseases Children*, 1923, **25**, 455—469).—Ingested calcium chloride behaves as an acid substance since the concentration of the chloride-ion absorbed is greater than that of the calcium-ion. The effect on acid-base metabolism of the ingestion of 1 g. of calcium chloride is equivalent to that of the ingestion of milk containing 75 c.c. of 0.1*N*-hydrochloric acid. This increase in acid over fixed alkali claiming excretion in the urine is compensated by an increase in urinary acidity and ammonia excretion resulting in a normal base concentration of blood plasma. The lowering of hydrogen carbonate following calcium chloride ingestion is due to a rise in chloride-ion concentration displacing an equivalent amount of bound carbon dioxide. Excretion of fixed alkali, especially of sodium and potassium in the urine, is increased following ingestion of calcium chloride, in consequence of a reduction in the volume of body-water rather than by actual withdrawal of base from body fluids.
CHEMICAL ABSTRACTS.

Tetany. II. The Effect of Ingestion of Hydrochloric Acid-producing Substances on the Acid-Base Metabolism of an Infant and the probable manner of their Action in the Treatment of Tetany. J. L. GAMBLE and G. S. ROSS (*Amer. J. Diseases Children*, 1923, **25**, 470—497).—Plasma bicarbonate is lowered following the administration of calcium chloride, ammonium chloride, and hydrogen chloride to an infant with tetany, in consequence of an increased metabolism of hydrogen chloride which produces an abnormally high chloride-ion content of the plasma at the expense of bicarbonate; the total base of the plasma remains stationary. The hydrogen-ion concentration of the plasma is considerably increased. The metabolism of these substances leads to an increased excretion of phosphates and of fixed alkali in the urine in consequence of a reduction of the volume of body-water due to diuresis. Ammonium chloride does not raise the lowered calcium content of the plasma found in tetany, its therapeutic action being ascribed to the production of an increased ionisation of calcium; calcium chloride and hydrogen chloride, however, cause in addition an increase in the calcium content of the plasma.
CHEMICAL ABSTRACTS.

Retention of Bismuth by the Brain. P. LEMAY and L. JALOUSTRE (*Compt. rend. Soc. Biol.*, 1923, **88**, 474; from *Chem. Zentr.*, 1923, i, 1517).—Comparatively large amounts of bismuth were found in the brains of two individuals to whom bismuth hydroxide had been administered.
G. W. R.

The Metabolism of Phosphorus of the Nervous System.

II. Phosphorus Content under Various Conditions. ELISABETH HECKER (*Z. physiol. Chem.*, 1923, **129**, 26—32).—The phosphorus content of the surviving central nervous system of the frog kept in isotonic sodium chloride solution and supplied with oxygen shows a decrease of about 15—16%. This decrease occurs almost entirely during the first eight hours. This loss of phosphorus is decreased by the application of a narcotic such as urethane, and is increased by electrical excitation, and there is no decrease if oxygen is excluded. W. O. K.

The Metabolism of Phosphorus of the Nervous System.

III. The Phosphorus-sparing Substances in the Metabolism of the Central Nervous Organs. ELISABETH HECKER (*Z. physiol. Chem.*, 1923, **129**, 205—219).—At rest or under stimulation the phosphorus content of the central nervous system decreases, but the presence of galactose, lævulose, or of cerebrin reduces this loss. In the presence of brain lecithin, there is practically no loss. Neutral phosphate solutions also cause a decrease of the loss of phosphorus, but the best effect is obtained by a combination of phosphates and brain lecithin. The temperature influences the magnitude of the changes and so also, in the case of the stimulated preparation, does the strength of the stimulation. W. O. K.

The Metabolism of Phosphorus of the Nervous System.

IV. The Phosphorus Metabolism of the Peripheral Nerves. ELISABETH HECKER (*Z. physiol. Chem.*, 1923, **129**, 220—222).—A nerve (ischiadicus) of the frog contains about 0.2% of phosphorus (calculated on the fresh substance). No change in the phosphorus content could be detected in the resting nerve, but under stimulation it decreased by about 10% in eight hours. W. O. K.

The Free Sugar Content of the Liver and its Relation to Glycogen Synthesis and Glycogenolysis. CARL F. CORI, G. T. CORI, and G. W. PUCHER (*J. Pharm. Expt. Ther.*, 1923, **21**, 377—389).—Under normal conditions, glycogen is synthesised in the liver when the free liver-sugar is high, but if insulin is administered, glycogen synthesis takes place at a much lower level of liver-sugar. Adrenaline causes glycogenolysis and the free liver-sugar is increased. W. O. K.

The Biological Decomposition of Uric Acid. H. STEUDEL and S. IZUMI (*Z. physiol. Chem.*, 1923, **129**, 188—194).—An extract prepared from finely divided ox-kidneys, which in the presence of oxygen converted uric acid into allantoin, was unable to form allantoin from uroxanic acid, $(\text{NH}_2\cdot\text{CO}\cdot\text{NH})_2\text{C}(\text{CO}_2\text{H})_2$. W. O. K.

Composition of a Cystic Liquid. E. MAURIN (*Ann. Chim. Analyt.*, 1923, [ii], **5**, 207—208).—A scrotal cyst yielded 155 c.c. of a slightly turbid, pink liquid, d 1.007. The liquid contained: total solids, 1.235%; ash, 1.062%; serine, 0.135%; globulin, 0.015%; nuclealbumin, trace; peptone, none; pseudomucin, none; urea, 0.075%; dextrose, none; cholesterol, trace; chlorides (as NaCl), 0.012%; phosphates (as P_2O_5), 0.020%. W. P. S.

Composition of Cyst Fluid (of Cattle). P. MAZZOCCO (*Compt. rend. Soc. Biol.*, 1923, **88**, 342—343; from *Chem. Zentr.*, 1923, i, 1334).—The colourless, transparent cyst fluid from cattle rarely becomes turbid on being heated. It has d_{15}^{20} 1.006—1.009. The reaction is alkaline to litmus, acid to phenolphthalein in the cold, and alkaline on warming. The total alkalinity to sulphuric acid is 0.010—0.018%. The composition is as follows: Na_2O , 0.53%; K_2O , 0.04—0.05%; CaO , 0.005—0.006%; Fe, trace; MgO , 0.005—0.007%; NaCl , 0.668—0.700%; SO_3 , 0.35—0.43%; P_2O_5 , 0.026—0.030%; SiO_2 , trace; dextrose, 0.03—0.4%; glycogen, trace; total fatty acids, 0.036—0.041%; unsaponifiable acids, 0.01—0.015%; cholesterol, 0.003—0.004%; proteins, 0.09—0.15%; total nitrogen, 0.069—0.080%; non-protein nitrogen, 0.034—0.040%; carbamide nitrogen, 0.025—0.028%; amino-acids, 0.025—0.028%; histidine, 0.0024—0.010%. The blood of the same animals contains twice as much dextrose and approximately the same amount of carbamide nitrogen and non-protein nitrogen.

G. W. R.

The Influence of Various Antipyretics on the Distribution of Nitrogen in the Urine. KIYOSHI MORINAKA (*Z. physiol. Chem.*, 1923, **129**, 111—129).—The effect of antipyretics on the various fractions of the nitrogen content of urine (rabbit, dog, and man) varies according to the particular drug used. Some, such as antifebrin, have little influence; others, such as elbon or phenacetin, cause amongst other effects, increased amino-acid nitrogen, probably to be associated with increased protein decomposition. The drugs investigated were elbon (cinnamoylhydroxyphenylcarbamide), phenacetin, sodium salicylate, aspirin, quinine, remigin (ethylhydrocupreine), antipyrine, pyramidone, and antifebrin.

W. O. K.

Distribution and Elimination of Organic Arsenic Compounds after Intravenous Administration. F. M. R. BULMER (*J. Pharm. Expt. Ther.*, 1923, **21**, 301—311).—After intravenous administration of salvarsan, arsenic first of all accumulates in the liver, but it disappears rapidly from that organ, being excreted in the bile, which seems to be the main route by which the organism eliminates arsenic. It also tends to accumulate in the lungs, where it remains for several days, whilst it is retained in the long bones for a longer period than in any of the other tissues analysed.

W. O. K.

Penetration of Arsenic into the Cerebrospinal Fluid. CARL VOEGTLIN, M. I. SMITH, HELEN DYER, and J. W. THOMPSON (*U.S. Public Health Repts.*, 1923, **38**, 1003—1021).—The penetration of arsenic into the cerebrospinal fluid, following the intravenous injection of a variety of arsenicals, has been studied by (a) the chemical analysis of the blood, brain, and cerebrospinal fluid for the presence of arsenic, and (b) the parasitocidal action obtainable in the cerebrospinal fluid. The distribution of arsenic in various tissues and body-fluids after injection of several preparations has also been studied. Normal rabbits fed on oats and kale contained 0.69 micro-mg. of arsenic per g. of cerebrospinal fluid. The brain of

normal animals contained an average of 0.02 micro-mg. arsenic per g. of fresh tissue. *Trypanosoma equiperdum* is killed in blood suspension in vitro by 7.5 micro-mg. of arsenic from "arsenoxide," in six minutes. Salvarsan, neo-salvarsan, and silver salvarsan have a relatively low effectiveness unless very large doses are used. Sulpharsphenamine is the most effective arsenobenzene derivative studied. A greater therapeutic effect can be expected from large single doses given at long intervals than from smaller doses administered more frequently. Sulpharsphenamine, tryparsamide, and 3-amino-4-hydroxyphenylarsinic acid are suggested as remedies of superior penetrative power.

CHEMICAL ABSTRACTS.

Chemistry of Vegetable Physiology and Agriculture.

The Importance of Sequence in Biology. III. L. KARCZAG and K. HAJÓS (*Biochem. Z.*, 1923, **139**, 345—351).—A continuation of the authors' work (A., 1922, i, 302) on the effect of varying the order of addition of the components of a reacting system. It is shown that, in the case of the Wassermann reaction, variations in (1) the sequence of addition of the components of the first phase (serum, antigen, complement, and salt) and (2) the order of addition of hæmolysin and erythrocytes has, in both cases, a marked effect on the intensity of the reaction. J. P.

Butylene Glycol Fermentation of Dextrose by *Bacillus proteus*. M. LEMOIGNE (*Compt. rend. Soc. Biol.*, 1923, **88**, 467—468; from *Chem. Zentr.*, 1923, i, 1460).—The formation of butylene glycol by the action of three types of *Bacillus proteus* on substrates containing dextrose was shown by isolation of acetylmethylcarbinol and β -butylene glycol from the products of fermentation.

G. W. R.

The Production of Carbon Dioxide and Volatile Acids by Propionic Bacteria, with special reference to their Action in Cheese. J. M. SHERMAN and R. H. SHAW (*Sci. Proc. Amer. Soc. Bacteriologists, Abstracts Bact.*, **6**, 16).—*Bacterium acidipropionici* (d) can produce carbon dioxide, propionic acid, and acetic acid from succinates, glycerol, peptone, and possibly to a slight degree from butter fat. In the case of succinates and glycerol, about twice as much propionic acid was produced as acetic acid; in the case of peptone, the amount of acetic acid was larger than in the other cases. Aspartic acid yielded only carbon dioxide and acetic acid.

CHEMICAL ABSTRACTS.

Intermediate Products of the Bacterial Decomposition of Cellulose. CARL NEUBERG and REINHOLD COHN (*Biochem. Z.*, 1923, **139**, 527—549).—In the bacterial fermentation of cellulose at 37° with production of hydrogen and methane, and at 53° to 55° by thermophilic bacteria, acetaldehyde was detected as an intermediate product and isolated as the sulphite compound and in combination

with dimethylhydrosoreinol. Of the breakdown products of cellulose, cellobiose and dextrose underwent fermentation by the cellulose bacteria with formation of butyric acid, in the former case, and acetaldehyde in both, whilst Hess's anhydrobiose gave negative results. The anhydrobiose is susceptible to fermentation by cultures of *Bacillus butylicus*, which also ferments cellobiose but not cellulose. Acetaldehyde was detected during the butyric acid fermentation of anhydrobiose and cellobiose and, in the latter case, traces of dextrose were also found. It is concluded that the hydrogen and methane fermentation of cellulose proceeds like a butyric acid fermentation with the subsequent intermediate formation of acetaldehyde. J. P.

Digestion of Cellulose by the Intestinal Flora of Man, *Bacillus cellulose dissolvens*, n.sp. (MME) Y. KHOUVINE (*Ann. Inst. Pasteur*, 1923, **37**, 711—752).—A detailed account is given of the isolation from the human intestinal flora in 60% of the cases of an anaërobie, *Bacillus cellulose dissolvens*, n.sp. It is best cultivated in media containing faecal extractives. Its separation as a pure culture from other bacteria is difficult, but depends on its great resistance to heat, the terminal spore resisting boiling for 40—50 minutes and also saturated chloropicrin solution. It does not appear to act on sugars, but only on cellulose, which it digests, with formation of carbon dioxide, hydrogen, ethyl alcohol, acetic, butyric, and probably lactic acids. It disintegrates 1 g. of cellulose in sixteen days, but in the presence of other bacteria it can cope with five times as much cellulose. The paper is illustrated by photomicrographs which show, inter alia, the attachment of the bacilli to the cellulose fibres by their non-sporulating terminations. H. K.

Micro-organisms Concerned in the Oxidation of Sulphur in the Soil. V. Bacteria Oxidising Sulphur under Acid and Alkaline Conditions. S. A. WAKSMAN (*J. Bact.*, 1922, **7**, 609—616).—In acid soils, *Thiobacillus thio-oxidans* rapidly oxidises sulphur, whilst *Thiobacillus-B*, which is commonly present in cultivated soils, is active in alkaline soils. CHEMICAL ABSTRACTS.

Influence of Ultra-violet Light on Alcoholic Fermentation. N. L. SÖHNGEN and C. COOLHAAS (*Woch. Brau.*, 1923, **40**, 187—188).—Contrary to the results obtained by R. and R. de Fazi (*A.*, 1922, i, 1219), ultra-violet light from a quartz lamp is found to exert a harmful influence both on the fermenting and on the reproductive capacity of yeast, unless the distance of the lamp from the solution is large and the time of illumination short, in which case no effect at all is noticeable. W. T. K. B.

Auto-fermentation of Yeast. H. VON EULER and KARL MYRBÄCK (*Z. physiol. Chem.*, 1923, **129**, 195—204).—The auto-fermentation of yeast as shown in the production of carbon dioxide is accelerated by the presence of toluene and inhibited by chloroform or by a mixture of toluene and ethyl acetate. The initial rate of production of carbon dioxide by dried yeast is reduced by the addition of dextrose. The auto-fermentation of fresh yeast is

slightly inhibited at p_H 6.3 by lactose which has little effect on the fermentation of dextrose. It is also inhibited markedly by sodium chloride. Alcohol as well as carbon dioxide is produced during the fermentation. The yeast gum is not attacked, but the yeast glycogen shows a marked decrease in quantity during autofermentation. W. O. K.

Effect of Infinitesimal Traces of Chemical Substances on Photosynthesis. J. C. BOSE (*Nature*, 1923, 112, 95—96).—The usual method of measuring the rate of photosynthesis of water-plants by counting the bubbles of oxygen evolved being untrustworthy, a device has been perfected whereby the evolution of equal volumes of oxygen is automatically recorded on a revolving drum. A definite relation has been found between the evolution of oxygen and the formation of carbohydrate in the leaf. In view of the fact that the coefficient of photosynthetic activity of the aquatic plant *Hydrilla verticillata* was doubled after a thunder-storm, presumably on account of the addition of traces of nitric acid, experiments were conducted which showed that the application of a solution of nitric acid at a dilution of 1 in 10^{11} induced no change, 1 in 10^{10} produced an increase in activity of 100%, whilst 1 in 2×10^9 caused a further increase of nearly 200%. Similar increases in carbon assimilation were obtained by the application of dilute solutions of extract of thyroid gland, and formaldehyde. Of the latter substance, a solution containing 1 part in 10^9 parts caused an increase of photosynthetic activity of 85%. A. A. E.

The Reaction of Protoplasm to some Reagents. WILLIAM SEIFRIZ (*Ann. Bot.*, 1923, 37, 489—509).—Experiments on the effect of ethyl alcohol and the glucosides, saponin, smilacin, and senegin, respectively, on the protoplasm of the leaf-cells of *Elodea*. The initial effect of ethyl alcohol is an increase in permeability with exosmosis, resulting in lowering of osmotic pressure. This is followed by partial decrease in permeability and increase in osmotic pressure. The ultimate effect is coagulation and death of the protoplasm. The glucosides at first cause increased permeability and decrease of osmotic pressure. Longer treatment results in increase of osmotic pressure. Different theories of permeability and narcosis are discussed. G. W. R.

Influence of Ammonium Sulphate on Plant Growth in Nutrient Solutions and its Effect on Hydrogen-ion Concentration and the Availability of Iron. LINUS H. JONES and JOHN W. SHIVE (*Ann. Bot.*, 1923, 37, 355—377).—A study of the effect of ammonium sulphate on the growth of soja beans in nutrient solutions and on the availability to plants of different forms of iron. In the solutions where nitrogen was supplied as nitrate, a decrease in hydrogen-ion concentration as a consequence of plant growth was observed. Where ammonium sulphate was substituted for nitrate an increase in hydrogen-ion concentration occurred. The availability of ferric phosphate was greater in the solutions containing ammonium sulphate than in those containing nitrates. Ferrous sulphate shows greater toxicity in the presence of ammonium

sulphate than in the presence of nitrate. Availability of iron compounds is apparently dependent on the changes in reaction of nutrient solutions induced by contact with plant roots. G. W. R.

The Soluble Carbohydrates in Wheat Grains during Growth.

H. COLIN and H. BELVAL (*Compt. rend.*, 1923, **177**, 343—346).—Immature wheat grains contain 6% of levosin (cf. Tanret, A., 1891, i, 661), 1.5% of sucrose and less than 1% of a reducing sugar, these constituting all the (soluble) reserve carbohydrates (starch, 5—6%). As maturity is approached, starch is formed in increasing quantities (50—60%), the soluble carbohydrates lose their importance and their relative proportions change. The rotatory powers before and after inversion steadily increase, and the dextrose : lævulose ratio gradually approaches unity. At maturity, only 0.15% of free reducing sugar, 0.40% of crystallisable sugar and roughly the same amount of levosin are present. E. E. T.

Phytochemical and Pharmacological Examination of the Seeds of *Chydenanthus excelsus*, Miers. M. DUYSER (*Pharm. Weekblad*, 1923, **60**, 777—799).—The tree is common in the Dutch Indies; the fruit and flowers are described in detail. The seeds contain a fatty oil, gallic acid, and a crystalline glucoside, *chydenanthin*, $C_{21}H_{34}O_{10}$. Hydrolysis separates this into arabinose, galactose, and a mixture of sapogenins, from which one, *chydenanthegeenin*, $C_{12}H_{20}O_3$, was separated and recrystallised; it contains two hydroxyl groups and an aldehyde group.

The action of strong acids on chydenanthin gives an amorphous substance, $C_9H_{15}O_4$, containing three hydroxyl groups; nitric acid, however, yields picric acid, whilst potassium hydroxide yields valeric and oxalic acids.

Chydenanthin possesses strong hæmolyzing action, coagulates the blood in low concentrations, acts as a poison on the heart, and depresses the blood pressure. S. I. L.

Comparative Plant Chemistry. VI. The Fruits of *Gleditschia triacanthos*, L. BINEM ASZKENAZY (*Monatsh.*, 1923, **44**, 1—8).—*Seeds*. Extraction with light petroleum showed the presence of an oil, which on oxidation with permanganate gave dihydroxystearic acid (m. p. 129.5—130.5°), sativic acid (m. p. 172—174°), and an isomeric tetrahydroxystearic acid (?) (m. p. 158°). The oil therefore consisted of a mixture of acids of the oleic and linoleic type, no linolenic acids being present, and only very small quantities of solid acids. A *phytosterol*, $C_{30}H_{50}O, 0.5H_2O$, was also isolated as leaflets, m. p. 152—153° (in closed tube). It is remarkable in possessing water of crystallisation (removable at 130°), in being optically inactive, and in being stable on exposure, in spite of the presence of two ethylenic linkings. The *acetyl* derivative forms leaflets, m. p. 164° (in closed tube).

Alcohol extracted only small quantities of material, which reduced Fehling's solution, was dextrorotatory, and gave no osazone. It is possibly allied to glycyrrhizin. The extract may have contained choline.

The hot aqueous extract was a viscous liquid, becoming a gel on cooling.

Proteins are present to a greater extent in the cotyledons than in the endosperm. The dried seeds contain : ether-soluble material, 4.08%; water-soluble material, 30.0%; water-soluble inorganic matter, 3.3%; raw fibre, 11.07%; pentosans, 7.95%; total ash, 3.78%; crude proteins, 22.81%. The weight unaccounted for (23%) is presumably due to polysaccharides which are insoluble in water.

Husks. These contain a phlobaphen and tannins, both of the protocathechuic type, dextrose, acetic acid, etc., the results of a complete analysis giving ether-soluble material, 1.67%; alcohol-soluble material, 26.00%; water-soluble material, 3.43%; soluble inorganic matter, 1.05%; raw fibre, 37.78%; pentosans, 12.41%; crude proteins, 7.81%; total ash, 4.11%. The 8% not accounted for is probably due to hemicelluloses of a non-pentosan type.

E. E. T.

The Chemical Constituents of Green Plants. XXVIII.
The Acids of the Tamarind (*Tamarindus indica*) Precipitable by Lead Acetate. HARTWIG FRANZEN and HANS KAISER (*Z. physiol. Chem.*, 1923, **129**, 80—94).—The acids of the tamarind precipitable by lead acetate consist very largely of tartaric acid, small amounts of malic acid, and traces of oxalic acid, succinic acid, and citric acid.

W. O. K.

Diurnal Variations in the Total Nitrogen Content of Foliage Leaves. ALBERT CHARLES CHIBNALL (*Ann. Bot.*, 1923, **37**, 511—518).—From a review of published results it is concluded that a withdrawal of nitrogen from leaves takes place at night. G. W. R.

The Constituents of Peach Leaves. TATSUO KARIYONE and YUSHIRO KIMURA (*J. Pharm. Soc. Japan*, 1923, No. **494**, 247—251; cf. Bourquelot and Fichtenholz, A., 1910, ii, 742; 1911, i, 803; ii, 142).—Analysis of leaves of *Pyrus sinensis*, Lindl. (I), and *Pyrus communis*, L. (II), gave the following results : I. (collected in July and September, respectively) : Water, 57.86%, 49.79%; Ash, 8.00%, 2.96%; Arbutin in dried leaves, 0.30%, 0.17%; Tannin (by Schröder's method), 2.41%, 2.91%. II. Corresponding figures (for July) are : 58.26%; 2.21%; 0.58%; 8.14%. K. K.

The Chemical Constituents of Green Plants. XXIX.
Some Water-soluble Constituents of the Leaves of the Bramble (*Rubus fruticosus*). HARTWIG FRANZEN and ERNST KEYSSNER (*Z. physiol. Chem.*, 1923, **129**, 309—319).—By the use of the ester-hydrazide method, the following acids have been found in bramble leaves; lactic acid (0.8%), succinic acid (0.009%), malic acid (0.00015%), oxalic acid (0.0003%). The figures refer to the quantities present in the dry leaf and are only approximate. In addition, the copper salt of an unidentified acid, and two unidentified hydrazides of m. p. 181—182° and 201—202°, respectively, have also been isolated.

W. O. K.

Presence of Quercitrin in the Leaves of *Camellia theifera* and in Dried Tea. J. J. B. DEUSS (*Rec. trav. chim.*, 1923, **42**, 623—624).—The presence of quercitrin in the fresh leaves of *Camellia theifera* and in dried tea may be demonstrated as follows. An aqueous extract of the material is filtered, treated with 1—2% of concentrated hydrochloric acid, and boiled under a reflux condenser while a rapid current of carbon dioxide is passed through. A brown precipitate is formed, and after about one to two hours the reaction is complete. The precipitate is washed with water and dried at 100° and extracted with ether, when the quercetin is removed and crystallised from water. Since the leaves contain no quercetin, this substance must have been formed by the hydrolysis of quercitrin in the leaves and consequently its formation constitutes a proof of the presence of the latter substance. The amount of quercitrin present is found to be about 0.1% and the amount is the same whether the leaves have been grown in the shade or exposed to the sunlight. J. F. S.

***Rapanea luteovirens*, Mez.** E. HERRERO DUCLOUX and MAX AWSCHALOM (*Anal. Asoc. Quim. Argentina*, 1923, **11**, 6—24).—The bark of *Rapanea luteovirens*, Mez., contains 59.552% of moisture. The dry matter contains ash 10.355%, total nitrogen 1.335%, proteins, 8.347%, crude fat 3.093%, cellulose 21.352%, carbohydrates 56.853%. The isolation of the acid and neutral saponin, respectively, is described and their reactions with a number of reagents are given. The neutral saponin was found to be more toxic to fish and to have a greater hæmolytic power than the acid saponin. The dry matter contains acid saponin 0.809% and neutral saponin 0.213%. G. W. R.

Chemistry of Japanese Plants. I. The Proximate Composition of Karafuto Wood. HISASHI NAKAMURA (*Mem. Coll. Sci. Kyoto*, 1923, **6**, 295—304).—Sawdust from the wood of two species of tree growing in the forests of the island of Karafuto was examined by hydrolysis for sugars, pentosans, and hexosans, lignin, and cellulose. Very little difference was found in the proximate analyses of the two woods. *d*-Mannose, *d*-galactose, and *l*-xylose were found in the acid extract after hydrolysis, the first being actually isolated in the crystalline state. H. H.

The Presence of Urease in the Nodules on the Roots of Leguminous Plants. E. A. WERNER (*Nature*, 1923, **112**, 202).—The presence of urease has been demonstrated in the nodules from the rootlets of *Trifolium procumbens*, *T. pratense*, *T. repens*, *Vicia sativa*, *Medicago sativa*, *Galega officinalis*, various lupins, and the garden pea. Urease was not found in any roots devoid of nodules, but it was clearly present in the cylindrical tuberous growths developed from the rootstock of *Ranunculus ficaria*. A. A. E.

The Presence of Loroglossine in Eleven New Species of Indigenous Orchids. P. DELAUNEY (*Bull. Soc. Chim. biol.*, 1923, **5**, 398—408; cf. A., 1921, i, 801).—Loroglossine has been isolated from a further eleven species of orchids. E. S.

Extraction and Separation of the Pigments of *Nereocystis luetkeana*. GRACE E. HOWARD (*Publ. Puget Sound Biol. Sta.*, 1921, **3**, 79—91).—Chlorophyll-*A* and -*B*, carotene, xanthophyll, and fucoxanthin can be extracted by Willstätter's method, but not with pure solvents. Colloidal chlorophyll carries a negative charge. Magnesium is present in chlorophyll, and chlorophyllase is probably present in kelp. CHEMICAL ABSTRACTS.

Soil Structure and Colloid Chemistry. G. HAGER (*Z. Pflanz. Düng.*, 1923, **2**, 292—311).—Theoretical. A discussion of the bearing of the phenomena of adsorption on soil structure with particular reference to the work of Mattson (*A.*, 1922, **i**, 800). G. W. R.

Arable Soil: Natural Zeolites. F. SCURTI (*Ann. Chim. Appl.*, 1923, **13**, 161—193).—The published analytical results of natural zeolites show that, in their typical forms at least, these compounds are alkali or alkaline earth salts of dimeta-*n*-ortho-silico-aluminic acids. The number of silicon atoms present is sometimes ten, but as yet no zeolites with eight atoms of silicon are known. As regards the water present, zeolites containing up to six atoms of silicon tend to absorb water extraneous to the mineral itself. As the silicon atom chain lengthens further, this process undergoes inversion, zeolites with seven atoms of silicon containing less than the theoretical proportion of water. The tendency to absorb water is evidently due to the aluminic hydroxyl groups and that to lose water to the silicic hydroxyl groups. The presence of these hydroxyls of different types explains the ability of zeolites to unite with either acids or bases and also the ease with which the alkali or alkaline-earth metal is replaceable by other metals or by ammonia. In this exchange, no matter what the concentration of the salt used, the new ion never replaces the original metal completely, the tendency of the new products to act in the inverse sense resulting in the establishment of a condition of equilibrium.

In such processes may be sought the general mechanism of the fixation of bases in arable soil, the absorbent power of the soil being interpreted as a true chemical combination obedient to the laws of mass action rather than as a physical absorption comparable with that of water by a sponge. The reactions of the zeolites also furnish ready explanations of the formation of alkaline soils and of the increase of acidity sometimes effected in soils. T. H. P.

Comparison of Active Aluminium and Hydrogen-ion Concentration of Widely Separated Acid Soils. PAUL S. BURGESS (*Soil Sci.*, 1923, **15**, 407—412).—From an examination of a large number of acid soils from different localities in the United States, it is concluded that there is a general correlation, with individual exceptions, between the content of active aluminium and hydrogen-ion concentration. [See, further, *J.S.C.I.*, 1923, 846A.]

G. W. R.

Variability of Nitrates and Total Nitrogen in Soils. ARTHUR L. PRINCE (*Soil Sci.*, 1923, **15**, 395—405).—A study of the variability of certain soils in total and nitrate nitrogen. It

is shown that the variability in nitrate content and nitrifying power is much greater than the variability in total nitrogen and a correspondingly larger number of samples must be taken in the former case in order to obtain trustworthy results. [See, further, *J.S.C.I.*, 1923, 846A.] G. W. R.

The Relation of Concentration of Soil Solution to Nitric Nitrogen in Soils containing Large Quantities of Available Nitrogen and their Effect on Plant Growth. (*New Mexico Agr. Exp. Sta. Ann. Rep.*, 1921, 24—25).—Soil which contains an excessive quantity of nitrates contains also other soluble salts in excessive quantities. As the quantity of total salts increased, the nitrate increased more rapidly. Injury is due chiefly to sulphates and chlorides rather than to nitrates. CHEMICAL ABSTRACTS.

Some Relations of Organic Matter in Soils. F. A. CARLSON (*Cornell Agr. Exp. Sta. Mem.*, 1923, 61).—Experiments with Dunkirk clay loam showed that plots in rotation with legumes contained more nitrogen than plots in rotation without legumes, the increase being greater in limed plots than in unlimed. There is a close relation between organic carbon and nitrogen.

CHEMICAL ABSTRACTS.

[Incorporation of] Organic Matter [in Soils]. F. J. SIEVERS (*Washington Agr. Expt. Sta. Bull.*, 1922, 167, 45—46).—The incorporation of straw having a nitrogen : carbon ratio of 1 to 75 in the soil produced a depressing effect on nitrate development, which persists until there is sufficient decomposition to cause the ratio to approach that in the soil, 1 to 13. When organic matter having a narrow nitrogen : carbon ratio like legumes is incorporated in the soil there is a rapid development of nitrate. There is less loss of carbon dioxide and indication of greater organic matter maintenance.

CHEMICAL ABSTRACTS.

The Influence of Precipitation on Soil Composition and on Soil Organic Matter Maintenance. F. J. SIEVERS and H. F. HALTZ (*Washington Agr. Expt. Sta. Bull.*, 1923, 176).—Soils receiving about 20·3 cm. of precipitation annually contain about one-fourth as much nitrogen in the surface layer 15·24 cm. deep as those receiving about 50·8 cm. annually. The ratio between the nitrogen and carbon remains practically constant. Variations in precipitation have no influence on the amount of total phosphorus and potassium in the soil, but that of the calcium (present as silicate) is slightly influenced; the organic matter content of the subsoil shows little change. The nitrogen : carbon ratio for the subsoil is slightly narrower than that for the corresponding surface soil.

CHEMICAL ABSTRACTS.

Organic Chemistry.

New Zealand Mineral Oils. THOMAS H. EASTERFIELD and NORMAN McCLELLAND (*Chemistry and Industry*, 1923, **42**, 936—938).—Three classes of mineral oil have been manufactured in New Zealand. Kauri oil is obtained by the distillation of peat containing kauri gum and is a mixture as complex as crude rosin oil. There are large deposits of oil shale in the Southland District and natural mineral oil occurs in many localities. The only considerable flow occurs at New Plymouth. This oil contains an unusually high percentage of solid paraffins, 12—13%, and the various fractions have generally higher specific gravities than fractions of similar boiling point from other sources. In the "benzene" fraction the following cycloparaffins have been identified: methylcyclopentane, cyclohexane, methylcyclohexane, α -decanaphthene, undecanaphthene, and dodecanaphthene. The aromatic hydrocarbons identified were benzene, toluene, the three xylenes, naphthalene, α -methylnaphthalene, and 1:4-dimethylnaphthalene. The oil is practically free from sulphur and acid and basic constituents. The paraffins from $C_{24}H_{50}$ to $C_{31}H_{64}$, excluding $C_{27}H_{56}$, were all identified. The paraffins are not decomposed by heating for a week in a vacuum at 350—400°. E. H. R.

The Addition of Water to Ethylene and Propylene. J. P. WIBAUT and J. J. DIEKMANN (*Proc. K. Akad. Wetensch. Amsterdam*, 1923, **26**, 321—328).—The reversibility of the dehydration of ethyl and *n*-propyl alcohols by means of alumina or aluminium sulphate at 300—400° has been studied, and very small quantities of acetaldehyde and acetone, respectively, were detected in the reaction mixture of olefine and water vapour after it had been passed over the heated catalyst. It is thought that water unites with ethylene to give ethyl alcohol which immediately decomposes into acetaldehyde and hydrogen. Similarly, in conformity with Markovnikov's rule, water unites with propylene to give *isopropyl* alcohol, which immediately breaks down into acetone and hydrogen.

Experiments were also carried out on the absorption of ethylene and propylene by means of sulphuric acid at various temperatures and concentrations, but only very small yields of ethyl and *isopropyl* alcohols were obtained. H. H.

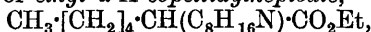
***n*-Amylethylene [Δ^a -Heptene] Oxide from Heptaldehyde.** JULIUS VON BRAUN and WERNER SCHIRMACHER (*Ber.*, 1923, **56**, [B], 1845—1850).—The fission of cholines (cf. Meyer and Hopff, A., 1921, i, 851; Karrer and Horlacher, A., 1922, i, 825) has been investigated in the hope that, in suitable cases, it might lead to $\alpha\beta$ -unsaturated alcohols. This does not appear to happen with the quaternary bases derived from β -dimethylaminoheptyl alcohol, which unexpectedly yields almost exclusively Δ^a -heptene oxide.

The production of an unsaturated alcohol is not observed when the dimethylamino-group is replaced by the *A*- or *B*-copellidyl residue.

Heptaldehyde is converted successively into heptoic acid and ethyl α -bromoheptoate. The latter compound, when treated with dimethylamine dissolved in benzene, yields *ethyl α -dimethylaminoheptoate*, an almost colourless liquid, b. p. $100^{\circ}/10$ mm. (*methiodide*, m. p. 126°). The ester is reduced by sodium and alcohol to β -*dimethylaminoheptyl alcohol*, $\text{CH}_3\text{Me} \cdot [\text{CH}_2]_3 \cdot \text{CH}(\text{NMe}_2) \cdot \text{CH}_2 \cdot \text{OH}$, a colourless liquid, b. p. 97 – $98^{\circ}/10$ mm. (the non-crystalline *hydrochloride*, the *picrate*, m. p. 98° , and the *methiodide*, m. p. 122° , are described). The methiodide is transformed by silver oxide into the corresponding hydroxide which when heated under diminished pressure yields Δ^{α} -heptene oxide, $\text{CH}_3 \cdot [\text{CH}_2]_4 \cdot \text{CH} < \text{O} \begin{smallmatrix} \text{CH}_2 \\ \text{O} \end{smallmatrix}$, b. p.

143 – 145° , $d_4^{13.5}$ 0.8385, $n_D^{13.5}$ 1.4164. It is converted by dilute sulphuric acid into heptaldehyde and by water at 180° into *heptene $\alpha\beta$ -glycol*, $\text{CH}_3 \cdot [\text{CH}_2]_4 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{OH}$, a colourless, viscous liquid, b. p. 128 – $130^{\circ}/11$ mm. Fuming hydrochloric acid transforms the oxide into α -*chloro- β -hydroxy-*n*-heptane*, a colourless liquid, b. p. 87 – $88^{\circ}/10$ mm.; α -*bromo- β -hydroxy-*n*-heptane*, b. p. 102 – $103^{\circ}/12$ mm., is prepared in a similar manner. Δ^{α} -Heptene oxide and dimethylamine in the presence of benzene yield α -*dimethylamino- β -hydroxy-*n*-heptane*, b. p. 83 – $85^{\circ}/11$ mm. (*picrate*, m. p. 63 – 65° ; *methiodide*, m. p. 106 – 108°); the compound is also obtained from α -chloro- or α -bromo- β -hydroxy-*n*-heptane by the action of dimethylamine.

The action of *A*-copellidine on ethyl α -bromoheptoate leads in part to the loss of hydrogen bromide from the latter and in part to the formation of *ethyl α -A-copellidylheptoate*,



a moderately mobile liquid, b. p. 160 – $163^{\circ}/10$ mm., d_4^{19} 0.9274, which yields only non-crystalline derivatives. *Ethyl α -B-copellidylheptoate* has b. p. 160 – $163^{\circ}/10$ mm., d_4^{19} 0.9326; its derivatives could not be caused to crystallise. Reduction of the esters by sodium and ethyl alcohol leads smoothly to the production of α -*A-copellidylheptyl alcohol*, a viscous liquid, b. p. 163 – $166^{\circ}/11$ mm. (which gives only non-crystalline derivatives) and α -*B-copellidylheptyl alcohol*, b. p. 163 – $166^{\circ}/11$ mm., which does not yield well-defined derivatives. The bases are converted into their methiodides and thence into the corresponding quaternary hydroxides, which are distilled under diminished pressure. The basic products of the reaction consist of mixtures of *A*- and *B-copellidylheptyl alcohols* with *A*- and *B-N-methylcopellidines*, respectively (the substances will be described in detail in a subsequent communication); the non-basic product is Δ^{α} -heptene oxide, the amount of which corresponds with that of the 1-methylcopellidine simultaneously formed. H. W.

Abnormal Reactions of Derivatives of Isoprene and of $\beta\gamma$ -Dimethylbutadiene. L. CLAISEN, F. KREMERS, F. ROTH, and E. TIETZE (*J. pr. Chem.*, 1922, [ii], 105, 65–92, 288).—The action of gaseous hydrogen bromide on ice-cold isoprene leads

primarily to the formation of the tertiary bromide, $\text{CMe}_2\text{Br}\cdot\text{CH}\cdot\text{CH}_2$. The product has b. p. indefinite, largely below $50^\circ/40$ mm., if an excess of hydrogen bromide is avoided and the distillation is carried out soon after the bromination; but if the product is kept a few hours before distillation, and particularly if hydrogen bromide is present, it is converted into the primary bromide, $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2\text{Br}$, b. p. $50\text{--}51^\circ/40$ mm., or $62\text{--}64^\circ/67$ mm. The constitution of the latter, which Mokiewsky (A., 1900, i, 509) regarded as the tertiary bromide, is proved as follows. It reacts in warm benzene solution with the sodio-derivative of formanilide, giving *formo-N- Δ^{β} -isopentenylanilide*, a thick oil, b. p. $163\text{--}164^\circ/16\cdot5$ mm., $d_{15}^{25} 1\cdot029$, which is hydrolysed by boiling with concentrated methyl-alcoholic potassium hydroxide to *N- Δ^{β} -isopentenylaniline*, an oil, b. p. $136\text{--}137^\circ/16\cdot5$ mm., $d_{15}^{25} 0\cdot9583$. The latter is benzooylated by warming with pyridine and benzoyl chloride, giving *benzo-N- Δ^{β} -isopentenylanilide*, hard, colourless rods, m. p. $80\text{--}81^\circ$, which is reduced by the aid of hydrogen and palladium to *benzo-N-isoamylanilide*, long, hard rods, m. p. 75° , identical with the product formed by benzoylating *isoamylaniline*. The primary bromide reacts with magnesium phenyl bromide to give *Δ^{β} -isopentenylbenzene* ($\gamma\gamma$ -dimethylallylbenzene) (Klages, A., 1906, i, 661), which is also prepared by the action of magnesium methyl iodide on ethyl hydrocinnamate, the dehydration of the intermediately formed carbinol being accomplished by distilling it with ammonium iodide, and then with phosphoric oxide. *isoPentenylbenzene* reduces mercuric acetate, although, according to Balbiano (A., 1915, i, 426), this is characteristic of aromatic propenyl derivatives, but not of allyl or Δ -butenyl derivatives. *isoPentenylbenzene* is converted into $\gamma\gamma$ -dimethylpropenylbenzene, when boiled with a small quantity of alkali hydroxide; when heated at 100° with hydrogen bromide in glacial acetic acid solution, it gives a colourless *hydrobromide*, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CMe}_2\text{Br}$, b. p. $126\text{--}128^\circ/14$ mm. The primary bromide is converted by the action of alcoholic sodium ethoxide solution into ethyl *Δ^{β} -isopentenyl ether*, a colourless liquid, b. p. $124\cdot7\text{--}125^\circ$, $d_{15}^{25} 0\cdot8005$, which is apparently identical with the ether previously described by Ipatiev (A., 1899, i, 657), and is reduced by means of palladium-hydrogen in alcoholic solution to ethyl *isoamyl ether*. The primary isoprene hydrobromide is unusually unstable towards water, being almost completely decomposed within thirty minutes with formation of the tertiary alcohol, $\text{OH}\cdot\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2$. The latter (Mokiewsky, *loc. cit.*) is evidently produced directly, and not by isomerisation of the primary alcohol, $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{OH}$, since this (Courtot, A., 1906, i, 788) shows no tendency to pass into its isomeride. The production of the alcohol from the bromide is best carried out in the presence of sodium carbonate, since the reaction is reversed by the action of hydrobromic acid, $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2\text{Br} \xrightleftharpoons[\text{HBr}]{\text{H}_2\text{O}} \text{OH}\cdot\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2$.

Hydrogen bromide reacts with cold $\beta\gamma$ -dimethylbutadiene to give *α -bromo- $\beta\gamma$ -dimethyl- Δ^{β} -butylene*, $\text{CMe}_2\cdot\text{CMe}\cdot\text{CH}_2\text{Br}$, a colourless, lachrymatory liquid, b. p. $51\text{--}54^\circ/20$ mm., $62\text{--}65^\circ/31$ mm.,

or 144—148° (decomp.) at the ordinary pressure, which is readily decomposed by the action of water, and reacts with bromine in chloroform solution to give an oily (?) *dibromide*, which gradually loses hydrogen bromide at the ordinary temperature, and passes on distillation into an oily *compound*, $C_6H_{10}Br_2$, b. p. 115—119°/14 mm. (cf. Courtot, *loc. cit.*). In the formation of the primary bromide, the tertiary bromide, $CMe_3Br \cdot CMe \cdot CH_2$, is evidently first produced, since the product has a low b. p., 27—50°/20 mm., if it is distilled soon after being prepared. The prolonged action of hydrogen bromide on ice-cold dimethylbutadiene gives a *dihydrobromide*, probably $CMe_2Br \cdot CHMe \cdot CH_2Br$, crystals resembling ammonium chloride, which volatilises at 160—180°. The primary bromide is converted by the action of sodium carbonate solution into the tertiary alcohol, $\alpha\beta$ -trimethylallyl alcohol (Courtot, *loc. cit.*), which gives a *benzoate*, a thick oil, b. p. 126—127°/12 mm.; the latter quickly decomposes into benzoic acid and dimethylbutadiene when heated under the ordinary pressure. The primary bromide reacts with sodium ethoxide to give the *ethyl ether*, b. p. 143—143·2°/757 mm., d_{15}^{15} 0·8167, and with magnesium phenyl bromide to give $\beta\gamma$ -*dimethyl- Δ^{β} -butenylbenzene*, $CH_2Ph \cdot CMe \cdot CMe_2$, b. p. 220—221°/750 mm., d_{15}^{15} 0·903. The latter is converted by the action of hydrogen bromide in glacial acetic acid solution at 100° into a *hydrobromide*, $C_6H_{12}PhBr$, b. p. 134—136°/15 mm., and is reduced by means of palladium-hydrogen to $\beta\gamma$ -*dimethylbutylbenzene*, b. p. 216·5—217·5°/755 mm., d_{15}^{15} 0·8765. *Formo- $\beta\gamma$ -dimethyl- Δ^{β} -butenylanilide*, a viscous oil, b. p. 169—171°/16 mm., is produced like the *isopentenyl* derivative, and is hydrolysed by means of methyl-alcoholic potash to $\beta\gamma$ -*dimethyl- Δ^{β} -butenylaniline*, b. p. 144—146°/16·5 mm., d_{15}^{15} 0·9622, which readily gives a *benzoyl* derivative, hard, quadratic tablets, m. p. 97·5—98·5°. The action of an ethereal solution of aniline on a light petroleum solution of $\beta\gamma$ -dimethyl- Δ^{β} -butenyl bromide gives aniline hydrobromide and a substance, rods grouped in rosettes, m. p. 58—59°, perhaps *di- $\beta\gamma$ -dimethyl- Δ^{β} -butenylaniline*. W. S. N.

The Preparation of Acetylenic Hydrocarbons by the Electrolysis of Unsaturated Acids. MARCEL BOUIS (*Bull. Soc. chim.*, 1923, [iv], 33, 1081—1084).—Electrolysis of a 40% aqueous solution of sodium acrylate by means of a current of 3 amperes leads to the formation of acetylene, which is identified by means of its reactions and the formation of its tetrabromide. The composition of the electrolytic gas in several experiments was determined and found to be: CO_2 , 68—76%; C_2H_2 , 4—8%; O_2 , 7—16%; CO , 8—13%. Similarly, sodium crotonate gives allylene, identified by means of its silver compound. The composition of the electrolytic gas is much the same in both cases. H. H.

The Components of Wood Spirit Oil. H. PRINGSHEIM and J. LEIBOWITZ (*Ber.*, 1923, 56, [B], 2034—2041).—The separation of wood spirit oil (the residue left after the isolation of methyl alcohol from wood spirit) cannot be effected advantageously by fractional distillation under atmospheric pressure, since the oxidisable

nature of the substances prevents the use of a long column, whilst under diminished pressure the separation is very incomplete. By combining the two methods, it is, however, possible to isolate methyl ethyl ketone, methyl propyl ketone, and dipropionylethane.

More promising results are obtained by treating the oil with sodium hydrogen sulphite solution, whereby it is separated into crystalline additive compounds (aldehydes and methyl ketones), compounds which are soluble in the solution (mesityl oxide and similar unsaturated ketones), and undissolved oil (hydrocarbons, alcohols, etc.). The crystalline compounds have been examined by decomposing the precipitate with dilute sulphuric acid, separating the liberated aldehydes and ketones as far as possible by fractional distillation, and converting them into crystalline derivatives. The presence of the following substances is established: α -dimethylpropionaldehyde, $\text{CMe}_3\cdot\text{CHO}$, b. p. 74° ; methyl ethyl ketone; isovaleraldehyde; methyl isopropyl ketone; Δ^7 -hexene- β -one, $\text{CH}_3\cdot\text{CO}\cdot\text{CH}:\text{CH}\cdot\text{CH}_2\text{Me}$; cyclopentanone.

Δ^7 -Hexene- β -one, b. p. 122 — 124° , is isolated with some difficulty, since it decomposes readily at a moderate temperature; with *p*-nitrophenylhydrazine it gives a crystalline derivative, $\text{C}_{12}\text{H}_{15}\text{O}_2\text{N}_3$, m. p. 126° . Its constitution is deduced from the observation that it is oxidised by potassium permanganate in the presence of acetone to pyruvic and propionic acids.

Treatment of the oil with potassium hydroxide solution which is subsequently acidified leads to the isolation of a single acid, $\text{C}_8\text{H}_{16}\text{O}_4$, a colourless liquid, b. p. $46^\circ/0.8$ mm. Analysis of the corresponding silver salt and of the derivative, $\text{C}_{20}\text{H}_{31}\text{O}_7\text{N}_3$, colourless needles, m. p. 198° , shows it to be a dihydroxyoctanemonocarboxylic acid. It is reduced by hydriodic acid and phosphorus to an octoic acid, $\text{C}_8\text{H}_{16}\text{O}_2$, b. p. 200 — 210° (decomp.). H. W.

The Photo-oxidation of Alcohol. III. The Catalytic Influence of some Ketones on the Photo-oxidation of Ethyl Alcohol. W. D. COHEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1923, 26, 443—455; cf. A., 1921, ii, 500).—The action of thirty-four ketones in promoting the photo-oxidation of ethyl alcohol was studied, and some general conclusions were drawn from the results. The velocities of activation appear to be independent of the concentration of ketone within fairly wide limits. The photo-activity of monoketones appears to be definitely associated with their aromatic character. $\alpha\beta$ -Diketones are especially active, whereas $\alpha\beta\gamma$ -triketones are inactive. The inactivity of the last class is ascribed to the possibility of the central carbonyl group forming an oxonium salt with the alcohol, thereby destroying the photocatalytically active double $\alpha\beta$ -diketonic structure. H. H.

The Unsaturated Reduction Products of Sugars and their Transformations. VI. δ -Hydroxyacetylbutyl Alcohol, a Simple Ketose. MAX BERGMANN and ARTHUR MIEKELEY (*Annalen*, 1923, 432, 319—344; cf. A., 1921, i, 763; 1922, i, 618; this vol., i, 653).—It has previously been observed (A., 1922, i, 618) that the cycloacetal of δ -acetyl-*n*-butyl alcohol is remarkably sensitive

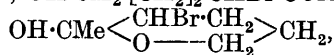
towards dilute mineral acids, a fact which illustrates the impossibility of distinguishing between the $\alpha\beta$ - and $\alpha\delta$ -oxide structures by means of their stability. A striking contrast is presented by the behaviour of the dicyclic anhydride of δ -hydroxy- δ -acetyl-*n*-butyl alcohol, which, although it contains an ethylene oxide ring, is unusually resistant to fission by means of hydroxylic reagents.

The oxidation of anhydroacetylbutyl alcohol in dry ethereal solution by means of perbenzoic acid gives $\beta\gamma$ - $\beta\zeta$ -*dioxido*hexane, $\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{>O}$, a colourless liquid, b. p. $56\cdot5$ – $57\cdot5^\circ/12$ mm., $\text{CH}_2\cdot\text{O}-\text{CMe}$

d_4^{20} 1·0331, d_4^{21} 1·0326, n_D^{20} 1·4441, n_D^{21} 1·4438, *phenylhydrazone*, m. p. 85 – 86° . This dicyclic anhydride reduces hot Fehling's solution, but does not give a red coloration with a pine shaving. It is stable towards methyl alcohol, or even towards water at 130° . If the oxidation is conducted in moist ethereal solution, the product is δ -hydroxy- δ -acetylbutyl alcohol, $\text{OH}\cdot\text{CH}_2\cdot[\text{CH}_2]_2\cdot\text{CH}(\text{OH})\cdot\text{COMe}$, or $\text{OH}\cdot\text{CMe}<\text{CH}(\text{OH})\cdot\text{CH}_2\text{>CH}_2$, m. p. 73° (sinters at 70°), b. p.

143 – $144^\circ/11$ mm., which reduces Fehling's solution even in the cold, and forms a *phenylosazone*, slightly yellowish-brown needles, m. p. 133° . It is converted into its anhydride by distilling with benzoic acid under 15 mm. pressure; the reverse change is difficult to accomplish, but may be effected by boiling the anhydride with *N*-sulphuric acid. The action of 0·01*N*-methyl-alcoholic hydrogen chloride on hydroxyacetylbutyl alcohol gives γ -hydroxy- β -methoxy- $\beta\zeta$ -*oxido*hexane, $\text{OMe}\cdot\text{CMe}<\text{CH}(\text{OH})\cdot\text{CH}_2\text{>CH}_2$, a colourless liquid,

b. p. 76 – $77^\circ/9$ – 10 mm., d_4^{18} 1·0813, n_D^{18} 1·4542, n_D^{19} 1·4540, which has a slight odour resembling that of camphor or turpentine. This compound is also produced in poor yield by the action of 0·1*N*-methyl-alcoholic hydrogen chloride on dioxidohexane, together with $\beta\gamma$ -*dimethoxy*- $\beta\zeta$ -*oxido*hexane, a colourless liquid, b. p. 69 – $70^\circ/12$ mm., d_4^{17} 1·0300, n_D^{19} 1·4400, n_D^{20} 1·4397, n_D^{17} 1·4405, which has a faint, camphoraceous odour and a bitter taste, and does not reduce Fehling's solution. The dimethoxy-derivative is converted by the action of 0·1*N*-hydrochloric acid at 50° into δ -acetyl- δ -methoxybutyl alcohol, a syrup, b. p. 88 – $90^\circ/1\cdot5$ mm. The oxidation of the dimethoxy-compound by means of chromic acid gives γ -acetyl- γ -methoxybutyric acid, a syrup, b. p. $115^\circ/5$ mm. Acetobutyl alcohol forms a white *oxonium* salt with ferrocyanic acid, the addition of which to a mixture of acetobutyl alcohol and methyl alcohol rapidly effects the formation of the *cyclo*acetal. A similar *oxonium* salt is obtained from dioxidohexane and ferrocyanic acid; its constituents are regenerated by the aid of alkali hydrogen carbonate solution and ether, but the action of a further quantity of dioxido-compound in methyl-alcoholic solution gives oxido- $\beta\gamma$ -dimethoxyhexane. The action of bromine (1 mol.) on an ice-cold chloroform solution of acetobutyl alcohol gives δ -bromo- δ -acetylbutyl alcohol, $\text{OH}\cdot\text{CH}_2\cdot[\text{CH}_2]_2\cdot\text{CHBr}\cdot\text{COMe}$, or



a slightly yellow, lachrymatory liquid, b. p. 70—75°/1.5 mm., which reduces warm Fehling's solution. It readily loses hydrogen bromide, even when warmed with water, with production of a second *anhydride* of hydroxyacetylbutyl alcohol, a colourless liquid, b. p. 63—64°/24 mm., or 50—51°/12 mm., n_D^{20} 1.4381, which becomes discoloured in contact with air, and reduces Fehling's solution. It reacts with phenylhydrazine, giving an oil. Bromoacetylbutyl alcohol reacts immediately with aqueous phenylhydrazine acetate solution, to give the osazone of hydroxyacetylbutyl alcohol, and with warm, anhydrous methyl alcohol, with formation of γ -bromo- β -methoxy- β - ζ -oxidohexane, $\text{OMe} \cdot \text{CMe} < \begin{smallmatrix} \text{CHBr} \cdot \text{CH}_2 \\ \text{O} \text{---} \text{CH}_2 \end{smallmatrix} > \text{CH}_2$, an oil, b. p. 78—81°/14 mm. The second anhydride mentioned above reacts with boiling 0.1N-methyl-alcoholic hydrogen chloride, with formation of a *liquid*, b. p. 63—65°/12 mm. W. S. N.

Alkylglycerols. II. Reactions of Alkylglycerols. Some Esters and Derivatives. III. Action of Organomagnesium Compounds on the Epibromohydrin of Ethylglycerol. R. DELABY (*Ann. Chim.*, 1923, [ix], 20, 33—81; cf. this vol., i, 741).—A republication, with additions, of work previously described (cf. this vol., i, 289, 531, 646; ii, 264). The action of diethylamine on $\alpha\gamma$ -dibromopentan- β -ol yields a *tetraethyldiaminopentanol*, b. p. 136—138°/20 mm., *picrate*, m. p. 102—103°. Oxidation of $\alpha\beta$ -dibromopentan- γ -ol by sodium dichromate in dilute sulphuric acid results in formation of $\alpha\beta$ -dibromopentan- γ -one together with acetic and propionic acids, whilst $\alpha\gamma$ -dibromopentan- β -ol yields the corresponding pentanone and acetic acid. The following are described: $\alpha\beta$ -dibromododecan- γ -ol, b. p. 170°/12 mm., a *diethylaminophenylpentanol*, b. p. 150—155°/19 mm. H. J. E.

The [Crystal] Structure of Pentaerythritol, and a Graphical Interpretation of Laue (Schichtlinien) Diagrams. H. MARK and K. WEISSENBERG (*Z. Physik*, 1923, 17, 301—315).—The mathematical analysis is detailed of a geometrical method applicable to the determination of crystallographic structure from a Laue diagram photographed on a cylindrical surface. It is shown that pentaerythritol crystallises in the di-tetragonal pyramidal system, with respective axes of lengths $a=6.16 \text{ \AA}$, $c=8.76 \text{ \AA}$. Moreover, the crystals belong to the space group type C_{4v}^2 , and the elementary crystal cell is space-centred and contains two molecules, $\text{C}_5\text{H}_{12}\text{O}_4$. The symmetry of the molecule and of the central carbon atom is represented by C_{4v} . The four substitution groups $\cdot\text{CH}_2\cdot\text{OH}$ are structurally equivalent and lie in the hemimorphic plane of symmetry. J. S. G. T.

Hydrolysis of $\beta\beta'$ -Dichlorodiethyl Sulphide and Action of Hydrogen Halides on Divinyl Sulphide. SIDNEY HARTLEY BALES and STANLEY ARTHUR NICKELSON (*T.*, 1923, 123, 2486—2489).

The Action of Methyl Iodide on Disulphides. WILHELM STEINKOPF and SIEGFRIED MÜLLER (*Ber.*, 1923, 56, [B], 1926—1930).—The action of methyl iodide on dimethyl disulphide takes

place in accordance with the schemes: $\text{MeS}\cdot\text{SMe} + \text{MeI} \rightarrow \text{SMe}_2\cdot\text{SMeI} \rightarrow \text{SMe}_2 + \text{SMeI}$; $\text{SMe}_2 + \text{MeI} \rightarrow \text{SMe}_3\text{I}$; $\text{SMeI} + \text{MeI} \rightarrow \text{SMe}_2\text{I}_2 \xrightarrow{+\text{MeI}} \text{SMe}_3\text{I}_3$. There does not appear to be any evidence of the formation of the radicle SMe . This conclusion is confirmed by the observation that diphenyl disulphide is attacked with greater difficulty by methyl iodide than is dimethyl disulphide, whereas dissociation into radicles, if possible, would be expected to occur more readily in the case of the diphenyl compound.

Dimethyl disulphide is transformed by more than four molecular proportions of methyl iodide at 100° into trimethylsulphonium iodide, decomp. $203\text{--}207^\circ$, according to the manner of heating, and trimethylsulphonium tri-iodide, m. p. 39° . Dimethyl sulphide di-iodide (which can be obtained in the crystalline form, m. p. $58\text{--}64^\circ$, according to the mode of heating, by the gradual addition of concentrated aqueous hydriodic acid solution to dimethylsulphoxide) and methyl iodide at 100° yield trimethylsulphonium tri-iodide. Dimethyl disulphide is converted by methyl bromide at 100° into trimethylsulphonium bromide, decomp. 172° .

Diphenyl disulphide is converted by prolonged heating with methyl iodide at 100° into phenyldimethylsulphonium tri-iodide, m. p. $53\cdot5^\circ$, and phenyl methyl sulphide; under the experimental conditions adopted, the latter substance does not unite with methyl iodide to give a sulphonium iodide. H. W.

Trimethylene Trisulphide. O. HINSBERG (*Ber.*, 1923, 56, [B], 1850—1852).—In reply to Fromm and Schultis (this vol., i, 580), the author reaffirms that β -trithioformaldehyde, m. p. 247° , is a well-defined chemical individual which is transformed when warmed with solvents into the stable α -variety, m. p. 216° . A second labile form of trithioformaldehyde also appears to exist; it has m. p. 216° , and passes when treated with solvents into the stable form of the same melting point. The theory of the sulphur atom is in harmony with these observations, since it predicts the possibility of the existence of four stereoisomeric trithioformaldehydes. H. W.

Ethyl Formate from Oxalic Acid, Glycerol, and Alcohol. WILFRID B. S. BISHOP (*J. Soc. Chem. Ind.*, 1923, 42, 401—402t).—Ethyl formate is conveniently prepared by distilling 46 g. of ethyl alcohol into a mixture of 200 g. of glycerol, 90 g. of anhydrous oxalic acid, and 90 g. of the hydrated acid heated at $105\text{--}110^\circ$. The vapours formed are passed through a reflux condenser kept at 62° and a still-head at $54\text{--}60^\circ$ into a condenser and receiver. The liquid collecting in the receiver is ethyl formate of commercial purity, and the yield is 80% of theory. When the temperature of the distilling liquid rises above 68° , the distillate is practically pure alcohol. The glycerol may be used for at least three fresh charges of oxalic acid and ethyl alcohol. E. H. R.

Fine Structure of some Sodium Salts of the Fatty Acids in Soap Curds. S. H. PIPER and E. N. GRINDLEY (*Proc. Physical Soc.*, 1923, 35, 269—272).—The structure of the soap curds of

sodium laurate, sodium myristate, and sodium palmitate has been investigated by the X-ray method. The X-ray photographs show lines due to reflections from planes with very wide spacings of the order 40 Å. These planar spacings increase uniformly with the number of methylene groups in the molecule, the actual spacings observed in the three cases being 33·5, 38·5, and 43·5 Å., respectively, the addition of two methylene groups to the carbon chain giving an increase of 5 Å. This indicates that the effective length of the methylene group is 1·25 Å. These and other lines observed are to be accounted for by the assumption that the curds are in the smectic state described by Friedel (this vol., ii, 223). J. F. S.

The Microscopic Structure of Soap. KENNETH MACLENNAN (*J. Soc. Chem. Ind.*, 1923, 42, 393—401t).—Examination of soaps with the polarising microscope at magnifications not greater than 100 diameters has revealed the unexpected fact that most soaps are built up of anisotropic material. The typical structures which can be recognised in a soap (the term including pure sodium salts of fatty acids) are: (a) crystals; solid crystals only occur in a few pure sodium soaps, but crystalline fluids, occurring as anisotropic, viscous liquids, syrups or jellies, are general; (b) soap fibres; these may be irregular, tangled masses, of which individual fibres are only faintly anisotropic, or orientated, rope-like or radial structures showing strong double refraction; (c) soap curds, consisting of a mass of fibres entangling a liquid phase; (d) soap gels, which are of infrequent occurrence, and (e) soap solutions. The soap fibres frequently pass when heated into the crystalline fluid form. This phenomenon is observed both in commercial soaps and with pure sodium stearate, palmitate, laurate, and elaidate. The fibres of sodium stearate and elaidate pass into the solid, crystalline form when matured. In each case, the fluid crystals stable at a high temperature revert on cooling into the fibre form. Completely dry fibres do not pass into the fluid, crystalline form when heated. This, and the fact that in presence of salt the fibres do not pass into a crystalline fluid, indicates that the latter is a more highly hydrated phase. Sodium octoate is peculiar in that the crystalline fluid phase is stable at the ordinary temperature. When the dry soap is exposed in a saturated atmosphere the passage of the original grains first into radially grouped fibres and then into a typically crystalline fluid can be observed. In dry air the reverse changes occur. E. H. R.

Arachidic Acid, isoBehenic Acid, and n-Eicosanoic Acid. R. EHRENSTEIN and H. STUEWER (*J. pr. Chem.*, 1923, [ii], 105, 199—207).—isoBehenic acid, formed by the degradation of lignoceric acid (Meyer, Brod, and Soyka, A., 1913, i, 1151), is identical with arachidic acid, obtained from earth-nuts. This acid is not n-eicosanoic acid, $\text{CH}_2\text{Me} \cdot [\text{CH}_2]_{17} \cdot \text{CO}_2\text{H}$, but an isodocosanoic acid, $\text{C}_{21}\text{H}_{43} \cdot \text{CO}_2\text{H}$; the radicle contained in the latter is also present in lignoceric acid, $\text{C}_{21}\text{H}_{43} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$. The acid, m. p. 76—77°, obtained from the oil from *Nephelium Lappaceum*, J. (Baczewski, A., 1896, ii, 209), is n-eicosanoic acid, which is also obtained by

fusing erucic acid with potassium hydroxide at 320° ; its *methyl* ester forms white, glistening scales, m. p. $46-47^{\circ}$, b. p. $215-216^{\circ}/10$ mm. W. S. N.

Erucic and Brassidic Acids and their Anhydrides. D. HOLDE and F. ZADEK (*Ber.*, 1923, **56**, [B], 2052—2058).—An attempt has been made to place beyond doubt the stereochemical relationship of erucic to brassidic acid.

The electrolytic conductivities of the acids and their anhydrides in very highly purified acetone have been measured. The constants of the substances employed are as follows: erucic acid, m. p. 35.5° ; erucic anhydride, m. p. $47.5-48^{\circ}$, n_D^{20} 1.4377; iodine number, 76.7; brassidic acid, m. p. 61.5° (corr.), n_D^{20} 1.4347; brassidic anhydride, m. p. $63.5-64.5^{\circ}$; iodine number, 76.3. The conductivity of the acetone is $\kappa = 1.01 \times 10^{-7}$. The conductivities of erucic acid and its anhydride are identical, whereas brassidic anhydride conducts rather better than brassidic acid. The conductivity of the brassidic compounds is noticeably higher than that of the erucic substances. Analogous differences in the conductivities of stereoisomeric substances have been observed with crotonic and isocrotonic acids and with tiglic and angelic acids. From this point of view, erucic acid is related to crotonic and tiglic acids, and brassidic acid to isocrotonic and angelic acids; as judged from the melting point, the relationships are in the inverse order.

The products obtained by the ozonisation of erucic or brassidic acids are nonaldehyde, b. p. $80-82^{\circ}/12$ mm., $d^{17.5}$ 0.893, $n_D^{17.5}$ 1.4276 (which is further identified as the semicarbazone, m. p. $83-84^{\circ}$, and by oxidation to pelargonic acid), and the semialdehyde of brassylic acid which is characterised as the *ethyl* ester *acetal*, $C_{19}H_{38}O_4$, a mobile liquid, b. p. $175-180^{\circ}/12$ mm., and by oxidation to brassylic acid, m. p. $109-111^{\circ}$. The *peroxide* of the semialdehyde of brassylic acid, $C_{13}H_{24}O_4$, is described. H. W.

Ethyl γ -Chloro- and γ -Bromo-ethoxymethyleneacetates and certain Derivatives. ERICH BENARY and FRANZ EBERT (*Ber.*, 1923, **56**, [B], 1897—1900).—The preparation of the substances mentioned in the title is described in detail; the production of cyclic compounds from them has not been effected with certainty.

Ethyl γ -chloro- α -ethoxymethyleneacetate,
 $CH_2Cl \cdot CO \cdot C(:CH \cdot OEt) \cdot CO_2Et$,
 slender, colourless needles, m. p. 98° , b. p. $160-165^{\circ}/13$ mm., is prepared by the action of orthoformic ester and acetic anhydride on ethyl γ -chloroacetate; the *copper* derivative is described. The ester is rapidly hydrolysed by warm water to *ethyl γ -chloro- α -hydroxymethyleneacetate*, large prisms, m. p. $18-19^{\circ}$, b. p. $131^{\circ}/12$ mm. (*copper* derivative, cornflower-blue platelets, decomp. about 156° after previous darkening). The hydroxy-ester is converted by successive treatment with phosphorus trichloride and ice-cold aqueous ammonia into *ethyl γ -chloro- α -aminomethyleneacetate* [*ethyl β -amino- α -chloroacetylacrylate*],
 $CH_2Cl \cdot CO \cdot C(:CH \cdot NH_2) \cdot CO_2Et$,

needles, m. p. 106° , and by methylamine into *ethyl γ -chloro- α -methyl-aminomethyleneacetoacetate*, $C_8H_{12}O_3NCl$, needles, m. p. 105° . The latter ester is converted by alcoholic potassium hydroxide or ammonia into solutions which give the pine shaving reaction, but from which only black, decomposed products could be isolated. Treatment of it with sodium hydrogen sulphide in absolute alcohol yields *α -methylaminomethylenethiotetronic acid*, $C_6H_7O_2NS$, needles, m. p. $188-189^{\circ}$.

Ethyl γ -bromo- α -ethoxymethyleneacetoacetate forms colourless needles, m. p. 85° (copper derivative, lustrous, cornflower-blue leaflets, decomp. about 152° after previous darkening). It is very readily hydrolysed to the corresponding *hydroxymethylene* compound, a colourless liquid, which is converted by aqueous ammonia into the compound, $C_{12}H_{14}O_6N_2$, lustrous, golden-yellow needles, m. p. $208-209^{\circ}$ (decomp.). *Ethyl γ -bromo- α -aminomethyleneacetoacetate* crystallises in needles, m. p. 73° . H. W.

Dissociation Constants of Polybasic Acids and their Application to the Calculation of Molecular Dimensions. NIELS BJERRUM (*Z. physikal. Chem.*, 1923, **106**, 219—242).—A theoretical paper in which the author discusses the relationships between the values of the ionisation constants of di- and poly-basic acids. The author deals particularly with the influence of the distance between carboxyl groups on the value of the ionisation constants.

J. F. S.

Esterification of Oxalic Acid. PAVITRA KUMAR DUTT (*T.*, 1923, **123**, 2714—2715).

The Relative Stability of Open-chain Dibasic Acids containing Odd and Even Numbers of Carbon Atoms. WILLIAM ARTHUR PERCIVAL CHALLENGER and JOCELYN FIELD THORPE (*T.*, 1923, **123**, 2480—2485).

Muconic and Hydromuconic Acids. II. The Isomerism of the Muconic Acids. ERNEST HAROLD FARMER (*T.*, 1923, **123**, 2531—2548).

Chemistry of the Sugars. V. H. KILIANI (*Ber.*, 1923, **56**, [B], 2016—2024; cf. *A.*, 1921, i, 304; 1922, i, 223, 321, 1111).—The removal of the excess of nitric acid left after the oxidation of the sugars by the author's process is relatively seldom so completely effected by the use of ether that the "uronic" or ketonic acids can be isolated by direct crystallisation. They must therefore be converted into derivatives. For this purpose phenylhydrazine and *p*-nitrophenylhydrazine are unsuitable, since they react slowly and do not yield crystalline precipitates. Under definite conditions (which are fully described in the original communication), semicarbazide hydrochloride is very suitable. Somewhat unexpectedly, it is found to give only semicarbazones, instead of semicarbazone-semicarbazide salts. The quantity employed can be based on an expected yield of oxidised product corresponding with 30—40% of that theoretically possible. Fission of the semicarbazones is

$p \text{ } p^* \text{ } 2$

conveniently effected by oxalic but not by hydrochloric or sulphuric acids. The difficulty of separating the "uronic" or ketonic acids from semicarbazide oxalate has not been completely overcome. The following examples of the new method are cited: conversion of *d*-galactonic into *l*-galacturonic acid [the *semicarbazone* of *l*-galacturonic lactone, $C_7H_{11}O_6N_3 \cdot H_2O$, has m. p. 190° (decomp.)]; the oxidation of *l*-mannonic acid into *l*-mannuronic acid [the *semicarbazone* of *l*-mannuronic lactone has m. p. 189° (decomp.) after darkening at 180°]; the oxidation of α -glucoheptonic acid and of isosaccharin.

It has been observed incidentally that the *sodium* salt of the lactone of *d*-saccharic acid can readily be caused to crystallise. Attempts have therefore been made to prepare the analogous potassium salt, which, however, crystallises with extreme difficulty or not at all, whilst, further, its presence greatly hampers the separation of potassium hydrogen *d*-saccharate. It therefore appears that all previous methods of preparing saccharic acid by the aid of the potassium hydrogen salt are subject to error, as is also the customary crystallisation of this salt from boiling water, since it undergoes partial conversion into the salt of the lactic acid.

H. W.

Preparation of Chloroacetaldehydesulphonic Acid.

CHEMISCHE FABRIKEN VORM. WEILER-TER MEER (D.R.-P. 362744: from *Chem. Zentr.*, 1923, ii, 1246).—Dichloroethylene is treated with fuming sulphuric acid, when the following reactions take place: $CHCl:CHCl + H_2S_2O_7 = SO_3H \cdot CHCl:CH:SO_3H + HCl$; $SO_3H \cdot CHCl:CH:SO_3H + H_2O = SO_3H \cdot CHCl:CHO + H_2SO_4$. Ice is added to the products of reaction. The solution is neutralised with sodium carbonate and evaporated in a vacuum. The residue is extracted with hot ethyl alcohol. After removal of the ethyl alcohol by distillation, *sodium chloroacetaldehydesulphonate semiacetal*, $SO_3Na \cdot CHCl:CH(OH) \cdot OEt$, remains. *Chloroacetaldehydesulphonic acid* and its *sodium* salt are very hygroscopic. With phenylhydrazine, both the semiacetal and the sulphonic acid give *glyoxalbisphenylhydrazone*. On heating the sulphonic acid with 80% sulphuric acid, chloroacetaldehyde is obtained. G. W. R.

The Ketonic Decomposition of Methyl Ethyl Ketone.

CHARLES DEWITT HURD and CYRIL KOCOUR (*J. Amer. Chem. Soc.*, 1923, **45**, 2167—2171; cf. Hurd and Cochran, this vol., i, 312).—When methyl ethyl ketone is passed through a tube at 600° , keten (identified by the formation of acetanilide by treating the vapour with anhydrous ethereal aniline) is formed in small yield, $COMeEt = CH_2:CO + C_2H_6$. Methylketen is apparently not produced, $COMeEt = CHMe:CO + CH_4$. It is shown that keten reacts much more slowly with water than with aniline or toluidine.

W. S. N.

Calorimetric Study of the Hydrolysis of Ketone Acetals by Water in the Presence of Acids. L. N. PARFENTIEV (*J. Russ. Phys. Chem. Soc.*, 1923, **54**, 455—461).—The hydrolysis of dimethylacetal by water in the presence of traces of the halogen acids or of

sulphuric acid was carried out in a Berthelot calorimeter and the thermal effect was found to be -5028 cal. Water alone does not effect hydrolysis; the catalytic effect of sulphuric acid is only two-fifths of that of the halogen acids; the velocity of the reaction is proportional to the amount of catalyst present. A few experiments with the acetals of methyl ethyl- and methyl butyl-ketones show that the above statements apply also in these cases; the velocity of the reaction appears to diminish with increasing complexity of the substance.

G. A. R. K.

The Acetals of Saturated Aliphatic Ketones. V. V. EVLAMPIEV (*J. Russ. Phys. Chem. Soc.*, 1923, **54**, 462—465).—Acetals were prepared from several ketones, using ethyl orthoformate in the presence of small quantities of sulphuric acid. It was found that the optimum amount of catalyst was not the same in all cases; the velocity of the reaction diminishes with increasing molecular weight and is greater in normal than in *iso*-compounds. No acetal could be obtained from pinacolin whilst methyl hexyl ketone reacted readily, but the product was a *compound*, $C_{10}H_{20}O$, b. p. $71.9^{\circ}/10$ mm., d^{20}_D 0.8232, d^{20}_D 0.8075, which was formed from the acetal by the loss of a molecule of ethyl alcohol. The *diethyl acetals* of the following ketones were prepared: of methyl ethyl ketone, b. p. $59.2^{\circ}/43$ mm., d^{20}_D 0.8586, d^{20}_D 0.8416; of methyl propyl ketone, b. p. $57.4^{\circ}/18.5$ mm., d^{20}_D 0.8574, d^{20}_D 0.8409; of methyl *isopropyl* ketone, b. p. $52.4^{\circ}/20$ mm., d^{20}_D 0.8627, d^{20}_D 0.8453; of methyl butyl ketone, b. p. $78.7^{\circ}/23.5$ mm., d^{20}_D 0.8573, d^{20}_D 0.8414; of ethyl propyl ketone, b. p. $74.8^{\circ}/18.5$ mm., d^{20}_D 0.8624, d^{20}_D 0.8470; of methyl *isobutyl* ketone, b. p. $72.4^{\circ}/18$ mm., d^{20}_D 0.8559, d^{20}_D 0.8396; of dipropyl ketone, b. p. $76.5^{\circ}/12$ mm., d^{20}_D 0.8577, d^{20}_D 0.8422.

G. A. R. K.

Pentosans. V. Hydrolysis of Xylan by Means of Dilute Nitric Acid. EMIL HEUSER and GEORG JAYME (*J. pr. Chem.*, 1923, [ii], **105**, 232—241).—The method for preparing xylose by hydrolysing xylan by means of dilute mineral acids (Heuser and Brunner, this vol., i, 184) has now been improved by using 3% nitric acid, and continuing the process for one hour. The product is colourless, and readily crystallises; the yield is 85% of the theoretical, and furfuraldehyde is not formed. The modified process is thus quicker and more economical. The conditions giving the best yield of xylose are also those for which the amount of sugar formed, as estimated by Bertrand's reduction method (*loc. cit.*), is a maximum (97.04% theory). It is remarkable that xylan passes completely into solution after being warmed for one to two minutes with 45 times its weight of 3% nitric acid at 100° . At this stage, according to the "reduction" estimation, 58.72% of xylose is already produced, but xylose is not obtained from the solution. Instead, a colloidal substance, resembling dextrin, undoubtedly a "xylo-dextrin," is obtained.

W. S. N.

Pentosans. VI. Oxidation of Xylan by Means of Nitric Acid. EMIL HEUSER and GEORG JAYME (*J. pr. Chem.*, 1923, [ii], **105**, 283—287).—E. Fischer has obtained trihydroxyglutaric acid

(A., 1891, 1173) by oxidising xylose by means of nitric acid, *d* 1.2. Hence xylan, which is hydrolysed to xylose by the action of nitric acid (cf. preceding abstract), should give the same product. This prediction is verified. Xylan is dissolved in two and a half times its weight of nitric acid, *d* 1.2, at 70°, and the solution kept at 45°. The yield, as the calcium salt, is 21.71% of the theoretical. If twice the above quantity of nitric acid is used, only a small quantity of trihydroxyglutaric acid is formed, together with much oxalic acid.

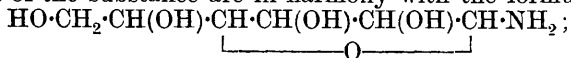
W. S. N.

The Isolation from Cabbage Leaves of a Carbohydrate hitherto undescribed containing three Carbon Atoms. HAROLD WILLIAM BUSTON and SAMUEL BARNETT SCHRYVER (*Biochem. J.*, 1923, **17**, 470—472).—The carbohydrate has the formula $C_3H_8O_4$. It crystallises in needles, m. p. 148°, which are soluble in cold water and hot glacial acetic acid, but insoluble in most other organic solvents. A tribenzoyl derivative, $C_3H_5O_4Bz_3$, m. p. 52—53°, was obtained from it. It is assumed, therefore, that the carbohydrate has the constitution $OH \cdot CH_2 \cdot CH(OH) \cdot O \cdot CH_2 \cdot OH$. The possible origin of the compound and its contribution to the formation of the anthocyanins in the plant are discussed. S. S. Z.

Observations on the Mutarotation of Dextrose in Aqueous-Alcoholic Solutions. HANS VON EULER and ELSA ERIKSON (*Biochem. Z.*, 1923, **140**, 268—272).—The mutarotation constants of dextrose were measured at p_H 3.0, using phosphate and citrate buffers in the presence of increasing percentage volumes of alcohol from 0 to 50%. The constants steadily diminished with increasing concentrations of alcohol, more especially in the presence of citrates. From the nature of the results, it is concluded that the inactivation of invertase in the presence of alcohol is not due to steric alterations of the substrate.

J. P.

A Compound of Dextrose with Ammonia. A. SCHMUCK (*Ber.*, 1923, **56**, [B], 1817—1819).—The action of gaseous ammonia on an alcoholic solution of dextrose leads to the production of a substance which has been designated glucosimine by Lobry de Bruyn. Further examination of the substance has shown that it readily reacts with nitrous acid with evolution of nitrogen, and hence contains the primary amino-group, whilst, also, the difficulty with which it is transformed into a pyrrole derivative indicates the absence of a ring containing nitrogen; it is converted by benzoyl chloride and aqueous sodium hydroxide into a *heptabenzoate*, $C_6H_5O_6NBz_7$, m. p. 91°, which gives a *nitroso*-derivative. The reactions of the substance are in harmony with the formula



the name *isoglucosamine* is proposed.

H. W.

Sources of the Rare Sugars. VIII. Preparation of Lævulose. T. SWANN HARDING (*Sugar*, 1923, 406—408; cf. A., 1922, i, 919).—A solution containing 250 g. of granulated sucrose is treated with invertase, concentrated in a vacuum to 85% solids, "seeded"

with dextrose, and set aside in a cool place. Sufficient ethyl alcohol is added to the mass of crystals to render it mobile, following which the dextrose is separated by centrifuging, the yield being about 25% of the sucrose taken. After distilling off the alcohol, the mother-liquor is diluted to 1,500 c.c., cooled to 5–10°, and treated with 115 g. of calcium oxide, previously slaked and cooled to at least 10°, the mixture being vigorously stirred for five minutes. The resulting calcium lævulosate is separated as quickly as possible by centrifuging, washed with iced lime-water, thrown into iced water, and the mixture neutralised with dilute sulphuric acid (25%). After filtering off the calcium sulphate, the solution is evaporated in a vacuum to a thick syrup, treated with two volumes of ethyl alcohol to precipitate the salts, a little decolorising carbon added, and the mixture set aside over-night. It is filtered, and concentrated in a vacuum to a syrup of 90–95% solids, from which the lævulose may be crystallised after the addition of alcohol containing nitric acid, the yield being 20–22% of the weight of sucrose taken. A further yield of dextrose may be obtained from the liquor from the centrifuging of the calcium lævulosate (which should meanwhile have been kept at a low temperature) by neutralising with dilute sulphuric acid, filtering, concentrating to a thin syrup, refiltering, continuing the concentration to a thick syrup, and adding ethyl alcohol containing 1% of nitric acid, the yield of the crystals thus obtained being about 15% of the sucrose employed.

J. P. O.

The Fission of Methylated Lactose. HANS HEINRICH SCHLUBACH and KARL MOOG (*Ber.*, 1923, **56**, [B], 1957–1963).—It has been shown by Haworth and Leitch (*T.*, 1918, **113**, 188) that heptamethyl- β -methyl-lactoside is hydrolysed by aqueous hydrochloric acid to 2:3:5:6-tetramethylgalactose and 2:3:6-trimethylglucose. The authors have expressed the opinion that the operation occurs in two stages, involving first the rupture of the disaccharide linking and then of the methylglucoside union. This hypothesis is now confirmed by the isolation of 2:3:6-trimethyl- β -methylglucoside as hydrolytic product.

The optimal conditions for the hydrolysis of heptamethyl- β -lactoside, m. p. 81.5–82°, n_D^{20} 1.4642, $[\alpha]_D^{17}$ -1.62° in water for $c=0.924$ (Haworth and Leitch give m. p. 77–82°, n_D^{20} 1.4675, $[\alpha]_D$ $+5.19^\circ$ for $c=0.771$), are established by preliminary kinetic measurements of the velocity of hydrolysis of the substance and of trimethyl- β -methylglucoside by aqueous hydrochloric acid. After hydrolysis, the tetramethylgalactose is removed as the anilide and trimethyl- β -methylglucoside is isolated from the residual oil by distillation (cf. Haworth and Leitch, *loc. cit.*); since, however, the production of the anilide is not quantitative and is strongly influenced by unknown factors (cf. Irvine and Hirst, *T.*, 1922, **121**, 1213), the yields of trimethyl- β -methylglucoside are very variable.

[With HELMUT FIRGAU.]—The isolation of trimethyl- β -methylglucoside is more readily affected when heptamethyl- β -methyl-

lactoside is hydrolysed with methyl-alcoholic hydrogen chloride (1%) at 100°. The product consists of a mixture of tetramethyl- α - and - β -methylgalactosides with trimethyl- β -methylglucoside, which cannot be separated into its components by fractional distillation. It is therefore treated with benzoyl chloride in the presence of pyridine, whereby the glucoside is converted into its benzoyl derivative, which differs by about 40° in boiling point from the galactosides. The glucoside is quantitatively regenerated from its benzoyl compound by means of alcoholic potassium hydroxide solution.

2 : 3 : 6-*Trimethyl- β -methylglucoside* crystallises in long needles, m. p. 60.5°, b. p. 81°/0.04 mm., n_D^{20} 1.4548, $[\alpha]_D^{15}$ -34.60° ($c=0.9908$). 5-*Benzoyl-2 : 3 : 6-trimethyl- β -methylglucoside* has b. p. 134—135°/0.08 mm., n_D^{20} 1.5020—1.5028, $[\alpha]_D^{15}$ -23.87° in aqueous alcoholic solution (50%) for $c=0.5654$. 5-*Acetyl-2 : 3 : 6-trimethyl- β -methylglucoside*, b. p. 106°/0.055 mm., $[\alpha]_D^{20}$ -14.17° in water ($c=1.2352$), is prepared from the glucoside and acetic anhydride in the presence of pyridine. 2 : 3 : 5 : 6-Tetramethyl- β -methylgalactoside has m. p. 48—48.5°, b. p. 87°/0.035 mm., n_D^{20} 1.4420, $[\alpha]_D^{20} +19.59^\circ$ in aqueous solution for $c=0.9872$ [Irvine and Cameron (T., 1904, **85**, 1073), give m. p. 44—45°, $[\alpha]_D +30.7^\circ$, for $c=4.968$]. 2 : 3 : 5 : 6-Tetramethyl- α -galactose, obtained by hydrolysis of the corresponding β -methylgalactoside or of the anilide, forms well-defined crystals, m. p. 71.5—72°, b. p. 96°/0.01 mm., n_D^{20} 1.4622, $[\alpha]_D^{17} +142.0^\circ \rightarrow 118.0^\circ$. H. W.

Sources of the Rare Sugars. IX. (Preparation of Trehalose.)

T. SWANN HARDING (*Sugar*, 1923, 476—478).—About 500 g. of trehala manna are extracted with 2,500 c.c. of 75% alcohol during two hours, using a reflux condenser, after which the operation is repeated with 750 c.c. The two extracts are united, filtered, concentrated to 400 c.c., diluted with 1,000 c.c. of water, and clarified by the addition of basic lead acetate, the excess of which after filtering is eliminated by precipitation as sulphide. On evaporating the filtrate to 100 c.c., and adding about 50 c.c. of 95% ethyl alcohol, crystallisation proceeds rapidly, more alcohol being added from time to time to prevent the formation of a solid cake. A yield of 20—25% is given by this method. A procedure using *Selaginella lepidophylla* ("resurrection plant") as raw material is also described, but in this case the yield is only 1—1.5%. Previous work done on the preparation of this sugar is summarised.

J. P. O.

Studies on Starch. I. The Nature of Polymerised Amylose and of Amylopectin. ARTHUR ROBERT LING and DINSHAW RATTONJI NANJI (T., 1923, **123**, 2666—2688).

Soluble Esters of Starch with the Higher Fatty Acids. H. GAULT (*Compt. rend.*, 1923, **177**, 592—593; cf. this vol., i, 757).—When starch is heated with lauryl chloride in presence of pyridine and (as solvent) toluene, *starch dilaurate*, $C_6H_8O_3(CO_2C_{11}H_{23})_2$, is obtained, in 80% yield, as scaly material, m. p. 130°, insoluble in hydroxylic and soluble in non-hydroxylic solvents. E. E. T.

The Action of Light on Cotton. A Summary of the Literature. PERCY W. CUNLIFFE (*J. Text. Inst.*, 1923, **14**, 314—318r).—The scanty literature dealing with the photochemistry of cotton is reviewed. It is not yet clear what part light plays in the deterioration of cotton fabrics apart from activating the surrounding atmosphere.
J. C. W.

The Swelling of Cotton Cellulose. A Summary of the Literature. GEORGE ERNEST COLLINS (*J. Text. Inst.*, 1923, **14**, 264—276r).—Two hundred papers dealing with the swelling of cotton cellulose in water, and in solutions of acids, alkalis, and salts, are summarised.
J. C. W.

Swelling of Cotton Cellulose. I. Cotton Hairs in Solutions of Sodium Hydroxide. GEORGE ERNEST COLLINS and ALEXANDER MITCHELL WILLIAMS (*J. Text. Inst.*, 1923, **14**, 287—295r).—Observations have been taken of the change in length, mean diameter, and number of convolutions per centimetre of single cotton hairs on immersion in water and in solutions of sodium hydroxide. For changes in length, a delicate instrument reading to 0.01 mm., modelled on Justin-Mueller's turgometer, was used. Diameters and convolution numbers were determined by direct observation in a glass cell mounted on the stage of a horizontal microscope fitted with a micrometer; polarised light was used, and the hairs appeared alternately red and green, especially in 9% sodium hydroxide, indicating frequent reversals of optical activity in the material. The technique and results are fully described.

It is found that the increase in length which is observed on immersion in water is due almost entirely to the straightening out of convolutions. Maximum swelling occurs in a 14.5% solution of sodium hydroxide, and hairs which have been immersed in solutions up to the highest concentration used (48%), on transference to more dilute solutions, also swell to the maximum extent in 15% alkali.

In one experiment, the cotton hairs were taken through solutions of sodium hydroxide up to 48%, then back through dilute solutions to water, and finally through hydrochloric acid of increasing concentration. Maximum extension, and presumably minimum swelling, occurred with 10% hydrochloric acid. Cotton cellulose appears, therefore, to be analogous to a heavy metallic hydroxide of definite acidic character; the point of maximum swelling (14.5% NaOH) corresponds with a point of maximum solubility, the reduction in swelling in more concentrated alkali with reduced solubility because of the repressed ionisation of the salt, the absence of swelling in acid with insolubility of the solid acid, and the minimum swelling in 10% hydrochloric acid with an isoelectric point.
J. C. W.

The Mercerisation of Cotton. A Review of the Literature. DOUGLAS ARTHUR CLIBBENS (*J. Text. Inst.*, 1923, **14**, 217—249r).—A critical summary, with seventy-nine references to the literature,

dealing with mercerisation under the following headings: history, microscopic characteristics of mercerised cotton, lustre of cotton mercerised under tension, shrinkage of cotton when treated with sodium hydroxide, tensile strength of mercerised cotton, reactivity and adsorptive capacity of mercerised cotton, nature of mercerised cotton and the mercerisation process, and tests for mercerised cotton. J. C. W.

The Hemicelluloses. I. The Hemicellulose of Wheat Flour. DONALD HERBERT FRANK CLAYSON and SAMUEL BARNETT SCHRYVER (*Biochem. J.*, 1923, 17, 493—496).—By removing from wheat flour the gliadin with 70% alcohol, the starch by the action of taka-diastrase, and the glutenin by extraction with 0.1% sodium hydroxide a hemicellulose is obtained. The compound is soluble in hot water, from which it separates in an amorphous form. It is also soluble in *N*-sodium hydroxide and is precipitated on the addition of acids. The pure compound, precipitated from hot water or obtained from the copper salt, has $[\alpha]_D^{20} + 150^\circ$ in 0.5*N*-sodium hydroxide. It is not an intermediate product in the digestion of the starch by taka-diastrase. S. S. Z.

The Hemicelluloses. II. The Hemicellulose Content of Starch. SAMUEL BARNETT SCHRYVER and ETHEL MARY THOMAS (*Biochem. J.*, 1923, 17, 497—500).—Employing the same method of extraction (see preceding abstract), hemicellulose was obtained from the starches of sago, maize, wheat, rice, tapioca, and potato. The yields varied practically from 0 in the case of potato starch up to nearly 4% in that of sago. The compound has a composition which corresponds with the formula $C_{18}H_{34}O_{17}$ ($=3C_6H_{10}O_5 \cdot 2H_2O$), and yields, on hydrolysis, dextrose as the only reducing sugar, mixed with small amounts of other products, probably of a dextrin-like nature. S. S. Z.

The Hemicelluloses. III. The Hemicellulose of American White Oak. MARGARET HELENA O'DWYER (*Biochem. J.*, 1923, 17, 501—509).—The hemicellulose was prepared by extracting the washed sawdust with 4% sodium hydroxide and precipitating the extract with acetic acid. A rough quantitative estimation of the products of hydrolysis showed the presence of 51.5% of xylose, and 18.5% of arabinose; the remaining 30% consisted of mannose and galactose. Untrustworthy figures were obtained in the estimation of the relative quantities of mannose and galactose. S. S. Z.

Hydrochloric Acid-Lignin. ERIK HÄGGLUND (*Ber.*, 1923, 56, [B], 1866—1868).—Pine wood is readily attacked by hydrochloric acid (45%) at 0°, leaving a residue of hydrochloric acid-lignin. The latter substance can be further hydrolysed by treatment with boiling dilute hydrochloric or sulphuric acid, and the residue from this operation is again susceptible to treatment with the cold concentrated acid. It is not yet established whether complete solution of the lignin can be obtained by repeated alternate treatments. The pentoses (chiefly arabinose) formed by hydrolysis correspond approximately with half the loss in weight

of the lignin. It is probable that methylpentoses are also present, since the furfuraldehyde distillates of the residues contain appreciable quantities of methylfurfuraldehyde. H. W.

Lignin. IV. The Oxidation of Alkali Lignins by Hydrogen Peroxide. OTTO ANDERZÉN and BROR HOLMBERG (*Ber.*, 1923, **56**, [B], 2044—2048; cf. Holmberg and Wintzell, A., 1921, i, 850).—The oxidation of α - or γ -lignin by hydrogen peroxide in the presence of water yields formic, acetic, oxalic, malonic, and succinic acids. The formation of the latter acid is somewhat remarkable, but is in harmony with the assumption that the coniferyl or vanillyl residue is a component of the lignin molecule. It may be obtained by the oxidation of vanillin. The oxidation of alkali lignins in alkaline solution leads to the production of oxalic, formic, and acetic acids, the yield of the latter not exceeding 1—1.6%. Since yields of 7—10.5% of the latter acid are obtained by the oxidation of hot, acid solutions, it appears that a portion of it is derived from primarily formed malonic acid. H. W.

Pectin-Sugar-Acid Gels. R. SUCHARIPIA (*J. Assoc. Off. Agric. Chem.*, 1923, **7**, 57—68).—Gels may be prepared by adding 5 g. of 4% pectin solution to 15 g. of 75% sucrose syrup containing 0.75% of citric acid; heating does not accelerate the setting of such gels, low temperature and evaporation being the promoting factors. The formation of such gels is due to the coagulation of pectin in the sucrose-acid medium. Pectin is very slightly soluble in sucrose-acid solutions. The mother-liquor separates from even very tough jellies, although in smaller amount than from soft jellies; the solid (after washing with alcohol) contains pectin only, whilst the liquid part contains all the acid, sugar, traces of pectin, and a small amount of methyl alcohol. The cleavage of methoxyl groups is, however, of very limited extent, since the recovered pectin will again form good gels. Pectins with different methoxyl contents have been prepared; they yield solutions of varying viscosity, and the gels prepared with them increase in strength with increase in the methoxyl content. The jelly-forming property of pectin is destroyed by prolonged heating, high temperature, and pressure. W. P. S.

Syntheses from Hydrocyanic Acid by Means of the Silent Discharge. III. Behaviour of Amylene. L. FRANCESCONI and A. CIURLO (*Gazzetta*, 1923, **53**, 521—522; and *Atti R. Accad. Lincei*, 1923, [v], **32**, ii, 34—35).—Like other hydrocarbons (this vol., i, 764, 1004), amylene reacts with hydrocyanic acid under the influence of the silent discharge, yielding nitrile and isonitrile compounds in fluctuating proportions. T. H. P.

Synthesis of Amines by Means of the Silent Discharge. I. L. FRANCESCONI and A. CIURLO (*Gazzetta*, 1923, **53**, 598—600; cf. this vol., i, 764, 1004, and preceding abstract).—The action of the silent discharge on a mixture of dry ethylene and ammonia in an ordinary Berthelot ozoniser at the ordinary temperature results in the formation of ethylamine in about 10% yield with reference

to the ethylene, and of an oily product (cf. Losanitsch, A., 1908, ii, 32). T. H. P.

The Ammonium Radicle. IV. Tetraethylammonium. III. The Similarity to the Alkali Metals. HANS HEINRICH SCHLUBACH and GUSTAV VON ZWEHL (*Ber.*, 1923, **56**, [B], 1889—1892).—A continuation of previous work (Schlubach and Ballauf, A., 1922, i, 15). Solutions of tetraethylammonium in liquid ammonia have been prepared under conditions so modified as to exclude the possibility of contamination with alkali metals. The colorations given by these solutions with organic substances containing unsaturated bonds (benzophenone, phenyl diphenyl ketone, dimethylpyrone, β -benzpinacolin, benzil, phenanthraquinone, anthracene, stilbene, tetraphenylethylene, benzylideneaniline, azobenzene, tolane, toluonitrile) are described in detail, and are shown to be closely similar to those given by these compounds with the alkali metals. Tetraethylammonium appears, therefore, to function as a true pseudo-metal. H. W.

The Ammonium Radicle. V. Onium Radicles. HANS HEINRICH SCHLUBACH and HERMANN MIEDEL (*Ber.*, 1923, **56**, [B], 1892—1896).—An examination of the influence of substituents on the stability of the ammonium radicle and of the possible existence of radicles which contain a central atom other than nitrogen.

The substituted ammonium salts are submitted to electrolysis, liquid ammonia being used as solvent. The formation of a radicle is indicated by the production of a blue colour in the solution, or, more accurately, by the development of a coloration in the presence of 2 : 6-dimethylpyrone.

For the formation of ammonium radicles, it appears necessary that an alkyl group should be attached to the nitrogen atom. Successive replacement of the ethyl groups of tetraethylammonium by benzyl radicles increases the instability of the ammonium complex; the effect is still more pronounced when the triphenylmethyl or phenyl group takes the place of benzyl. Instability is also conferred on the substituted ammonium radicle when the ethyl group is replaced by hydrogen.

Electrolysis of tetraethylphosphonium and tetraethylarsonium iodides dissolved in liquid ammonia gives rise to radicles which do not cause the solution to become blue, but are detected by the colorations given with 2 : 6-dimethylpyrone. Diphenyliodonium iodide, under similar conditions, does not appear to give a radicle.

It appears, therefore, that a large class of complexes exists, to which the name "onium radicles" is assigned, owing to their preparation from onium salts. These differ from the usual radicles in that the valency of the central atom is greater by one unit than that observed in the stable hydrogen compound of the atom, whereas in the usual radicles it is less by one unit. H. W.

The Preparation of β -Methylhydroxylamine by the Aid of Potassium Hydroxylamineisodisulphonate. WILHELM TRAUBE and ALFRED P. SCHULZ (*Ber.*, 1923, **56**, [B], 1856—1860).—The recent investigations of Raschig (this vol., ii, 161) on the preparation

of potassium hydroxylamineisodisulphonate, $\text{SO}_3\text{K}\cdot\text{NH}\cdot\text{O}\cdot\text{SO}_3\text{K}$, have rendered possible the convenient preparation of β -methylhydroxylamine.

Potassium hydroxylamineisodisulphonate is dissolved in rather more than the quantity of aqueous potassium hydroxide solution which is theoretically necessary for the production of the basic salt, and the solution is treated with methyl sulphate or methyl iodide, whereby *potassium* β -methylhydroxylamineisodisulphonate, $\text{SO}_2\text{K}\cdot\text{NMe}\cdot\text{O}\cdot\text{SO}_3\text{K}$, minute rhombohedra, is readily obtained; the corresponding *silver*, *lead*, and *barium* salts are described. The isolation of the potassium salt is not necessary for the preparation of β -methylhydroxylamine, for which purpose the solution is heated with acid. The direct isolation of β -methylhydroxylamine in the form of one of its salts from the resulting solution does not appear to be practicable. The solution is therefore rendered slightly alkaline and treated with successive small quantities of benzaldehyde, care being taken to maintain the alkalinity by periodical additions of potassium hydroxide. It is filtered through a wet paper, and the *N*-methylbenzaldoxime is extracted from the filtrate by chloroform. The oxime is purified and subsequently decomposed by hydrochloric, sulphuric, or oxalic acid. The yield of β -methylhydroxylamine hydrochloride, calculated on the hydroxylamineisodisulphonate taken, is 60—70% of that theoretically possible.

The following salts of β -methylhydroxylamine are described; the *hydrochloride*, very hygroscopic crystals, m. p. 87° ; the normal *oxalate*, $2\text{CH}_3\text{ON}\cdot\text{H}_2\text{C}_2\text{O}_4$, long needles, m. p. 159° ; the hygroscopic, normal *sulphate*, m. p. 130° ; the *picrate*, m. p. 268° . H. W.

Synthesis of γ -Aminobutyric Acid from Ethyl Glutaryl-aminoacetate. THEODOR CURTIUS and WILHELM HECHTENBERG (*J. pr. Chem.*, 1923, [ii], **105**, 319—326).—Glutaryl chloride and ethyl aminoacetate hydrochloride react in boiling benzene solution to give the *half-chloride*, $\text{COCl}\cdot[\text{CH}_2]_3\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, a thick, yellow oil, b. p. 179 — $180^\circ/14$ mm., which is converted, on keeping with concentrated aqueous ammonia solution for several days, into the corresponding *amide*, $\text{NH}_2\cdot\text{CO}\cdot[\text{CH}_2]_3\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$, glistening, colourless needles, m. p. 188° . The half-chloride reacts vigorously with hydrazine hydrate, giving *ethyl hydrazidoglutaryl-aminoacetylhydrazide*, $\text{NH}_2\cdot\text{NH}\cdot\text{CO}\cdot[\text{CH}_2]_3\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$, small, glistening, colourless leaflets, m. p. 166° (decomp.), *dihydrochloride*, m. p. 190° (decomp.), *dibenzylidene* derivative, m. p. 220° . The dihydrazide is converted by treatment with nitrous acid in aqueous solution into the *diazide*, a thick, colourless, unstable oil, which reacts with alcohol in ethereal solution to give the *diurethane*, glistening leaflets, m. p. 143° . The latter gives γ -aminobutyric acid (hydrochloride), when hydrolysed by means of concentrated hydrochloric acid at 100° . W. S. N.

Resolution of Non-naturally Occurring Amino-Acids and Polypeptides. III. EMIL ABDERHALDEN and KIKO GOTO (*Fermentforsch.*, 1923, **7**, 95—105).—Ferments are capable of

hydrolysing the amide linking of non-naturally occurring peptides. *dl- α -Amino-octoic acid* was prepared by the action of aqueous ammonia on α -bromo-octoic acid. It melts at 263–264°. It was converted by the action of chloroacetyl chloride and α -bromo-isohexoyl chloride, respectively, into *chloroacetyl-dl- α -amino-octoic acid*, m. p. 82–83°, and *α -bromoisohexoyl-dl- α -amino-octoic acid*, m. p. 123°. By the action of alcoholic ammonia these halogenated acids gave the dipeptides, *glycyl-dl- α -amino-octoic acid*, m. p. 196°, and *dl-leucyl-dl- α -amino-octoic acid*, m. p. 230°. The hydrochlorides of the *ethyl* and *methyl* esters of α -amino-octoic acid melt at 53–54° and 76–77°, respectively. The formyl derivative of *dl- α -amino-octoic acid* was resolved by means of brucine, the salt of *d*-formyl-amino-octoic acid separating first, and giving on hydrolysis *l- α -amino-octoic acid*, m. p. 276°, and $[\alpha] -12.99^\circ$. From the mother-liquors *d- α -amino-octoic acid* was eventually obtained having $[\alpha] +12.28^\circ$. By the action of yeast on *dl- α -amino-octoic acid*, the dextrorotatory component was selectively utilised, leaving a slight preponderance of the *l*-form. The dipeptides *glycyl-dl- α -amino-octoic acid* and *dl-leucyl-dl- α -amino-octoic acid* were submitted to the action of yeast press juice with suitable buffering. In the former case *d- α -amino-octoic acid* and glycine were isolated, and in the latter *l*-leucine with a trace of *d- α -amino-octoic acid*.

H. K.

Resolution of Non-naturally Occurring Racemic Amino-acids by Ferments. III. EML ABDERHALDEN and MUNENARI TANAKA (*Fermentforsch.*, 1923, 7, 153–159).— α -Aminomyristic acid was combined with chloroacetyl chloride, yielding *chloro- α -acetamidomyristic acid*, m. p. 205°. The reaction proceeds better if the ethyl ester (2 molecules) is coupled with chloroacetyl-chloride in chloroform solution. *Ethyl α -aminomyristate hydrochloride* melts at 83°, the *methyl ester hydrochloride* at 105°, and the *chloroacetyl* derivative of the ethyl ester at 58°. The latter is transformed by alcoholic ammonia at 37° into the dipeptide, *α -glycylamidomyristic acid*, m. p. 212°. Under parallel conditions, α -bromoisohexoyl chloride converts the ethyl ester of α -aminomyristic acid into *ethyl α -bromoisohexoyl- α -amidomyristate*, m. p. 44°, which yields *dl- α -leucylamidomyristic acid*, m. p. 218°. This latter acid forms an *acid chloride* on treatment with thionyl chloride. By the action of yeast on *dl- α -aminomyristic acid*, a weakly lævoro-rotatory acid was obtained of doubtful purity. Yeast press juice was allowed to act on the dipeptides mentioned above but with inconclusive results.

H. K.

Synthesis of Methyl β -Methylaminopropene- α -carboxylate, $\text{NHMe}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{Me}$. G. KORSCHUN and (MME) C. ROLL (*Bull. Soc. chim.*, 1923, [iv], 33, 1106–1107).—When methyl acetoacetate is agitated with 33% aqueous methylamine in the cold, *methyl β -methylaminopropene- α -carboxylate*, m. p. 60.5°, is formed. It is hydrolysed quantitatively by dilute sulphuric acid, and this reaction may be used for its estimation, provided that

the hydrolysis is carried out without the application of heat (about twenty-four hours are required) to avoid loss of methylamine.

H. H.

$\alpha\delta$ -Diamino- γ -valerolactone and a New Synthesis of Hydroxyproline. WILHELM TRAUBE, R. JOHOW, and W. TEOHL (*Ber.*, 1923, 56, [B], 1861—1866; cf. Leuchs, A., 1905, i, 545).—Ethyl chlorovalerolactonecarboxylate is transformed by aqueous ammonia (25%) into δ -amino- γ -valerolactone- α -carboxylamide, $\text{CO} < \text{CH}(\text{CO}\cdot\text{NH}_2)\cdot\text{CH}_2$
 $\text{O} \text{-----} \text{CH}\cdot\text{CH}_2\cdot\text{NH}_2$, rectangular plates, m. p. 176—

178°. It is converted by barium hydroxide solution into the corresponding free *acid*, which could not be obtained in a completely homogeneous condition; its constitution is deduced by its transformation with loss of carbon dioxide into the oxypiperidone, m. p. 144—145°. The aqueous solution of the acid is treated with bromine and subsequently heated until evolution of carbon dioxide ceases, whereby α -bromo- δ -amino- γ -valerolactone hydrobromide, $\text{CHBr}\cdot\text{CH}_2 > \text{CH}\cdot\text{CH}_2\cdot\text{NH}_2$, HBr, m. p. 215—216°, is obtained. The latter substance is transformed by water and silver oxide into γ -hydroxyproline.

Bromination of aminovalerolactonecarboxylamide dissolved in water or glacial acetic acid leads to the production of the lactone of 3-bromo-5-hydroxypiperidone-3-carboxylic acid (annexed formula), m. p. 240° (decomp.), which is converted by concentrated alcoholic ammonia into $\alpha\delta$ -diaminovalerolactonecarboxylamide, $\text{C}_6\text{H}_{11}\text{O}_3\text{N}_3$, m. p. 215—220° after becoming changed at 200°. Treatment of the latter substance with sodium hydroxide solution gives an *acid*, $\text{C}_6\text{H}_{14}\text{O}_6\text{N}_2$, needles, m. p. 210—212°, which is either the corresponding carboxylic acid (+2H₂O), or, possibly, α -carboxy- $\alpha\delta$ -diamino- γ -hydroxyvaleric acid (+H₂O). When warmed with dilute nitric acid, it yields $\alpha\delta$ -diamino- γ -valerolactone, $\text{CH}(\text{NH}_2)\cdot\text{CH}_2 > \text{CH}\cdot\text{CH}_2\cdot\text{NH}_2$, a

viscous liquid which readily absorbs atmospheric moisture and carbon dioxide; it is characterised as the corresponding *nitrate*, $\text{C}_5\text{H}_{10}\text{O}_2\text{N}_2\cdot 2\text{HNO}_3$, rectangular plates, m. p. 153—155°, the *hydrochloride*, $\text{C}_5\text{H}_{10}\text{O}_2\text{N}_2\cdot 2\text{HCl}\cdot\text{H}_2\text{O}$, rhombic plates, m. p. 239—240°, and the *carbamide* derivative, $\text{C}_7\text{H}_{12}\text{O}_4\text{N}_4$, slender needles, m. p. 204—206°.

Ethyl chlorovalerolactonecarboxylate is converted by guanidine in boiling alcoholic solution into the *compound*, $\text{C}_7\text{H}_9\text{O}_3\text{N}_3$, slender needles which have no definite melting point.

H. W.

The Fission of Polypeptide Esters by Lipase. EMIL ABDERHALDEN and ALFRED ÄLKER (*Fermentforsch.*, 1923, 7, 77—84).—Attempts to resolve polypeptides by selective hydrolysis of the esters by lipase were not successful. *Glycyl-dl-leucylglycine*, prepared by the action at 37° of 25% ammonia on *chloroacetyl-*

dl-leucylglycine (m. p. 127—137°) decomposes at 227° and gives a weak biuret reaction. Its *ethyl* ester was amorphous. dl-Leucylglycyl-dl-leucylglycine, m. p. 235°, was prepared by the action of ammonia on dl- α -bromoisohexoylglycyl-dl-leucylglycine, m. p. 195° (decomp.). The former tetrapeptide gave an intense red biuret reaction. Its *ethyl* ester was amorphous and gave a rose-coloured biuret reaction. Lipase failed to hydrolyse either of these esters.

H. K.

Glutathione. IV. Constitution. JUDA HIRSCH QUASTEL, CORBET PAGE STEWART, and HUBERT ERLIN TUNNICLIFFE (*Biochem. J.*, 1923, **17**, 586—592).—The following evidence is produced in support of the formula

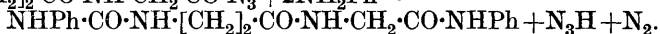


When the free amino-group of the compound is condensed with 2:3:4-trinitrotoluene, the resulting compound on hydrolysis yields cysteine, but not free glutamic acid. On replacing the free amino-group of glutathione by a hydroxyl group, α -hydroxyglutaric acid is obtained on hydrolysis. Oxidation of glutathione by hydrogen peroxide yields succinic acid only after hydrolysis of the oxidation product, thus demonstrating which carboxyl group of glutamic acid is condensed with the amino-group of cysteine.

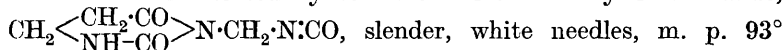
S. S. Z.

Synthesis of β -Alanine from Ethyl Succinylamidoacetate. THEODOR CURTIUS and WILHELM HECHTENBERG (*J. pr. Chem.*, 1923, [ii], **105**, 289—318).—The action of an excess of hydrazine hydrate on ethyl succinylamidoacetate gives *hydrazidosuccinylglycinehydrazine*, $\text{NH}_2\cdot\text{NH}\cdot\text{CO}\cdot[\text{CH}_2]_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$, colourless, anisotropic tablets, m. p. 167° (decomp.). If the materials are not well cooled during the reaction, a *compound*, m. p. 210°, is also formed. The dihydrazide forms a *dihydrochloride*, needles, m. p. 174°, a *dibenzylidene* derivative, tablets, m. p. 218° (decomp.), and a *diisopropylidene* derivative, m. p. 174°. The action of sodium nitrite on a cold hydrochloric acid solution of the dihydrazide (dihydrochloride) gives *azidosuccinylglycineazide*, $\text{N}_3\cdot\text{CO}\cdot[\text{CH}_2]_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{N}_3$, white, glistening leaflets, which is converted by warming with alcohol in ethereal solution into the corresponding *diurethane*, small, colourless, anisotropic prisms, m. p. 150—152° (decomp.). The hydrolysis of the latter by heating at 100° with alcoholic hydrogen chloride solution does not give ethyl β -aminopropionate, but a product which reacts with benzene-sulphonyl chloride to give a *compound*, m. p. 125—127°; this result is not due to decomposition of the expected amino-ester, since this is unaffected by alcoholic hydrogen chloride at 100°. However, ethyl β -aminopropionate hydrochloride is produced by hydrolysing the urethane, using aqueous hydrochloric acid, although the yield never exceeds 30% of theory. It was expected that the hydrolysis of the above diazide, by means of boiling alcoholic hydrogen chloride, would give formaldehyde ammonia, carbon dioxide, and β -aminopropionic acid (cf. Curtius and Sieber, A., 1921, i, 653), but hydrazoic acid, succinic acid, and aminoacetic acid are formed

instead. The action of aniline on a freshly prepared, ethereal solution of the diazide gives a small quantity of a crystalline substance, m. p. 195°, perhaps the normal dianilide, together with the semi-inverted *dianilide*, colourless prisms, m. p. 223—224°, $\text{N}_3\cdot\text{CO}\cdot[\text{CH}_2]_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{N}_3 + 2\text{NH}_2\text{Ph} =$



The constitution of this dianilide follows, since it gives aniline, aminoacetic acid, and phenyl- β -carbamidopropionic acid, $\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, when hydrolysed by heating at 100° with concentrated hydrochloric acid. The cyclic *carbimide*,



(decomp.), is obtained by boiling a carbon tetrachloride solution of the diazide; it is very readily converted by the action of heat, even during its preparation, into an amorphous, infusible substance. The freshly prepared carbimide readily reacts with ethyl alcohol to give the analogous *urethane*, colourless prisms, m. p. 124°, and not the diurethane, m. p. 150—152° (decomp.) (above). It is evident that the cyclic carbimide is formed by isomeric change from the open-chain isomeride, $\text{CO}\cdot\text{N}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{N}:\text{CO}$, which is not isolated. The cyclic carbimide reacts immediately in carbon tetrachloride solution with aniline or *p*-toluidine to give, respectively, the *anilide*, a colourless, microcrystalline powder, m. p. 183° (decomp.), or the *p*-toluidide, m. p. 205°. The hydrolysis of the cyclic urethane by means of hot (100°) concentrated hydrochloric acid gives β -aminopropionic acid, as expected, together with an infusible, colourless, somewhat insoluble compound, long, tabular crystals, which is converted into β -aminopropionic acid by further heating with acid at 110°; moreover, this compound is not isolated if the original hydrolysis is conducted at this temperature.

Ethyl *N*-succinylamidoacetate is formed when succinyl chloride reacts with the hydrochloride of ethyl aminoacetate, but if the free ester is used, the product is ethyl succinyldiamidoacetate. This reacts with cold hydrazine hydrate to give the *dihydrazide*, $\text{C}_2\text{H}_4(\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et})_2$, glistening tablets, m. p. 220°, which gives a *dibenzylidene* derivative. If the condensation with hydrazine hydrate is carried out in alcoholic solution, a flocculent *hydrazide*, m. p. 225°, is produced, which gives a compound, m. p. 196°, by reaction with benzaldehyde.

The dihydrochloride, m. p. above 270° (colourless tabular crystals), of ethylenediamine is produced by keeping a hydrochloric acid solution of the diazide of succinic acid, formed by diazotising the dihydrazide. When the diazide is boiled in chloroform solution, *ethylenedicarbimide*, $\text{C}_2\text{H}_4(\text{N}:\text{CO})_2$, b. p. 75°/25 mm., or 105°/50 mm., is produced, from which the known diurethane is formed by warming with anhydrous ethyl alcohol. The dicarbimide readily reacts with water, giving carbon dioxide and ethylenecarbimide, together with a small quantity of a compound (? $\text{C}_5\text{H}_7\text{O}_2\text{N}_3$), small, thin, elongated, felted prisms, m. p. above 300°, which is also formed when the dicarbimide is kept in contact with moist air. The

dicarbimide reacts in carbon tetrachloride solution with aniline to give *ethylenediphenylcarbamide*, $C_6H_4(NH\cdot CO\cdot NHPh)_2$, prisms, m. p. 245° (decomp.). The action of aniline in ethereal solution on the diazide gives the dianilide of succinic acid. W. S. N.

The Constitution of Carbamides. XV. A Delicate and Trustworthy Test for the Recognition of Cyanic Acid. EMIL ALPHONSE WERNER (T., 1923, 123, 2577—2579).

Substituted Biurets and Allophanic Esters. HEINRICH BILTZ and ARNOLD JELTSCH (*Ber.*, 1923, 56, [B], 1914—1926).—Up to the present the systematic preparation of alkylated biurets has not been effected. It can be accomplished by the action of ammonia or amines on allophanic esters, which may be prepared from carbamides and chloroformic esters or from carbamic esters and carbamyl chloride. A second method depends on the action of alkylcarbimides on carbamides, reaction occurring initially at the primary amino-group. The new biurets closely resemble in their behaviour those described previously. The action of nitrous acid leads to the introduction of the nitroso-group at the terminal secondary nitrogen atom. Treatment with acetyl chloride causes the introduction of an acetyl group at a terminal nitrogen atom; it has not been established whether the change occurs at the primary or secondary amino-group.

It is proposed to distinguish the terminal nitrogen atoms by the expression N^w , whereas the intermediate atom is designated N^{ms} .

Ethyl allophanate, m. p. $190-191^\circ$, and methyl allophanate, m. p. 208° , are prepared from carbamide and the requisite chloroformic ester according to the method of Dains and Wertheim (A., 1921, i, 61). Methyl N^w -methylallophanate, from methylcarbamide and methyl chloroformate at $110-115^\circ$, has m. p. 163° . Methyl N^{ms} -methylallophanate, indistinct leaflets, m. p. 146° , is prepared from methyl methylcarbamate and carbamyl chloride; it is transformed by ammonia into ms -methylbiuret. Methyl- N^{ms} -ethylallophanate, m. p. $160-161^\circ$, is prepared in a similar manner to the corresponding methylallophanate; it is converted by aqueous or alcoholic solution of ammonia or ethylamine into ammonium N^{ms} -ethylallophanate, m. p. $226-228^\circ$, and ethylammonium N^{ms} -ethylallophanate, m. p. $222-223^\circ$, respectively. Phenylurethane and carbamyl chloride yield ethyl N^{ms} -phenylallophanate, short, four-sided prisms or rhombic plates, m. p. 184° . Attempts to cause interaction between urethanes and dimethylcarbamyl chloride or between chloroformic esters and *s*- or *as*-dimethylcarbamide at 100° were unsuccessful.

ω -Methylbiuret is prepared from allophanic ester and aqueous methylamine (33%) at 100° from methyl N^w -methylallophanate and ammonia or from carbamide and methylcarbimide; it has m. p. $167-168^\circ$. ω -Nitroso- ω -methylbiuret forms minute crystals, decomp. $139-140^\circ$; it is decomposed by warm water in accordance with the equation: $NH_2\cdot CO\cdot NH\cdot CO\cdot NMe\cdot NO + H_2O = CO(NH_2)_2 + CO_2 + N_2 + MeOH$. Acetyl- ω -methylbiuret, from ω -methylbiuret and acetyl chloride at 100° , has m. p. 212° .

ω -Ethylbiuret is readily prepared from aqueous ethylamine and methyl (but not ethyl) allophanate; it has m. p. 154° (cf. Pickard, Allen, Bowdler, and Carter, T., 1902, 81, 1572). ω -Nitroso- ω -ethylbiuret forms small, flat prisms, m. p. 119 — 120° (decomp.), whereas acetyl- ω -ethylbiuret crystallises in four-sided, oblique prisms, m. p. 160 — 162° .

The action of dimethylamine on methyl allophanate leads to the formation of *as*-dimethylcarbamide, m. p. 180° ; dimethylcarbamyl chloride could not be caused to react with carbamide, methylcarbamide, or *s*-dimethylcarbamide.

$\omega\omega'$ -Dimethylbiuret, long, four-sided, flattened prisms, m. p. 162 — 163° , is prepared from methyl N^{ω} -methylallophanate and methylamine or from methylcarbamide and methylcarbimide. ω -Nitroso- $\omega\omega'$ -dimethylbiuret, short, slender prisms, decomp. about 108° , $\omega\omega'$ -dinitroso- $\omega\omega'$ -dimethylbiuret, yellow, four-sided prisms, decomp. 94° , and ω -acetyl- $\omega\omega'$ -dimethylbiuret, minute crystals, m. p. 216 — 217° (decomp.), are described. Attempts to prepare $\omega\omega\omega'$ -trimethylbiuret from methyl N^{ω} -methylallophanate and aqueous dimethylamine led to the production of *as*-dimethylcarbamide and methylcarbamide. Ethylcarbamide and ethylcarbimide at 100° yield a substance, $C_6H_{11}ON_3$, leaflets, m. p. 191° , in place of the expected $\omega\omega'$ -diethylbiuret.

ms-Methylbiuret, colourless, four-sided prisms, m. p. 189° , is prepared from methyl N^{ms} -methylallophanate and aqueous ammonia at 100° ; it does not yield a nitroso-compound. ω -Acetyl-*ms*-methylbiuret forms indistinct crystals, m. p. 280° . Attempts to prepare ω -*ms*-dimethylbiuret from methyl N^{ms} -methylallophanate and methylamine or from carbamyl chloride and *s*-dimethylcarbamide did not lead to the desired result; the action of cyanic acid on a solution of *s*-dimethylcarbamide in chloroform give a substance, $C_4H_8O_3N_2$, m. p. 189 — 190° .

The preparation of *ms*-ethylbiuret is beset with difficulty owing to the ready hydrolysis of N^{ms} -ethylallophanic esters by ammonia and amines, but, under certain conditions, it may be obtained from the methyl ester and aqueous ammonia; it crystallises in monoclinic or triclinic plates, m. p. 178 — 179° . ω -Acetyl-*ms*-ethylbiuret forms lustrous, hexagonal platelets, m. p. 228 — 230° . ω -*ms*-Diethylbiuret could not be prepared from methyl N^{ms} -ethylallophanate and ethylamine since hydrolysis of the ester could not be avoided.

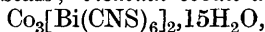
ms-Phenylbiuret, leaflets, m. p. 192° , is readily prepared from ethyl N^{ms} -phenylallophanate and concentrated aqueous ammonia at 100° . ω -Methyl- ω' -phenylbiuret, coarse, four-sided prisms, m. p. 172 — 173° , is obtained from methylcarbamide and phenylcarbimide at 120 — 130° .

s-Dimethylcarbamide and methylcarbimide at 100° yield ω -*ms*- ω' -trimethylbiuret, long, slender, colourless needles, m. p. 125 — 126° . The microcrystalline dinitroso-derivative, decomp. 102° , and the monoacetyl compound, m. p. about 165° , are described. Corresponding attempts to prepare ω -*ms*- ω' -triethylbiuret were unsuccessful.

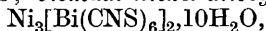
H. W.

Some Complex Thiocyanates of Bismuth. A. PACIELLO and N. FOÀ (*Gazzetta*, 1923, **53**, 526—531).—The addition of potassium thiocyanate solution to bismuth thiocyanate solution yields an orange-red coloration, which indicates the formation of the complex ion $\text{Bi}(\text{CNS})_6'''$. This indication is confirmed (1) by the existence of a series of salts capable of representation by a common scheme, this holding for the salt of cobalt, which exhibits a marked tendency to the formation of complex ions; (2) by the comparative stability of these salts towards the hydrolysing action of water, and (3) by the migration of complex bismuth-ions towards the positive pole in solutions of the salts. It seems probable that solutions of bismuth thiocyanate in thiocyanic acid contain bismuththiocyanic acids of the formula $\text{HBi}(\text{CNS})_4$ in concentrated solutions or $\text{H}_3\text{Bi}(\text{CNS})_6$ in dilute solutions; the structure of bismuth thiocyanate may be regarded as $\text{BiBi}(\text{CNS})_6$.

Bismuth zinc thiocyanate, $\text{Zn}_3[\text{Bi}(\text{CNS})_6]_2$, forms large, non-hygroscopic, orange-red crystals; *bismuth cobalt thiocyanate*,



reddish-brown crystals; *bismuth nickel thiocyanate*,



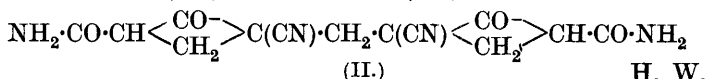
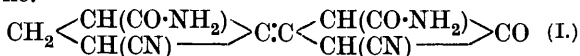
a greenish-yellow, crystalline mass becoming brownish-yellow when pounded; *bismuth vanadyl thiocyanate*, $(\text{VO})_3[\text{Bi}(\text{CNS})_6]_2, 7\text{H}_2\text{O}$, a reddish-violet powder; *bismuth iron thiocyanate*, $\text{FeBi}(\text{CNS})_6$, lustrous, green crystals; *bismuth thallium thiocyanate*, $\text{TlBi}(\text{CNS})_4$, red crystals, giving an orange-red powder. T. H. P.

Methylenebismalononitrile and Hexacyanopentane and their Behaviour towards Hot Water. OTTO DIELS and BRUNO CONN (*Ber.*, 1923, **56**, [B], 2076—2082).—A further investigation of the condensation of formaldehyde with malononitrile (cf. Diels, Gärtner, and Kaack, this vol., i, 25).

It has not yet been found possible to isolate the primary product of the action of formaldehyde on malononitrile in the presence of piperidine, but the production of methylenemalononitrile may be assumed from the formation of methylenebismalononitrile (m. p. 160—180° after softening very sharply at 136—137°, which is previously recorded as the melting point), and of *pentane- $\alpha\alpha$ - $\gamma\gamma$ - $\epsilon\epsilon$ -hexanitrile*, colourless leaflets, m. p. 226°, decomp. 275° after darkening at about 180°. The production of these substances is explained by the schemes: $\text{CH}_2\cdot\text{C}(\text{CN})_2 + \text{CH}_2(\text{CN})_2 \rightarrow \text{CH}_2[\text{CH}(\text{CN})_2]_2$ and $\text{CH}(\text{CN})_2\cdot\text{CH}_2\cdot\text{CH}(\text{CN})_2 + \text{CH}_2\cdot\text{C}(\text{CN})_2 \rightarrow (\text{CN})_2\text{C}[\text{CH}(\text{CN})_2]_2$. Support of this hypothesis is found in the observation that the hexanitrile is obtained by the action of hot water on pure methylenebismalononitrile under definite conditions and by the spontaneous evaporation of alcoholic solutions of methylenebismalononitrile at the atmospheric temperature.

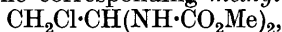
Methylenebismalononitrile is decomposed in a complicated manner by hot water, yielding the ammonium salts of two acids, $\text{C}_{12}\text{H}_{10}\text{O}_3\text{N}_4$, small, pale yellow prisms, decomp. 290°, and $\text{C}_{13}\text{H}_{12}\text{O}_4\text{N}_4$, long, thin prisms, decomp. 293°, to which the constitutions (I) and (II) are assigned. The substance

$C_{12}H_{10}O_3N_4$ is also obtained by the action of hot water on pentane-hexanitride.



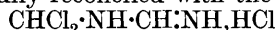
H. W.

The Sandmeyer Synthesis of Ethyl Chloroimidocarbonate, and the Formhydroximic Esters as a Step towards Alkyl Cyanates. J. HOUBEN (*J. pr. Chem.*, 1922, [ii], 105, 7—26) [with E. PFANKUCH and K. KÜHLING].—The preparation of ethyl *N*-chloroimidocarbonate is improved by working at twice the dilution employed by Sandmeyer (A., 1886, 611). In this reaction, β -chloroethylidenediurethane is also formed, evidently by the condensation of chloroacetaldehyde with 2 mols. of urethane; this compound is most conveniently prepared, in 93% yield, by gently warming a mixture of 2 mols. of urethane and 1 mol. of $\alpha\beta$ -dichloro-ether. The corresponding *methyl* ester,

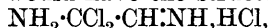


forms colourless crystals, m. p. 136° . The action of chlorine on an ice-cold, aqueous solution of urethane gives *N*-dichlorourethane, $NCl_2 \cdot CO_2Et$, a golden-yellow oil, b. p. $66\text{--}67^\circ/18$ mm., which has an extraordinarily penetrating and stupefying odour. It is volatile in steam, and dissolves in warm ammonium chloride solution. It decomposes potassium nitrite solution, giving a green coloration, and liberates iodine from potassium iodide solution. On being heated above its boiling point (147° /ordinary pressure), it decomposes with violence. When kept in alcoholic solution it passes into β -chloroethylidenediurethane. The analogous *methyl* ester, $NCl_2 \cdot CO_2Me$, prepared similarly, is a yellow oil, b. p. $56\text{--}57^\circ/21$ mm., having properties similar to those of its homologue. Ethyl imidocarbonate reacts in alcoholic solution with aniline hydrochloride to give a small quantity of *s*-diphenylcarbamide, together with *ethyl phenylimidocarbonate*, $NPh \cdot C(OEt)_2$, a somewhat oily, but mobile liquid, b. p. $136\text{--}137^\circ/16$ mm., which is readily decomposed by means of dilute mineral acids into aniline and ethyl carbonate. The oxime of ethyl formate, *ethyl formhydroximate*, $OH \cdot N \cdot CH \cdot OEt$, long, colourless needles, m. p. 80° , b. p. $76\text{--}77^\circ/15$ mm. (slight decomp.), is prepared by the action of free hydroxylamine on free ethyl imidoformate (both liberated from their hydrochlorides by means of potassium hydroxide) in ice-cold, aqueous solution, or by the action of hydroxylamine on ethyl imidoformate hydrochloride in dry ethereal solution. It readily reacts with acetic anhydride, giving the *acetate*, $OEt \cdot CH \cdot NOAc$, an oil, b. p. $82^\circ/17$ mm. *Methyl formhydroximate*, needles, m. p. $99\text{--}100^\circ$, and *n*-propyl formhydroximate, long needles, m. p. $61\text{--}62^\circ$, can only be prepared in anhydrous ethereal solution, using free hydroxylamine. These three oximino-esters give a transient, bluish-green coloration with chlorine in carbon tetrachloride solution, and a slight reddish-brown or reddish-yellow coloration

with aqueous ferric chloride solution. *Formylformamidoxime*, $\text{CHO}\cdot\text{NH}\cdot\text{CH}\cdot\text{NOH}$, m. p. 140° (slight decomp.), is prepared by the action of hydrogen cyanide sesquihydrochloride, $2\text{HCN}\cdot 3\text{HCl}$ (Claisen and Matthews, *Ber.*, 1883, **16**, 311) (1 mol.), on an ice-cold, aqueous-ethereal solution containing 1 mol. of free hydroxylamine and 2 mols. of potassium hydroxide. The production of this compound is readily reconciled with the formula

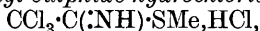


(Gattermann, A., 1898, i, 546), for the sesquihydrochloride, whereas if the latter is derived from Nef's imidoformyl cyanide (A., 1896, i, 71), $\text{NH}\cdot\text{CH}\cdot\text{CN}$, it would have the structure



and would give, by the action of hydroxylamine, the isomeric, known oximidoacetamide, $\text{NH}_2\cdot\text{CO}\cdot\text{CH}\cdot\text{NOH}$. It seems likely, therefore, that Nef's dimeric hydrogen cyanide has the structure $\text{NH}\cdot\text{CH}\cdot\text{NC}$.
W. S. N.

Trichloroacetimidomethyl Sulphide. WILHELM STEINKOPF and SIEGFRIED MÜLLER (*Ber.*, 1923, **56**, [B], 1930—1932).—*Trichloroacetimido methyl sulphide hydrochloride*,



large, rhombic crystals, m. p. $126\text{--}129^\circ$, according to the manner of heating, is prepared by the action of dry hydrogen chloride on a solution of trichloroacetonitrile in methyl mercaptan. It is converted by cold water into a mixture of the *S*-methyl ester of trichlorothioacetic acid, $\text{CCl}_3\cdot\text{CO}\cdot\text{SMe}$, and *trichloroacetimido methyl sulphide*. The latter substance, a pale yellow liquid, b. p. $93\cdot 5^\circ/20$ mm., which slowly decomposes when preserved at the atmospheric temperature, is obtained in the homogeneous condition by the addition of the hydrochloride to a saturated, ice-cold solution of potassium carbonate in water in the presence of ether. H. W.

Diallylhydrazine and its Conversion into Tetra-allyltetrazen by Dehydrogenation with Azodicarboxylic Ester. OTTO DIELS (*Ber.*, 1923, **56**, [B], 1933—1938).—Ethyl azodicarboxylate appears to be a generally applicable reagent for the conversion of disubstituted hydrazins into tetrazens. A tetrazen appears to be produced initially which subsequently passes into the tetrazen and the hydrazo-ester: $2\text{NR}_2\cdot\text{NH}\cdot\text{N}(\text{CO}_2\text{Et})\cdot\text{NH}\cdot\text{CO}_2\text{Et} \rightarrow 2\text{NH}(\text{CO}_2\text{Et})\cdot\text{NH}\cdot\text{CO}_2\text{Et} + \text{NR}_2\cdot\text{N}\cdot\text{N}\cdot\text{NR}_2$ (cf. Busch, Müller and Schwarz, this vol., i, 864).

Methyl hydrazinemonocarboxylate is converted by allyl bromide into *methyl diallylhydrazinemonocarboxylate*, $\text{N}(\text{C}_3\text{H}_5)_2\cdot\text{NH}\cdot\text{CO}_2\text{Me}$, colourless, lustrous needles, m. p. 68° ; the corresponding *hydrochloride* is very hygroscopic. The ester combines with bromine in the presence of chloroform to give *methyl tetrabromodipropylhydrazinemonocarboxylate*, colourless crystals, m. p. 108° . Allyl bromide and ethyl hydrazinemonocarboxylate give a mixture of *ethyl diallylhydrazinemonocarboxylate*, short, lustrous needles, m. p. 52° , and *ethyl monoallylhydrazinemonocarboxylate*, a colourless liquid, b. p. $102^\circ/18$ mm. Methyl diallylhydrazinemonocarboxylate is converted by hydrazine hydrate at 150° into *as-diallylhydrazine*,

a colourless, mobile liquid, b. p. $145^{\circ}/752$ mm., which is transformed by furfuraldehyde into *furfuraldehydediallylhydrazone*, a colourless liquid, b. p. $108^{\circ}/2$ mm., and by phenylcarbimide into *phenyldiallylsemicarbazide*, $\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{N}(\text{C}_3\text{H}_5)_2$, a colourless, viscous liquid, b. p. $185^{\circ}/0.5$ mm. Diallylhydrazine is converted by ethyl azodicarboxylate in well-cooled, ethereal solution into *tetra-allyltetrazen*, $\text{N}(\text{C}_3\text{H}_5)_2\cdot\text{N}\cdot\text{N}\cdot\text{N}(\text{C}_3\text{H}_5)_2$, a pale yellow, mobile liquid, b. p. $113^{\circ}/752$ mm., which explodes violently when heated above its boiling point; the corresponding picrate and the additive compound with mercuric chloride do not crystallise readily.

Diphenylhydrazine and azodicarboxylic ester give tetraphenyltetrazen and the hydrazo-ester.

Phenylmethylhydrazine is converted by ethyl azodicarboxylate into diphenyldimethyltetrazen, m. p. 137° ; simultaneously phenyl azide, b. p. $70^{\circ}/11$ mm., and phenylmethylurethane, b. p. $116^{\circ}/8$ mm., are produced. H. W.

Certain Simple Aliphatic Azo-compounds. F. ARNDT, E. MILDE, and G. ECKERT (*Ber.*, 1923, **56**, [B], 1976—1984).—*Dimethylazodicarbothioamide*, $\text{NH}\cdot\text{C}(\text{SMe})\cdot\text{N}\cdot\text{N}\cdot\text{C}(\text{SMe})\cdot\text{NH}$, is prepared by the oxidation of the corresponding hydrazo-compound by potassium ferricyanide in alkaline solution; it crystallises in orange-red needles, m. p. 92 — 93° , which can be preserved at 0° during one to two days, but decompose within a few hours at the atmospheric temperature. It decomposes violently when heated at about 110° into the hydrazo-compound, nitrogen, cyanogen, dimethyl disulphide, and methyl thiocyanate, in accordance with the equations: $2\text{C}_4\text{H}_8\text{N}_4\text{S}_2 = \text{C}_4\text{H}_{10}\text{N}_4\text{S}_2 + \text{N}_2 + \text{C}_2\text{N}_2 + \text{SMe}\cdot\text{SMe}$ and $2\text{C}_4\text{H}_8\text{N}_4\text{S}_2 = \text{C}_4\text{H}_{10}\text{N}_4\text{S}_2 + \text{N}_2 + 2\text{Me}\cdot\text{SCN}$. It is immediately dissolved by dilute mineral acids with the formation of colourless solutions which do not evolve gas and contain mainly the hydrazo-compound. The course of the action has been more fully investigated by using the *azo-hydrochloride*, $\text{C}_4\text{H}_{10}\text{N}_4\text{S}_2\text{Cl}_2$, a reddish-brown substance which rapidly becomes white when exposed to moisture. It is thereby decomposed into the hydrazo-hydrochloride, urazole, methylsulphonyl chloride, ammonium chloride, and the *hydrochloride* of the *methylsulphone* of *dithiourazole dimethyl ether* in accordance with the scheme: $6\text{C}_4\text{H}_8\text{N}_4\text{S}_2\cdot 2\text{HCl} + 6\text{H}_2\text{O} = 4\text{C}_4\text{H}_{10}\text{N}_4\text{S}_2\cdot 2\text{HCl} + \text{C}_5\text{H}_8\text{O}_2\text{N}_2\text{S}_3\cdot\text{HCl} + \text{C}_2\text{H}_3\text{O}_2\text{N}_3 + \text{Me}\cdot\text{SO}_2\text{Cl} + 2\text{NH}_4\text{Cl}$. The *methylsulphone* of *dithiourazole dimethyl ether*, $\begin{smallmatrix} \text{N}\cdot\text{C}(\text{SMe}) \\ | \\ \text{N}\cdot\text{C}(\text{SMe}) \end{smallmatrix} > \text{N}\cdot\text{SO}_2\text{Me}$, m. p. 102° ,

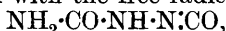
is readily prepared from dithiourazoledimethyl ether and methylsulphonyl chloride in ammoniacal solution.

Methyl hydrazodithiocarboxylate, $\text{SMe}\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}\cdot\text{CO}\cdot\text{SMe}$, needles, m. p. 173° , prepared from hydrazine and methyl chlorothioformate, is oxidised by nitric acid (60—66%) to the corresponding *azo-ester*, $\text{C}_4\text{H}_6\text{O}_2\text{N}_2\text{S}_2$, lustrous, orange-red needles, m. p. 69° , which is unstable at the atmospheric temperature. It is decomposed by heat in accordance with the schemes: $\text{SMe}\cdot\text{CO}\cdot\text{N}\cdot\text{N}\cdot\text{CO}\cdot\text{SMe} \rightarrow \text{MeS}\cdot\text{SMe} + \text{N}_2 + 2\text{CO}$ or $\rightarrow \text{MeS}\cdot\text{CO}\cdot\text{CO}\cdot\text{SMe} + \text{N}_2$. (*Methyl dithiooxalate*, a yellow, crystalline powder, m. p. 80° , b. p. $218^{\circ}/760$ mm.,

is also prepared from oxalyl chloride and methyl mercaptan in the presence of anhydrous ether.) Dilute sodium hydroxide solution decomposes it instantaneously, giving the hydrazo-ester, dimethyl disulphide, nitrogen, and carbon dioxide.

Methyl chlorothioformate, $\text{COCl}\cdot\text{SMe}$, a colourless, mobile, highly refractive liquid, b. p. 110° , is prepared by the interaction of well-cooled carbonyl chloride and methyl mercaptan in the presence of a trace of aluminium chloride. *Methyl chlorodithioformate*, $\text{CSCl}\cdot\text{SMe}$, a golden-yellow liquid, b. p. $50\text{--}52^\circ/15\text{ mm.}$, is prepared in a similar manner from thiocarbonyl chloride and methyl mercaptan. H. W.

The Decomposition of Carbamyl Azide, $\text{NH}_2\cdot\text{CO}\cdot\text{N}_3$, alone and in Aromatic Hydrocarbons. THEODOR CURTIUS and FRIEDRICH SCHMIDT (*J. pr. Chem.*, 1923, [ii], **105**, 177—198).—Carbamyl azide decomposes when heated alone, with the formation of isocyanic acid and hydrazoic acid, $\text{NH}_2\cdot\text{CO}\cdot\text{N}_3=\text{NH}\cdot\text{CO}+\text{N}_3\text{H}$; the latter gives nitrogen and ammonium azide. Decomposition also occurs in the sense of the equation: $\text{NH}_2\cdot\text{CO}\cdot\text{N}_3=\text{N}_2+\text{NH}_2\cdot\text{CO}\cdot\text{N}<$, giving a free radicle, two molecules of which may then combine to form azodicarbonamide. The latter is converted by boiling with water, whilst working up the product, into hydrazodicarbonamide. Urazole is also produced, perhaps by the interaction of isocyanic acid with the free radicle to give



which spontaneously passes into urazole, $\text{NH}<\begin{smallmatrix} \text{CO}\cdot\text{NH} \\ \text{CO}\cdot\text{NH} \end{smallmatrix}$. But perhaps

decomposition is accompanied by rearrangement: $\text{NH}_2\cdot\text{CO}\cdot\text{N}_3=\text{N}_2+\text{NH}_2\cdot\text{N}\cdot\text{CO}$; this rearranged residue could also combine with isocyanic acid to give $\text{NH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{N}\cdot\text{CO}$, which would then isomerise to urazole. The relative merits of these explanations remains undecided, although the formation (momentarily) of a free radicle seems probable, because a diarylcarbamide is also produced if the heating is conducted in a solution in an aromatic hydrocarbon, the first product being presumably a monoaryl-carbamide, which then suffers rearrangement: $\text{NH}_2\cdot\text{CO}\cdot\text{N}_3+\text{C}_6\text{H}_6=\text{N}_2+\text{NH}_2\cdot\text{CO}\cdot\text{NHPh}$. Carbamyl azide reacts with boiling ethyl alcohol to give urethane and hydrazoic acid. The complex carbamide, $(\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH})_2$ (Pellizari, A., 1907, i, 833), gives amino-urazole, $\text{NH}_2\cdot\text{N}<\begin{smallmatrix} \text{CO}\cdot\text{NH} \\ \text{CO}\cdot\text{NH} \end{smallmatrix}$, when heated at 150° with water.

W. S. N.

Low Temperature Tar. III. FRANZ SCHÜTZ, WILHELM BUSCHMANN, and HEINRICH WISSEBACH (*Ber.*, 1923, **56**, [B], 1967—1975; cf. this vol., i, 195, 525).—The phenols and bases present in the low temperature tar obtained from the Fürst Hardenburg coal in rotary furnaces at a temperature not exceeding 500° are described.

The phenols are isolated in the usual manner from the low temperature tars and are subjected to preliminary purification by fractional distillation, thus yielding almost colourless fractions

which alter little on exposure to air. The viscosity increases rapidly with increasing temperature, but the separation of a solid is not observed in any case. They contain small amounts of substances containing sulphur and nitrogen, together with very unstable products of unknown nature, which, however, are readily removed by hot water. Mercaptans are removed by precipitation with lead acetate in alcoholic solution. The separation of the individual phenols by fractional distillation is exceedingly tedious and only completely successful in the case of phenol, whereas the higher homologues are almost inextricably mixed. Their isolation can only be accomplished by the application of physical and chemical methods, which vary from case to case (they are described fully in the original). The presence of the following eight phenols has been established: phenol, *o*-, *m*-, and *p*-cresols, and 1:3:5-, 1:2:4-, 1:3:4-, and 1:4:2-xenols. The fractions of higher boiling point have not been completely investigated; they do not appear to contain naphthols.

The bases investigated are derived exclusively from the crude light oils of the tar in which they are present to the extent of about 1%. On distillation, the mixture gives the fractions, b. p. 93—150° (18%), 150—200° (27%), and 200—250° (55%). Resinifiable or pitch-like substances or compounds which are readily polymerised by acids or alkalis are not present. Pyridine is easily isolated from the fractions of lower boiling point. The separation of individuals from the fractions of higher boiling point is very incomplete. The identification of the components is therefore effected by methods which are suited to each particular case. The presence of pyridine, 2-methylpyridine, 2:3-dimethylpyridine, 2:4-dimethylpyridine, 2:4:6-trimethylpyridine, aniline, quinoline, and 2-methylquinoline is established. H. W.

Certain Derivatives of 1-Methyl- Δ^1 -cyclohexene. S. NAMETKIN and ANNA JARZEV (*Ber.*, 1923, 56, [B], 1803—1804).—The authors have undertaken an examination of the influence of the particular agent used in the oxidation of unsaturated hydrocarbons on the configuration of the glycol so produced; the oxidation of 1-methyl- Δ^1 -cyclohexene is described.

1-Methyl- Δ^1 -cyclohexene, b. p. 109—110°/753 mm., d_4^{20} 0.8122, n_D^{20} 1.4503, is conveniently prepared by the action of dilute nitric acid (d 1.075) at 100—110° or of sulphuric acid (50%) on 1-methylcyclohexan-1-ol. It is oxidised by benzoyl peroxide in ethereal solution (cf. Prileschaeff, A., 1910, i, 86, 295; 1911, i, 255, 604; 1912, i, 633) to 1-methylcyclohexene 1-oxide, $C_7H_{12}O$, b. p. 137.5—138°/756 mm., d_4^{20} 0.9300, n_D^{20} 1.4430, which is converted by water at 107—110° into *cis*-1-methylcyclohexane-1:2-diol, small, four-sided prisms, m. p. 84° (cf. Brunel, A., 1905, i, 869); the latter compound does not appear to become isomerised by treatment with water at 180°. *trans*-1-Methylcyclohexane-1:2-diol, m. p. 67°, is obtained by the oxidation of 1-methyl- Δ^1 -cyclohexene with permanganate.

H. W.

4-Methyl- Δ^1 -cyclohexene and certain of its Derivatives.

S. NAMETKIN and LYDIA BRÜSOV (*Ber.*, 1923, **56**, [B], 1807—1810).—4-Methyl- Δ^1 -cyclohexene has been frequently described previously in the literature, but the products do not appear to have been homogeneous; the pure substance, b. p. 102.5—102.7°/772 mm., d_4^{20} 0.8001, n_D^{20} 1.4419, is prepared by the successive treatment of 4-methylcyclohexane-1-ol with sodium, carbon disulphide, and ethyl sulphate, followed by thermal decomposition of the *xanthate* thus produced. Oxidation of the hydrocarbon by benzoyl peroxide in ethereal solution leads to the formation of 4-methylcyclohexene 1-oxide, $C_7H_{12}O$, b. p. 147—147.5°/16 mm., d_4^{20} 0.9364, n_D^{20} 1.4473, which is transformed by water at 108—110° into *cis*-1-methylcyclohexane-4 : 5-diol, small rhombic crystals, m. p. 63—64°. *trans*-1-Methylcyclohexane-4 : 5-diol, long needles, m. p. 35—37°, is obtained by treatment of 4-methyl- Δ^1 -cyclohexene with cold permanganate solution (1%). The physical constants of the diols indicate that in each case a mixture of the two theoretically possible *cis*- and *trans*-forms is produced.

H. W.

Constitution of Benzene. RONALD FRASER (*T.*, 1923, **123**, 2712—2713).

Space Formulæ of Benzene, Naphthalene, and Anthracene.

B. ÖRELKIN (*J. Russ. Phys. Chem. Soc.*, 1923, **54**, 493—532).—The existing formulæ for aromatic compounds are criticised on the ground that none of them explains the peculiar "aromatic" character of the compounds or the reason why true aromatic character is not shown by cyclic compounds with five- or eight-membered rings, and an attempt is made to devise a formula satisfying the latter requirements.

In the first place, it is suggested that when an atom containing several electrons unites with a hydrogen atom with the formation of a ring or "octet" of eight electrons, the positive nucleus of the hydrogen atom may or may not enter the electronic sphere. In cases where the nucleus remains outside the sphere, the new compound will readily ionise and exchange the hydrogen atom for another atom, as in the example of hydrogen chloride; if the positive nucleus is within the electronic sphere the mobility of the hydrogen atom is diminished and the compound is less reactive or indifferent (*i.e.*, not ionised), as in ammonia or methane. From this argument it follows that a methyl group should be very similar to an atom of a halogen, and it is shown from crystallographic data that this assumption is justified; thus *p*-xylene is practically isomorphous with the *p*-dihalogenobenzenes. A double bond is described as an arrangement of four electrons disposed at the corners of a square so that the centres of the two atoms can be joined by a line perpendicular to the plane of this square and passing through its centre; the instability of the double bond is due to the displacement of the electrons necessitated by this arrangement. In a triple bond there are six electrons similarly

arranged at the corners of a hexagon; it is clear that free rotation is impossible with these two systems.

As regards the benzene formula itself, it is suggested that of the thirty electrons in benzene, twelve are used for the union of hydrogen with carbon; another twelve suffice to hold together the ring of six carbon atoms, whilst six electrons remain "free" and must assume some symmetrical arrangement within the molecule; this means that they must be disposed at the corners of a regular octahedron and one of the axes of this octahedron must coincide with the axis of symmetry of the molecule. This is achieved by disposing the nuclei of the carbon atoms in two parallel planes at the corners of equilateral triangles the sides of which are not parallel but form an angle of 60° ; in other words, in projection their apices form a regular hexagon. The six electrons occupy positions in the centres of the sides of these triangles. It is shown that taking the distance between two such electrons as 1, the distances between the centres of the nuclei of two meta-carbon atoms is equal to 2; that between the ortho-atoms is represented by $\sqrt{2}$, and between the para-atoms by $\sqrt{6}$; or taking the ortho-distance as unit, we have $o : m : p = 1 : \sqrt{2} : \sqrt{3}$, that is, the same as in Sachse's formula. The electrons uniting the six-membered carbon ring are so disposed that the two electrons forming the ortho-bonds occupy two of the corners of a square, the other two corners being also occupied by electrons. This disposition simulates a double linking, but does not constitute one, because two of the four electrons are also involved in another similar arrangement. It is to this that the peculiar character of the aromatic nucleus is ascribed, and mathematical proof is given that such an arrangement is impossible with any number of carbon atoms other than six. The position of the electrons which unite the hydrogen atoms to the nucleus is somewhat difficult to describe without reference to drawings. A formula for naphthalene is constructed by fusing two benzene formulæ in the ortho-position, and a repetition of the process leads to that of anthracene and chrysene.

From these formulæ the crystal structure of benzene, naphthalene, and anthracene is deduced and is shown to agree satisfactorily with experimental data. The chief objection to the formulæ is the fact that benzene should exist in two enantiomorphous modifications, but it is suggested that the lack of symmetry in the new formula may be insufficient to cause rotation of polarised light.

G. A. R. K.

Diamond- and Graphite-structure in Organic Compounds.

A. SCHLEICHER (*J. pr. Chem.*, 1922, [ii], **105**, 350—354).—The author traces a connexion between the structure of diamond and of graphite, and the phenomena connected with the ethylation of benzene, and the phenylation of ethane.

W. S. N.

Additive Compounds of Aluminium Chloride with Hydrocarbons. A. SCHLEICHER [with E. BÜTTGENBACH] (*J. pr. Chem.*, 1922, [ii], **105**, 355—360).—By the action of aluminium chloride

on a mixture of benzene and ethyl bromide, a yellow oil is obtained one fraction of which has b. p. $135\text{--}138^\circ/12$ mm. (slight decomp.). The oily product formed by heating aluminium chloride with hexaethylbenzene at a temperature not exceeding 90° is less easily attacked by water than aluminium chloride itself. These results, it is claimed, prove the existence of additive compounds of aluminium chloride with triethylbenzene and hexaethylbenzene, confirming the conclusions of Gustavson (A., 1905, i, 696). W. S. N.

The Refractometric Behaviour of Cymene from Sulphite-Cellulose Liquors. A. KARVONEN (*Ber.*, 1923, 56, [B], 1824—1828).—The author notes the many discrepancies between the published values for the refractive index and the density of cymene from various sources. He therefore submits *p*-cymene from the sulphite liquors of the Finnish cellulose industry to severe chemical and physical treatment, finally washing with strong sulphuric acid and distilling over sodium. In this way, nine samples are obtained, b. p. $174\cdot8^\circ/746\cdot5$ mm., with n_D^{20} between 1.49032 and 1.49089, mean 1.49060, and d_4^{20} 0.85668—0.85704, mean 0.85688.

H. H.

The Aryl and Alkyl Sulphonamides. PERCIVAL WALTER CLUTTERBUCK and JULIUS BEREND COHEN (*T.*, 1923, 123, 2507—2515).

Hydrogenated Polycyclic Ring Systems. II. The Stereoisomerism of Dicyclohexane. WALTHER SCHRAUTH and KURT GÖRIG (*Ber.*, 1923, 56, [B], 1900—1906).—In a recent theoretical paper, Mohr (A., 1919, ii, 229) has considered the stability of the cyclohexane ring and has shown that the number of known isomerides is readily explicable by means of Sachse's model (in which the carbon atoms do not lie in one plane) if, at the same time, a free or only partly hindered rotation is assumed. For the establishment of the theory it is necessary that cyclohexane itself or one of its monosubstituted products should be isolated in at least two isomeric forms. The problem appears to be beset with unexplained difficulties in so far as simple derivatives are concerned. The authors have therefore directed their attention to compounds containing a second ring, and bring forward evidence of the existence of at least three dicyclohexanes.

The action of phosphoric oxide on a mixture of cyclohexanol and phenol leads to the production of a mixture of *p*-cyclohexylphenol, slender needles, m. p. 130° , b. p. $165^\circ/15$ mm., and *o*-cyclohexylphenol, needles, m. p. 57° , b. p. $147^\circ/17$ mm. Hydrogenation of the former compound in the presence of a nickel catalyst at $180\text{--}220^\circ$ yields a mixture of *cis*-*p*-cyclohexylcyclohexanol, needles, m. p. 105° , b. p. $159^\circ/20$ mm., and *trans*-*p*-cyclohexylcyclohexanol, m. p. $83\text{--}84^\circ$, b. p. $157\text{--}158^\circ/20$ mm. *o*-cyclohexylcyclohexanol has b. p. $273\text{--}274\cdot5^\circ/750$ mm., d_4^{20} 0.9835, and appears to possess a spatial configuration of the carbon skeleton differing from that of the compound described in the literature.

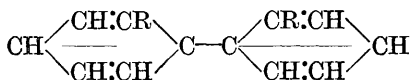
The action of zinc chloride on the two forms of *p*-cyclohexyl-

cyclohexanol yields *cyclohexyl-Δ¹-cyclohexene*, b. p. 236—237·5°/755 mm., which is hydrogenated to *dicyclohexane*, b. p. 227—228°/750 mm., the compound being identical with that described by Wallach. On the other hand, *o-cyclohexylcyclohexanol* does not yield a homogeneous hexene, the physical properties of the product appearing to be subject to uncontrollable factors. Hydrogenation of the material gives two different *dicyclohexanes* which have b. p. 219·5—221·5°/750 mm., d_4^{20} 0·8809, n_D^{20} 1·47758, and b. p. 235—237°/750 mm., d_4^{20} 0·8818, n_D^{20} 1·47795, respectively. The variety b. p. 235—237°/750 mm. appears to be the stable form, since it is unchanged by light or by energetic transforming agents. The remaining isomerides are transformed by warming with aluminium chloride or by protracted exposure to light into a mixture of the three forms, in which that of boiling point 235—237°/750 mm. predominates.

Evidence is brought forward to show that the hexene derivative mentioned previously can also exist in a labile form, b. p. 231·5—232·5°.

H. W.

Stereoisomerism among Derivatives of Diphenyl. E. E. TURNER (*Nature*, 1923, **112**, 439).—The possibility of the existence of a stable para-bond in benzene and diphenyl derivatives suggests that any 2 : 2'-derivative of diphenyl should be capable



of optical activity on the basis of the annexed formula (cf. Kenner and others, T., 1922, **121**, 614, etc.). Four asymmetric carbon atoms exist also in the isomeric dinitrobenzidines and some of their derivatives (Brady and McHugh, T., 1923, **123**, 2047), although none are known to exhibit optical activity.

A. A. E.

Stereoisomerism among Derivatives of Diphenyl. J. KENNER (*Nature*, 1923, **112**, 539—540).—Although the formula considered by Turner (preceding abstract) contains four asymmetric carbon atoms, it does not demand the existence of a correspondingly large number of stereoisomeric forms of 2 : 2'-derivatives of diphenyl. The respective distributions of the groups attached to the pair of asymmetric carbon atoms in either benzene nucleus are not mutually independent, so that only one asymmetric atom in each nucleus is effective as a source of stereoisomerism.

A. A. E.

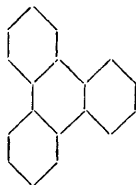
The [Crystal] Lattice of Triphenylmethane. H. MARK and K. WEISSENBERG (*Z. Physik*, 1923, **17**, 347—350).—Contrary to the conclusion of Becker and Rose (this vol., i, 550), the authors find, by Röntgen-ray analysis, that 8 molecules, and not 3, are contained in the elementary crystal cell of the stable crystalline modification of triphenylmethane. The respective lengths of the sides of the cell are : *a*, 15·16 Å.; *b*, 26·25 Å.; *c*, 7·66 Å., in agreement with values of the axial ratios deduced from goniometric

crystallographic measurements and with the results of Huggins (this vol., i, 329). J. S. G. T.

The [Crystal] Lattice of Triphenylmethane. KARL BECKER and H. ROSE (*Z. Physik*, 1923, **17**, 351—352).—The authors reply to criticism of their results by Mark and Weissenberg (preceding abstract), and remark that possibly the crystals of triphenylmethane investigated by themselves possessed hexagonal symmetry. The question as to whether the different conclusions originate in the existence of different crystalline modifications of triphenylmethane is to be settled by a mutual interchange and reinvestigation of the crystals. J. S. G. T.

Hydrogenated Polycyclic Ring Systems. III. Perhydro-9:10-benzophenanthrene. WALTHER SCHRAUTH and KURT GÖRIG (*Ber.*, 1923, **56**, [B], 2024—2027).—The author has previously expressed the opinion that the carbohydrates of plants during their life, and more particularly during the formation of coal, give a primary condensation product which contains the carbon skeleton of 9:10-benzophenanthrene. The preparation of perhydro-9:10-benzophenanthrene has therefore been effected; it is possibly identical with the compound prepared by Willstätter and Kalb (*A.*, 1922, i, 989) by the reduction of lignin, cellulose, or sugar with phosphorus and hydriodic acid.

The action of phosphoric oxide on a mixture of *o*-cyclohexylcyclohexanol and phenol leads to the formation of 1-*o*-dicyclohexyl-2-phenol, needles, b. p. 220—224°/14 mm., m. p. 112—115°, together with a residue, m. p. 86—87°, which greatly resembles colophony. The phenyl is reduced by hydrogen in hexahydro-toluene solution in the presence of a nickel catalyst to 1-*o*-dicyclohexylcyclohexane-2-one, a colourless, very viscous liquid, b. p. 212—214°/14 mm., d_4^{20} 0.9874, which solidifies when cooled to a glassy, non-crystalline mass. Treatment of the ketone with zinc chloride at 180° yields $\Delta^{9,14}$ -hexadecahydro-9:10-benzophenanthrene, a colourless liquid, b. p. 186—188.5°/12 mm., d_4^{20} 0.9518, which is hydrogenated in the presence of a nickel catalyst to *perhydro*-9:10-benzophenanthrene (annexed formula), a colourless liquid, b. p. 175—176°/7 mm., d_4^{20} 0.9425, n_D^{20} 1.51959. H. W.



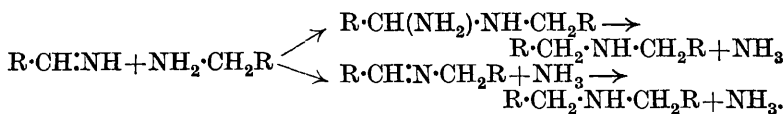
n_D^{20} 1.51959.

The Hydroferrocyanides and Hydroferricyanides of the Organic Bases. II. WILLIAM MURDOCH CUMMING (*T.*, 1923, **123**, 2457—2464).

The Utilisation of Monomethylaniline in the Production of Tetryl [2:4:6-Trinitrophenylmethylnitroamine]. THOMAS JOSEPH NOLAN and HENRY W. CLAPHAM (*Sci. Proc. Roy. Dubl. Soc.*, 1923, **17**, 219—223).—Nitration of methylaniline with nitric acid in presence of sulphuric acid gives rise to a considerable amount of 2:3:4:6-tetranitrophenylmethylnitroamine (*m*-nitrotetryl) in addition to tetryl, and since, by hydrolysis, this gives *m*-hydroxy-

tetryl, which reduces the stability of tetryl, the method is not suitable for the manufacture of tetryl. On the other hand, phenyl-methylnitrosoamine can be nitrated to give tetryl without the formation of any appreciable quantity of *m*-nitrotetryl. It is necessary to isolate the phenylmethylnitrosoamine and to nitrate it in freshly prepared sulphuric acid solution. There appears to be an equilibrium between nitrous acid, methylaniline, and phenyl-methylnitrosoamine in sulphuric acid solution. Consequently, if the nitrosoamine is prepared in sulphuric acid solution, or if the nitrosoamine is dissolved in sulphuric acid and time allowed for equilibrium to be attained, methylaniline will be present and a good quality tetryl cannot be obtained on nitration. E. H. R.

Catalytic Hydrogenation under Pressure in the Presence of Nickel Salts. VI. Nitriles. JULIUS VON BRAUN, GEORG BLESSING, and FRIEDRICH ZOBEL (*Ber.*, 1923, **56**, [B], 1988—2001).—The catalytic hydrogenation of nitriles in the presence of nickel salts occurs rapidly and smoothly except in the cases of the simpler aliphatic nitriles, in the presence of which the catalyst rapidly becomes poisoned. It leads to the production of mixtures of primary and secondary, but apparently not of tertiary amines, the yields being 80—95% of those theoretically possible. Alteration in pressure does not appear to affect the course of the reaction; the influence of temperature is not very marked and is variable. On the other hand, the effect of solvent and of concentration is unusually marked. The total amount of reduced product is always somewhat greater in the presence of alcohols or ethers than in that of hydrocarbons, and a very marked displacement of the yield in the direction either of primary or secondary amine can be effected by variation of the oxygenated solvent. Increase in concentration in the cases of all solvents favours the production of primary base frequently to a very marked degree. The primary product of the change is assumed to be the compound $R\cdot CH:NH$, which is either reduced further to primary amine or reacts with primary amine to produce the secondary base in accordance with the schemes :



The comparatively greater yield of primary amines in more concentrated solution is thereby explained. Confirmation of the hypothesis is found in the observation that under similar conditions the yields of secondary bases from ortho-substituted benzonitriles are less than from the corresponding meta- and para-derivatives, thus conforming to the expected influence of steric hindrance. Further, if alcohols with a particularly mobile hydroxyl group $R'\cdot OH$ are used as solvents during the reduction of a nitrile, $R\cdot CN$, in addition to the bases $R\cdot CH_2\cdot NH_2$ and $NH(CH_2\cdot R)_2$, mixed bases of the type $R\cdot CH_2\cdot NHR'$ are produced, the formation

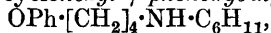
of which is explained by the scheme: $R\cdot CH\cdot NH + R'\cdot OH \rightarrow R\cdot CH(OH)\cdot NHR' \rightarrow R\cdot CH\cdot NR' \rightarrow R\cdot CH_2\cdot NHR$.

Hydrogenation is usually effected at $110-130^\circ$, and is continued until further appreciable absorption of the gas does not occur. The products are readily separated from one another by fractional distillation in all cases in which the solvent does not enter into the reaction; where this is the case, the separation of the two secondary bases is difficult.

Acetonitrile and propionitrile are only hydrogenated to a slight extent under the experimental conditions.

Octonitrile gives *n*-octylamine, b. p. $72-73^\circ/14$ mm. (*hydrochloride*, m. p. 198° ; *phenylthiocarbamide* derivative, m. p. 55°), and *dioctylamine*, b. p. $175^\circ/14$ mm. (*hydrochloride*, m. p. 238°).

γ -Phenoxy-*n*-butyronitrile yields δ -phenoxybutylamine, b. p. $140^\circ/12$ mm., and *di- δ -phenoxybutylamine*, $(OPh\cdot[CH_2]_4)_2NH$, a colourless, crystalline substance, m. p. $51-52^\circ$, b. p. $266^\circ/15$ mm. (*hydrochloride*, leaflets, m. p. 165° ; *nitroso*-derivative, m. p. 50° ; the *picrate*, *acetyl* derivative, and *benzoyl* compound could not be caused to crystallise). The secondary base is transformed by fuming hydrobromic acid to *di- δ -bromobutylamine hydrobromide*, colourless leaflets, m. p. 200° . When liberated from its salt the base immediately becomes converted into dipyrrolidinium bromide, m. p. $256-258^\circ$. Catalytic reduction of δ -phenoxy-*n*-butyronitrile in the presence of *cyclohexanol* yields, in addition to the two bases just described, *cyclohexyl- γ -phenoxybutylamine*,



a colourless liquid, b. p. $177-179^\circ/16$ mm. (*picrate*, m. p. 110° ; the *hydrochloride* is very hygroscopic; the *nitroso*-derivative is not crystalline).

Benzonitrile yields benzylamine and dibenzylamine, the former being very advantageously prepared if decahydronaphthalene or amyl alcohol is used as solvent. In the presence of *cyclohexanol*, *cyclohexylbenzylamine*, b. p. $145-147^\circ/15$ mm. (*hydrochloride*, m. p. 284° ; *nitroso*-derivative, m. p. 43° ; *benzenesulphonyl* compound, m. p. 90°) is also produced; the yield increases at the expense of the simple secondary base with increasing dilution of the solution. When *m*-methylcyclohexanol is used as solvent, *m*-methylcyclohexylbenzylamine, b. p. $155^\circ/15$ mm., is also produced, but the yield is relatively less than that of the lower homologue, doubtless owing to the diminished mobility of the hydroxyl group; the non-crystalline *nitroso*-derivative, the *hydrochloride*, colourless prisms, m. p. 249° , and the *hydrobromide*, m. p. $245-248^\circ$, are described.

Hydrogenation of the naphthonitriles is effected at about 190° , and leads mainly to the production of primary amines; it is remarkable that the nucleus does not appear to be attacked under these conditions. α -Naphthylmethylamine has b. p. $155^\circ/12$ mm., the *hydrochloride*, m. p. $262-264^\circ$, the *picrate*, m. p. 223° , the *phenylcarbamide* compound, m. p. 216° , the *acetyl* derivative, colourless needles, m. p. 134° , the *benzenesulphonyl* compound, m. p. 148° , and α -naphthylmethyltrimethylammonium iodide, lustrous leaflets,

m. p. 213°, are described. *Di-α-naphthylmethylamine*, m. p. 73—74°, yields a *hydrochloride*, m. p. 239°, a *picrate*, m. p. 202°, a *nitroso-derivative*, rectangular leaflets, m. p. 147°, and *di-α-naphthylmethyldimethylammonium iodide*, $\text{NMe}_2(\text{CH}_2\cdot\text{C}_{10}\text{H}_7)_2\text{I}$, m. p. 209—210°. β -Naphthylmethylamine, b. p. 148—149°/12 mm., m. p. 60°, gives a *hydrochloride*, m. p. 269°, a *picrate*, m. p. 226°, an *acetyl derivative*, m. p. 126°, and β -*naphthylmethyltrimethylammonium iodide*, colourless prisms, m. p. 168°. *Di-β-naphthylmethylamine*, m. p. 95°, yields a *hydrochloride*, m. p. 285°, a *picrate*, m. p. 126°, a *nitroso-derivative*, m. p. 132°, and *di-β-naphthylmethyldimethylammonium iodide*, m. p. 217°.

The hydrogenation of phenylacetonitrile has been studied under varied conditions. β -Phenylethylamine and di- β -phenylethylamine, colourless crystals, m. p. 28—30°, b. p. 195°/18 mm. (*picrate*, m. p. 150°, *nitroso-derivative*, m. p. 53°; *phenyllithiocarbamide* compound, m. p. 113°), are the usual products. In the presence of cyclohexanol, phenylacetonitrile yields also β -*phenylethylcyclohexylamine*, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_{11}$, a liquid, b. p. 163—169°/13 mm., the *hydrochloride*, m. p. 199°, the *sulphate*, and the *picrate*, m. p. 154°, of which are also described. In the presence of benzyl alcohol, the only secondary amine which is formed is *benzyl-β-phenylethylamine*, a liquid, b. p. 186—187°/15 mm. (*hydrochloride*, m. p. 254°, *nitroso-derivative*, m. p. 142°; *benzoyl derivative*, m. p. 123°; *picrate*, m. p. 146°). Similarly, in the presence of *p*-methylbenzyl alcohol, the sole secondary base produced is *p-xylyl-β-phenylethylamine*, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\text{Me}$, b. p. 191—193°/14 mm. (*hydrochloride*, m. p. 238—240°; *picrate*, m. p. 139—141°).

β -Phenylpropionitrile is hydrogenated in the presence of decahydronaphthalene or β -phenylethyl alcohol to γ -phenylpropylamine, b. p. 112—114°/18 mm., and di- γ -phenylpropylamine, b. p. 220—222°/18 mm. In the presence of benzyl alcohol, it gives also *benzyl-γ-phenylpropylamine*, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CH}_2\text{Ph}$, a liquid which forms a *hydrochloride*, m. p. 184—185°, and a non-crystalline *nitroso-derivative*.

o-Toluenitrile is transformed into *o*-xylylamine and *di-o-xylylamine*, $\text{NH}(\text{CH}_2\cdot\text{C}_6\text{H}_4\text{Me})_2$, b. p. 190°/16 mm. (*hydrochloride*, m. p. 202°; *picrate*, m. p. 133°). *Di-m-xylylamine*, b. p. 189—191°/14 mm., gives a *hydrochloride*, m. p. 199°, and a *benzoyl derivative*, m. p. 100°. *Di-p-xylylamine*, b. p. 220°/13 mm., solidifies when cooled in ice.

α -Tetrahydronaphthonitrile is reduced in tetrahydronaphthalene solution to *ar-α-tetrahydronaphthylmethylamine*, $\text{C}_{10}\text{H}_{11}\cdot\text{CH}_2\cdot\text{NH}_2$, b. p. 150°/14 mm. (yield 70%) and *di-ar-α-tetrahydronaphthylmethylamine*, m. p. 93° (*hydrochloride*, m. p. 212°; *nitroso-derivative*, m. p. 90—91°). Similarly, β -tetrahydronaphthonitrile yields β -tetrahydronaphthylmethylamine, b. p. 147°/11 mm., and *di-β-tetrahydronaphthylmethylamine*, b. p. 265—267°/11 mm. (*hydrochloride*, m. p. 245°; *benzoyl derivative*, m. p. 241—242°; *nitroso-compound*, m. p. 76°). The yield of primary amine from the β -nitrile is much smaller than from the α -compound, whilst that of the secondary base is much greater.

H. W.

q q*

Reductions with Co-operation of Metallic Hydrides. KARL KINDLER (*Ber.*, 1923, 56, [B], 2063—2064).—Evidence is adduced to show that cathodic reduction is not entirely attributable to cathodic over-voltage but also to the intermediate formation of metallic hydrides.

[With O. GIESE.]—The yield of β -phenylethyldimethylamine obtained by the electrolytic reduction of phenylacetodimethylamide at a lead cathode is greatly increased by the addition of antimony pentoxide or arsenious oxide to the cathode solution; the action is attributed to the formation of arsine and stibine, respectively.

H. W.

Slow Formation of a Definite Compound in Mixed Crystals. PAUL PASCAL (*Compt. rend.*, 1923, 177, 587—589).—When mixtures of benzylideneaniline and anisylideneaniline are slowly cooled, a slight cloudiness appears at a temperature (t) just before rapid solidification sets in, a similar result being obtained by slow heating of the solidified mixture. By plotting concentration of the two components against t , it is seen that they form a compound (2 : 1), m. p. 33·5°, with partial dissociation. Whereas the solidification temperature curves are smooth, with a minimum at 21—23°, the temperature-concentration curve has a well-defined maximum (33·5°), the eutectics lying at 27·5° and 25·5° for 70% and 40% of benzylideneaniline, respectively. The cloudiness is apparently not due to the formation of an anisotropic liquid.

E. E. T.

New Secondary Bases in the Indene Series. CH. COURTOT and A. DONDELINGER (*Compt. rend.*, 1923, 177, 536—538).—1-Bromoindene reacts at the ordinary temperature with aniline to give *phenylindanyllamine*, yellowish-brown leaflets, m. p. 74—75°. The reactivity of this bromine atom (cf. Grignard and Courtot, A., 1912, i, 250) has previously been ascribed to the contiguity of the ethylenic linking, but it is now found that Weissgerber's 1-chloroindane (A., 1911, i, 623) reacts readily at the ordinary temperature with aniline, *p*- and *o*-toluidines and xylidine, and at 50—60° with *m*- and *p*-nitroanilines, the following compounds being so prepared: *Phenylindanyllamine*, m. p. 40—41°, b. p. 202—203°/15 mm., *p*-tolylindanyllamine, m. p. 64—65°, *o*-tolylindanyllamine, m. p. 71°, *xylindanyllamine*, b. p. 218°/17 mm., and *p*-nitrophenylindanyllamine, yellow, m. p. 126—127°.

1-Bromoindene and 1-chloroindane react with phenols in the cold with production of hydrogen chloride, and, presumably, of the corresponding ethers.

E. E. T.

Preparation of N-Mono- and Di-carboxylic Acid Esters of Unsymmetrically Substituted Alkylenediamines. SOCIETY OF CHEMICAL INDUSTRY IN BASLE (Brit. Pat. 203608).—The above esters are prepared by the interaction, in water or an organic solvent (ether, benzene), of an ester of a halogenated formic acid and an unsymmetrically substituted alkylenediamine. With equimolecular proportions, a monocarboxylic ester is obtained, whilst a mixture of 2 mols. of formic ester with 1 mol. of diamine (or equimolecular proportions of monocarboxylic ester and diamine)

yields a dicarboxylic ester. The free bases are oils which cannot be distilled under atmospheric pressure, and are insoluble in water but soluble in most organic solvents. Of their salts, those formed with halogen acids are readily soluble in water, whilst some dissolve also in organic solvents. Of the new compounds, which find therapeutic application, the preparation of the following is described: *Benzyl diethylaminoethylcarbamate*: a nearly odourless oil, b. p. $127^{\circ}/0.015$ mm., giving a crystalline *hydrochloride* melting at $105-106^{\circ}$. The corresponding *dimethylamino-ester* is a viscid, clear oil, the *hydrochloride* of which is syrupy and hygroscopic. *Phenylethyl diethylaminoethylcarbamate* is a colourless, nearly odourless oil, b. p. $147^{\circ}/0.025$ mm.; the *hydrochloride* forms an amorphous, hygroscopic mass. *Phenylethyl piperidyl-N-ethylcarbamate*, viscid, clear oil, b. p. $152^{\circ}/0.015$ mm.; the *hydrochloride* melts indefinitely at $60-75^{\circ}$. *Menthyl diethylaminoethylcarbamate* is an oil, b. p. $142^{\circ}/0.015$ mm.; the *hydrochloride* is a very viscid oil, boiling, with partial decomposition, at about $170^{\circ}/0.02$ mm.; the *hexahydrobenzyl ester* is a viscous, clear oil, b. p. $150^{\circ}/0.05$ mm.; the *phenylethyl diethylaminoethyliminodicarboxylate* has b. p. $200-202^{\circ}/0.05$ mm.

W. T. K. B.

β -Nitroarylhydroxylamines. II. Picrylhydroxylamine.

W. BORSCHÉ (*Ber.*, 1923, 56, [B], 1939—1943).—A continuation of previous work (this vol., i, 778).

Trinitrophenylhydroxylamine is smoothly prepared by heating a solution of trinitrophenetole in alcohol with a small excess of hydroxylamine during several hours. It crystallises in lustrous, reddish-brown, oblique prisms, m. p. 113° (decomp.). The following derivatives are described: the *sodium* compound; the *aniline* compound which is not suitable for the characterisation of the substituted hydroxylamine; the *p-toluidine* derivative, $C_{13}H_{13}O_7N_5$, m. p. 122° (slow decomp.); α -*acetyl*- β -*picrylhydroxylamine*, $C_6H_2(NO_2)_3 \cdot NH \cdot OAc$, obtained by means of acetic anhydride, dark yellow needles, m. p. 130° ; α -*benzoyl*- β -*picrylhydroxylamine*, thin red leaflets, m. p. 167° (decomp.). Trinitrophenylhydroxylamine is readily reduced to 1:2:3:5-tetraminobenzene, but its oxidation to 2:4:6-trinitro-1-nitrosobenzene has not yet been effected. It is converted by fuming nitric acid ($d < 1.54$) into 1:2:3:5-tetranitrobenzene, coarse, pale yellow needles, m. p. $125-126^{\circ}$, which is readily converted by dilute sodium hydroxide solution or by nitric acid ($d 1.395$) into picric acid, by aqueous or alcoholic ammonia into picramide, and by aniline into 2:4:6-trinitrodiphenylamine.

The preparation of 2:4:6-trinitrophenylhydroxylamine by the action of picryl chloride on hydroxylamine hydrochloride in boiling alcoholic solution has been described in the literature; a further examination of the change has shown that the product is a mixture of picric acid and picramide, but it is not certain whether these substances are formed independently. H. W.

Use of the Salts of the Arylsulphonhalogenoamides in the Estimation and Iodination of Phenols. ELWYN ROBERTS (*T.*, 1923, 123, 2707—2712).

Nitrosation of Phenols. I. 3-Chloro-4-nitrosophenol and its Conversion into Two Isomeric Chloroquinonemonoximes. HERBERT HENRY HODGSON and FRANCIS HARRY MOORE (T., 1923, 123, 2499—2507).

Derivatives of 3:5-Dinitrophenol. II. GUSTAV HELLER (*Ber.*, 1923, 56, [B], 1873—1876).—A continuation of previous work (A., 1909, i, 567).

[With HANS GEORGI.]—2:3-Dibromo-5-nitrophenol, needles, m. p. 106° (the sodium derivative, golden-yellow leaflets, is described), is prepared by diazotising 2-bromo-5-nitro-3-aminophenol and treatment of the diazonium salt with hydrobromic acid and copper powder. It is reduced by ferrous sulphate and ammonia to 2:3-dibromo-5-aminophenol, pale yellow needles, m. p. 133°, which undergoes resinification when subjected to diazotisation. 2:4:6-Tribromo-3:5-diaminophenol crystallises in pale yellow needles, m. p. 138°. 2:5-Dinitro-3-acetamidophenol, pale yellow needles, m. p. 223° (decomp.), is obtained by the action of nitric acid (*d* 1.4) on 5-nitro-3-acetamidophenol in the presence of glacial acetic acid.

3-Nitro-5-acetamidoanisole crystallises in colourless needles, m. p. 201°; it is converted by hydrochloric acid into 3-nitro-5-aminoanisole. The latter substance is transformed by bromine in glacial acetic acid solution into 2-bromo-5-nitro-3-aminoanisole, pale yellow needles, m. p. 156—157° (hydrobromide, colourless needles, m. p. 204°), and 2:4:6-tribromo-5-nitro-3-aminoanisole, long, pale brown needles, m. p. 113°. 2-Bromo-5-nitro-3-aminoanisole is converted by diazotisation and subsequent treatment of the diazonium salt (which does not couple directly with an alkaline solution of β -naphthol) with hydrobromic acid and copper powder into 2:3-dibromo-5-nitroanisole, pale brown needles, m. p. 121°, which is reduced by cautious treatment with zinc dust and hydrobromic acid in glacial acetic acid solution to 2:3-dibromo-5-aminoanisole, pale yellow needles, m. p. 244—245°. The latter substance is converted through the diazo-compound into 5:6-dibromoresorcinyl 1-methyl ether, brown crystals, m. p. 108°. If the diazotised solution of bromonitroaminoanisole is diluted with water, warmed on the water-bath until evolution of gas ceases and subsequently cooled in ice, 5-nitroanisole-2:3-quinone-3-diazide, ochre-coloured needles, decomp. 172—173°, separates.

[With MAX KAMMANN.]—2-Bromo-5-nitro-3-aminophenol is converted through the corresponding diazo-compound into 2-bromo-5-nitroresorcinol, orange-yellow needles, m. p. 201° (slight decomp.).
H. W.

Electrolytic Preparation of *p*-Aminophenol. J. C. WARNER and O. W. BROWN (*J. Physical Chem.*, 1923, 27, 652—673).—The electrolytic reduction of *p*-nitrophenol has been investigated under various conditions. It is shown that lead is superior to copper as cathode material in this reduction, since lead cathodes permit the use of higher current densities during the reduction. An electrolyte containing sodium hydroxide gives

higher current efficiencies and higher material yields of *p*-aminophenol than electrolytes containing sodium carbonate, sodium hydrogen carbonate, or sulphuric acid. With a copper or a lead cathode, the highest current efficiencies and material yields are obtained with an electrolyte containing about 8% of sodium hydroxide. At a copper cathode, the highest current efficiencies and material yields are obtained when a current density of 1—2 amperes per sq. dcm. is used. The most favourable concentration of *p*-nitrophenol in the cathode liquor is 2.0—3.0 g. in 100 c.c. of solution. With a current density of 4.0 amperes per dcm.², the most favourable temperature for the reduction is 65—75°. With a current density of 10 amperes per dcm.², the reduction is best effected near to the boiling point. When a solution of 10 g. of *p*-nitrophenol in 400 c.c. of 8% sodium hydroxide is reduced at a copper cathode with a current density of 2.0 amperes per dcm.² at 72—74°, a theoretical current efficiency is obtained as long as the concentration of *p*-nitrophenol does not fall below 1.0 g. in 100 c.c., and the material yield increases as the number of ampere-hours is increased until 10% in excess of the theoretical amount of current is used. The use of a larger excess of current causes no further increase in the material yield. *p*-Aminophenol of high purity (99.0—99.5%) can be obtained from alkaline solutions of the amine by neutralising with sulphuric acid in the presence of sodium hydrogen sulphite, filtering, washing with water, and drying in a vacuum. The *p*-aminophenol remaining in the mother-liquor after precipitation with sulphuric acid can almost all be recovered by making the mother-liquor slightly acid, evaporating to dryness on a steam-bath, and extracting the dry residue with small portions of boiling absolute alcohol. On keeping, alkaline *p*-aminophenol solutions decompose quite rapidly. If small quantities of sodium hydrogen sulphite are added this decomposition is prevented. J. F. S.

***o*-Chloro-*p*-methylaminophenol Sulphate, a New Photographic Developer.** WALTER G. CHRISTIANSEN (*J. Amer. Chem. Soc.*, 1923, 45, 2192—2194).—*o*-Chloro-*p*-nitrophenol has m. p. 110° (cf. Kollrepp, A., 1886, 1018); it is reduced by means of sodium hyposulphite and sodium hydroxide in boiling aqueous solution to *o*-chloro-*p*-aminophenol, white needles, m. p. 150—151°. When this aminophenol is treated in hot, aqueous alkaline solution with formaldehyde in the presence of an excess of zinc dust, methylation of the amino-group occurs; *o*-chloro-*p*-methylaminophenol sulphate, slender, white needles, is isolated from the product by adding sulphuric acid. It gives a red coloration, changing to deep purple, with ferric chloride solution. Both this compound and the hydrochloride of the unmethylated aminophenol are good photographic developing agents, but the former is the better, being equal to, but not better than, *p*-methylaminophenol sulphate (metol). W. S. N.

Preparation of *p*-Aminothymol. A. C. GRAYBEAL and R. E. KREMERS (*J. Amer. Pharm. Assoc.*, 1922, 11, 252—255; from *Chem. Zentr.*, 1923, i, 1618).—In modification of Wallach's method

(A., 1895, i, 546), *p*-aminothymol is prepared from *d*-limonene by way of the nitrosochloride. *d*-Limonene nitrosochloride is obtained by acting on limonene with freshly prepared ethyl nitrite in acetic acid-ethyl alcohol solution with gradual addition of strong hydrochloric acid. Carvoxime is obtained by treatment of the nitrosochloride with alcoholic potash, and changed into *p*-aminothymol by Wallach's method. G. W. R.

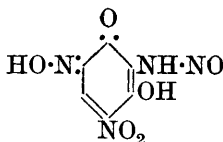
C-Alkylation (Nucleus Alkylation) of Phenols. L. CLAISEN (*Z. angew. Chem.*, 1923, **36**, 478—479).—The reaction between alkyl halides and the sodium derivatives of monohydric phenols of the benzene and naphthalene series results in O-alkylation when the medium is methyl or ethyl alcohol (also acetone, as a rule), whereas in non-dissociating media, *e.g.*, benzene or toluene, C-alkyl derivatives preponderate. Unsaturated radicles (*e.g.*, allyl, cinnamyl) are more easily introduced into the nucleus than saturated radicles, and the substituent enters in the ortho-position to the hydroxyl, provided this is unsubstituted. The following substituted phenols were prepared. Allylphenol: a yield of more than 90% of the ether is obtained from allyl bromide and alcoholic sodium phenoxide, whilst, in benzene or toluene, 70% of the C-allylphenol (including a little diallylphenol) is formed. Allyl-*p*-cresol: the proportions are as in the foregoing; by repeating the process with *o*-allyl-*p*-cresol, a good yield of *o*:*o*-diallyl-*p*-cresol is obtained. *o*-(α : γ -Dimethylallyl)-*p*-cresol: a colourless oil, b. p. 134—136°/13 mm., giving an alkali-insoluble isomeride, b. p. 244°, when treated with acid. *o*-Cinnamylphenol: in alcoholic solution the ether (m. p. 65—66°) is exclusively formed, whereas in benzene the product is almost exclusively monocinnamylphenol (crystals, m. p. 56°, b. p. 214°/12 mm.). *o*-Cinnamyl-*p*-cresol: a thick oil, b. p. 218—220°/13 mm., giving a *phenylcarbamate* melting at 124.5—125°. *o*-Benzylphenol: colourless crystals, m. p. 21°, b. p. 312°/760 mm. *o*-Benzylguaiacol: the ether is the main product, even in benzene solution; the C-substituted phenol melts at 38° and boils at 195°/13 mm. *o*-Benzyl- α -naphthol: obtained, in 50% yield, as colourless needles, m. p. 73.5—74°, b. p. 237—240°/13 mm. *o*-Benzyl- β -naphthol: obtained, in 60—70% yield, as a crystalline mass, m. p. 111—112°, which is probably identical with the compound obtained by Bakunin and Altieri (*cf.* A., 1904, i, 313) from β -naphthol, benzyl chloride, and zinc; the acetyl and benzoyl derivatives melt at 65—65.5° and 97° respectively.

W. T. K. B.

4-Nitro-2-aminoresorcinol and 2-Nitro-4-aminopyrocatechol. GUSTAV HELLER, PAUL LINDNER, and HANS GEORGI (*Ber.*, 1923, **56**, [B], 1868—1872).—Heller and Sourlis (A., 1910, i, 749) have described the production of a stable primary nitrosoamine by the action of nitrous acid on 2-nitro-4-aminoresorcinol; a similar compound has now been isolated from the isomeric 4-nitro-2-aminoresorcinol.

2:4-Dinitroresorcinol, dissolved in glacial acetic acid, is reduced

by the calculated quantity of stannous chloride and hydrochloric acid, and the product is converted by acetic anhydride into 4-nitro-2-acetamidoresorcinol, long, pale yellow needles, m. p. 213°, which is hydrolysed by concentrated hydrochloric acid to 4-nitro-2-aminoresorcinol, red needles, m. p. 182° (the *hydrochloride*, which darkens above 225°, is described). The amine is transformed by nitrous acid into 5-nitro-3-nitrosoamino-4-hydroxy-o-quinoneoxime (annexed formula), small, yellow, hexagonal rods; the substance is not converted by hydrochloric acid into a diazonium



compound which can undergo coupling, whilst also chlorine cannot be introduced by means of Gattermann's copper powder.

The constitution of 4-nitro-2-aminoresorcinol is established by the conversion of 2-aminoresorcinol into 2-acetamidoresorcinyldiacetate, colourless needles, m. p. 104°, which is subsequently transformed into 4-nitro-2-acetamidoresorcinyldiacetate, almost colourless plates, m. p. 123°; the latter compound is hydrolysed to 4-nitro-2-aminoresorcinol, m. p. 182°, which is identical with the product described above.

2-Nitro-4-aminopyrocatechol is conveniently prepared by the partial reduction of 2:4-dinitropyrocatechol by stannous chloride. The constitution of the compound is established by the observation that 4-aminopyrocatechol is converted by acetic anhydride and sodium acetate into 4-acetamidopyrocatechyl diacetate, colourless needles, m. p. 198°, which is nitrated to 6-nitro-4-acetamidopyrocatechyl diacetate, almost colourless needles, m. p. 207°. The nitroaminopyrocatechol obtained by the hydrolysis of this compound is identical with that derived from 2:4-dinitropyrocatechol. H. W.

The Moderated Bromination of Organic Compounds.

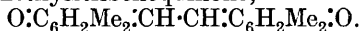
KARL W. ROSENMUND, W. KUHNHENN, and W. LESCH (*Ber.*, 1923, 56, [B], 2042—2044; cf. Rosenmund and Kuhnenn, this vol., i, 782).—Further examples of the authors' method of bromination are cited. Generally, bromine is added to a solution of quinoline sulphate and the compound to be brominated in glacial acetic acid, but in some cases quinoline hydrochloride is to be preferred. When this process leads to perbromination, a solution of quinoline sulphate and bromine in glacial acetic acid is first prepared and then added to the substance to be brominated.

The following examples are described in detail: *Bromoacetylpyrogallol*, $\text{COMe}\cdot\text{C}_6\text{HBr}(\text{OH})_3\cdot\text{H}_2\text{O}$, long needles, m. p. 186°, from acetylpyrogallol (bromoacetylpyrogallyl triacetate has m. p. 108°); *Bromoacetylresorcinol*, $\text{COMe}\cdot\text{C}_6\text{H}_2\text{Br}(\text{OH})_2$, colourless needles, m. p. 139°; *Bromochloroacetylpyrocatechol*, $\text{C}_8\text{H}_6\text{O}_3\text{ClBr}$, small, colourless needles, m. p. 137°; 3-*Bromotyrosine*, $\text{C}_9\text{H}_{10}\text{O}_3\text{NBr}\cdot 2\text{H}_2\text{O}$, m. p. 223° (decomp.).

In reply to the criticisms of Krause (this vol., i, 891; cf. A., 1918, i, 415), it is pointed out that identical results are not obtained by bromination in pyridine solution and by the authors' method.

H. W.

The Dehydrogenation of Mesityl. STEFAN GOLDSCHMIDT and HANNS BERNARD (*Ber.*, 1923, 56, [B], 1963—1967).—Porter and Thurber (*A.*, 1921, i, 505) have described the isolation of a red, crystalline substance, m. p. 50°, by the oxidation of a solution of mesitol in benzene by silver oxide, which they have considered to be derived by the combination of a molecule of mesitol with a second molecule of the same substance which has been oxidised in such a manner as to contain either univalent oxygen or tervalent carbon. This conception appears so improbable to the authors that they have repeated the work and thus drawn the conclusion that Porter and Thurber's compound has the composition $C_{18}H_{18}O_2$ instead of $C_{18}H_{23}O_2$ and is most probably 3 : 5 : 3' : 5'-tetramethylstilbenequinone,



The oxidation of mesitol by silver oxide yields the compound, $C_{18}H_{18}O_2$, red crystals, which decompose without melting above 200°. It is reduced by phenylhydrazine dissolved in chloroform to 4 : 4'-dihydroxy-3 : 5 : 3' : 5'-tetramethylstilbene, colourless crystals without a distinct melting point, which gives a *diacetate*, colourless prisms, m. p. 237°; the hydroxy-compound is converted by silver oxide into the red quinone, decomp. above 200°.

Dihydroxytetramethylstilbene is prepared by the condensation of chloral hydrate and *m*-2-xyleneol in the presence of glacial acetic and concentrated sulphuric acid to *trichloro*-4 : 4'-dihydroxy-3 : 5 : 3' : 5'-tetramethyldiphenylethane, $CCl_3 \cdot CH(C_6H_2Me_2 \cdot OH)_2$, m. p. 202—207° (corr.), and treatment of the latter with zinc dust in the presence of boiling alcohol. H. W.

Studies in the Anthracene Series. VI. EDWARD DE BARRY BARNETT and MARCUS AURELIUS MATTHEWS (*T.*, 1923, 123, 2549—2557).

Studies in the Anthracene Series. VII. EDWARD DE BARRY BARNETT and JAMES WILFRED COOK (*T.*, 1923, 123, 2631—2642).

The Preparation of the Isomeric Methoxybenzyl Bromides. JOHN BALDWIN SHOESMITH (*T.*, 1923, 123, 2698—2703).

Application of the Grignard Reaction to some Acetylenic Compounds. I. Preparation of Diacetylenic Glycols. FORSYTH JAMES WILSON and WILLIAM MCNINCH HYSLOP (*T.*, 1923, 123, 2612—2618).

Catechin. V. Structurally Isomeric Catechins. M. NIERENSTEIN (*Ber.*, 1923, 56, [B], 1877—1879; cf. Nierenstein, *T.*, 1922, 121, 609).—It has been shown previously (*loc. cit.*) that tetramethylacacatechin, $C_{13}H_7O(OMe)_4(:CH):CH \cdot OH$ can be converted into a pentamethyl derivative, $C_{13}H_7O(OMe)_4(:CH_2):C \cdot OMe$, which is now shown to be identical with the pentamethyl derivative of catechin-*C* which occurs in small amount in cube-gambier and in Pegu catechin; it is designated *isoacacatechin*. The two pentamethyl derivatives can be partly demethylated, yielding, respectively, tetramethylacacatechin and *tetramethylisoacacatechin*.

$C_{13}H_7O(OMe)_4:(CH_2):C\cdot OH$, small, prismatic needles, m. p. 171—172°.

Monoacetyltetramethylisocatechin crystallises in small needles, m. p. 157—158°, whereas the corresponding *benzoyl* derivative has m. p. 141—142°. H. W.

Stereoisomeric 1-Phenylcyclohexane-1:2-diols. S. NAMETKIN and N. IVANOV (*Ber.*, 1923, 56, [B], 1805—1807).—The oxidation of 1-phenyl- Δ^1 -cyclohexene occurs in a manner closely analogous to that of 1-methyl- Δ^1 -cyclohexene (Nametkin and Jarzev, this vol., i, 1081).

1-Phenylcyclohexane-1-ol is converted by treatment with sulphuric acid on the boiling water-bath into 1-phenyl- Δ^1 -cyclohexene, b. p. 128°/16 mm., d_4^{20} 0.9939, n_D^{20} 1.5695. The hydrocarbon is oxidised by benzoyl peroxide in ethereal solution to 1-phenylcyclohexene 1-oxide, a colourless, oily liquid, b. p. 142—143°/25 mm., d_4^{20} 1.0561, n_D^{20} 1.5434, which is transformed by water at 110° into *cis*-1-phenylcyclohexane-1:2-diol, $C_{12}H_{16}O_2$, four-sided prisms, m. p. 95°. On the other hand, the hydrocarbon is oxidised by permanganate to *trans*-1-phenylcyclohexane-1:2-diol, a viscous liquid, b. p. 166—167°/12 mm., and δ -benzoylvaleric acid.

H. W.

The Chemistry of the Three-carbon System. II. Tautomeric Nitriles and Cyano-esters. STANLEY FRANCIS BIRCH and GEORGE ARMAND ROBERT KON (*T.*, 1923, 123, 2440—2448).

Attempt to Prepare Dihydrocampholytolactone by the Aid of the Windaus "Glutaric Acid Degradation." MARIA BREDT-SAVELSBERG (*J. pr. Chem.*, 1922, [ii], 105, 149—157).—The action of iodine and sand on silver *cis*-camphorate at 150° gives *cis*-camphoric acid, and not, as expected, dihydrocampholytolactone. Under similar conditions, *tert*-silver *sec*-methyl camphorate is partly converted into camphoric anhydride. The Windaus method for distinguishing substituted glutaric and succinic acids (*A.*, 1921, i, 392) cannot, therefore, be applied, without possibility of error, to ring-bound dibasic acids. W. S. N.

Chlorination of Benzoyl Chloride. II. EDWARD HOPE and GEORGE CLIFFORD RILEY (*T.*, 1923, 123, 2470—2480).

The Sweetness of "Saccharin." The Electrolytic Dissociation of *o*-Benzoylsulphimide. O. J. MAGIDSON and S. W. GORBATSCHOV (*Ber.*, 1923, 56, [B], 1810—1817).—From a consideration of the sweetness of various derivatives of "saccharin," the authors draw the conclusion that it is the "saccharin"-ion and not the molecule which causes its solutions to have a sweet taste. It is shown that, in accordance with this view, its sweetening power and molecular conductivity are affected very similarly by dilution. Similarly, the sweetness of "sodium-saccharin," or "crystalline" is depressed in the presence of other sodium-ions, exactly as would be expected in accordance with theory. "N-Saccharinacetic acid" [*o*-benzoic-sulphinidoacetic acid] was prepared

by the action of ethyl chloroacetate on "sodium saccharin," and crystallises in needles, m. p. 212—215°. It has a bitter, acid taste, and its dissociation constant ($k=0.14 \times 10^{-4}$) is practically that of acetic acid. H. H.

The Resolution of Hydratropic Acid. HENRY STANLEY RAPER (T., 1923, 123, 2557—2559).

Action of Dimethyl Sulphate on Salicylic Acid, Methyl Salicylate, and o-Methoxybenzoic Acid. Sulphonation and Methylation. L. J. SIMON and M. FRÈREJACQUE (*Compt. rend.*, 1923, 177, 533—536; cf. this vol., i, 462).—Salicylic acid, when heated with potassium methyl sulphate, gives a 40% yield of methyl salicylate, but on heating with methyl sulphate at 110—120° affords a mixture of roughly equal amounts of methyl sulphosalicylate, $[\text{OH} : \text{SO}_3\text{H}=1 : 4]$, and its methyl ester (Blau, A., 1897, i, 413). One mol. of methyl sulphate gives a mixture of unchanged salicylic acid and methyl sulphosalicylate, the latter also resulting by the action of either sulphuric acid or methyl sulphate on methyl salicylate. When o-methoxybenzoic acid is heated with 3 mols. of methyl sulphate, the sulphonic acid of its methyl ester, the dimethyl ester of sulphosalicylic acid, and small quantities of methyl sulphosalicylate are produced. E. E. T.

The Isomerism and Polymerism of Salicylides. RICHARD ANSCHÜTZ (*J. pr. Chem.*, 1922, [ii], 105, 158—164).—The facts at present known about α -disalicylide, β -disalicylide, tetrasalicylide, and polysalicylide are collected, classified, and discussed.

W. S. N.

A New Method for the Resolution of Asymmetric Compounds. A Reply. JULIUS BEREND COHEN (T., 1923, 123, 2716).

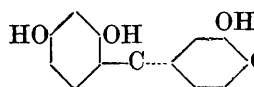
Preparations from Maleic and Fumaric Acids. HAROLD G. ODDY (*J. Amer. Chem. Soc.*, 1923, 45, 2156—2160).—The best conditions are described for the preparation of β -benzoylacrylic acid (Pechman, A., 1882, 1074; Gabriel and Colman, A., 1899, i, 390) and of β -toluoylacrylic acid (Pechman, *loc. cit.*; Kosniewski and Marchlewski, *Chem. Zentr.*, 1906, ii, 1190) from benzene, or toluene, respectively, and maleic anhydride, in the presence of aluminium chloride. The acid prepared from toluene gives, when boiled with 10% sodium hydroxide solution, a tolyl methyl ketone, from which *p*-toluic acid is obtained by the action of cold, alkaline potassium ferricyanide solution; hence the acid is β -*p*-toluoylacrylic acid. Its methyl ester forms long, colourless needles, m. p. 45.5—46°, b. p. 240—245°/115 mm. The acid reacts in the cold with concentrated hydrochloric acid to give α -chloro- β -*p*-toluoylpropionic acid, m. p. 144—144.5°, and with bromine in cold, acetic acid solution to give $\alpha\beta$ -dibromo- β -*p*-toluoylpropionic acid. The action of maleic anhydride on naphthalene in warm benzene

solution in the presence of aluminium chloride gives $\beta\beta$ -*naphthoylacrylic acid*, m. p. 189—190° (*silver salt, methyl ester, plates*, m. p. 94—95°), which gives β -*naphthoic acid* when oxidised by means of sodium dichromate and acetic acid at 100°. In the above condensation, a second *compound*, m. p. 158—159°, is also formed. The use of diphenyl and maleic anhydride leads to the formation of β -*p-phenylbenzoylacrylic acid*, yellow needles, m. p. 167—168° (*sodium salt, silver salt, methyl ester*, m. p. 73·5—74°), which reacts with bromine in hot, acetic acid solution to give α - β -*dibromo- β -p-phenylbenzoylpropionic acid*, m. p. 180—181° (white *methyl ester*, m. p. 120—121°), which gives *p-phenylbenzoic acid* on being fused at 160° with potassium hydroxide. Maleic anhydride and anthracene react at 60—70° in benzene solution in the presence of aluminium chloride to give β -*meso-anthroylacrylic acid*, colourless crystals, m. p. 261° (*sodium salt, ammonium salt*), which does not react with bromine in cold or hot acetic acid solution, and is unaffected by fusion at 250° with potassium hydroxide; its *methyl ester* forms long needles, m. p. 149·5—150°. *trans*-Di-*p-toluylethylene* has m. p. 134·5° (Conant and Lutz, this vol., i, 685, give m. p. 148°); it is changed to the *cis*-form by exposure to sunlight in acetic acid solution (cf. Conant and Lutz, *loc. cit.*). Either form is converted by means of bromine in acetic acid solution into *dibromodi-p-toluolethane*, colourless needles, m. p. 200—200·5°, which gives *p-toluic acid* when fused at 130° with potassium hydroxide. Fumaryl chloride and *m*-xylene react in the presence of aluminium chloride to give *trans-di-o : p-xyloylethylene*, yellow crystals, m. p. 125·5—126°, which is partly converted into the colourless *cis*-form, needles, m. p. 65—65·5°, by the action of sunlight on its methyl-alcoholic solution. Either forms give, on treatment with bromine in hot, acetic acid solution, *dibromodi-o : p-xylolethane*, white needles, m. p. 145°, which is converted into *o : p*-dimethylbenzoic acid by the action of fused potassium hydroxide at 135°. *Di-p-phenylbenzoylethylene*, a yellow powder, m. p. 247·5—248°, is prepared by keeping a mixture of fumaryl chloride, diphenyl, benzene, and aluminium chloride; it is apparently the *trans*-form, but is not changed by the action of sunlight on its chloroform solution. It reacts with bromine in chloroform solution to give *dibromodi-p-phenylbenzoylethane*, a white solid, m. p. 218—218·5°, the structure of which is assumed. Rubidge and Qua's method (A., 1914, i, 539) for the preparation of diphenylphthalide is not applicable to the preparation of diphenylcrotonolactone from maleic anhydride. Neither can this lactone be prepared by the action of benzene and aluminium chloride on the mixed *anhydride*, m. p. 113—114°, of acetic acid and β -benzoylacrylic acid.

W. S. N.

The Formation of 3 : 5-Dinitro- β -resorcylic Acid by the Action of Concentrated Nitric Acid on Extracts of Quebracho Wood and Mimosa Bark. HANS EINBECK and LUDWIG JABLONSKI (*Ber.*, 1923, 56, [B], 1906—1908).—3 : 5-Dinitro-3-resorcylic acid has been obtained by the action of nitric acid on the

extracts of quebracho wood and mimosa bark in addition to styphnic acid (cf. Einbeck and Jablonski, A., 1921, i, 505); the former substance appears to be the precursor of the latter in the reaction. It appears, therefore, that the quebracho tannin contains the grouping shown in the annexed scheme.

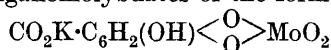


[With H. SCHWABE.]—The following derivatives of 3 : 5-dinitro- β -resorcylic acid are described : the *monopotassium* salt, pale yellow needles; the explosive *dipotassium* salt, pale, orange-coloured needles; the *monomethyl* ester, lustrous rodlets, m. p. 196°. H. W.

Hetero-poly-compounds of Gallic Acid with the Anhydrides, MoO_3 , WO_3 , and UO_3 . L. FERNANDES (*Gazzetta*, 1923, 53, 514—520).—With numerous organic hydroxy-acids molybdic anhydride forms compounds with a complex anion assumed to be formed by elimination of a molecule of water from the anhydride and the alcoholic hydroxyl group. This hypothesis is supported by the results obtained with gallic acid and the trioxides of the heavy elements of the sixth group of the periodic system. Thus, the intense coloration of the compounds obtained is characteristic of phenolic reactions, and the reaction occurs even better when the hydrogen of the carboxyl group is replaced by a metal, the formation of double salts being thus virtually excluded. Three series of compounds are formed, according as one, two, or three of the hydroxyls of the gallic acid are substituted by metals. Finally, cryoscopic determinations demonstrate the formation of complex anions which are only very slightly dissociated.

Sodium, *potassium*, and *ammonium monogallomolybdates* of the form $\text{MoO}_2[\text{O} \cdot \text{C}_6\text{H}_2(\text{OH})_2 \cdot \text{CO}_2\text{K}]_2$ form deep red, lustrous, scaly masses and are readily soluble in water and stable towards dilute acids.

The following digallomolybdates of the form



were prepared and analysed : *potassium*, at first red, darkening to chestnut later; *thallium*, green and amorphous; *barium*, pale chestnut; *nickel*, greenish-black and microcrystalline. The tri-substituted *potassium* compound, $\text{MoO}_2[\text{O} \cdot \text{C}_6\text{H}_2(\text{CO}_2\text{K}) < \overset{\text{O}}{\text{O}} > \text{MoO}_2]_2$, forms deep chestnut, slender needles.

The gallotungstates prepared were : *Potassium monogallotungstate*, $\text{WO}_2[\text{O} \cdot \text{C}_6\text{H}_2(\text{OH})_2 \cdot \text{CO}_2\text{K}]_2$, a deep chestnut, amorphous compound; *potassium digallotungstate*, $\text{CO}_2\text{K} \cdot \text{C}_6\text{H}_2(\text{OH}) < \overset{\text{O}}{\text{O}} > \text{WO}_2$; and *potassium trigallotungstate*, a brown, amorphous precipitate. The three corresponding *potassium gallouranates* were also prepared.

T. H. P.

The Isomerism of the Oximes. XIV. 3-Nitro- and 3-Bromo-*p*-dimethylaminobenzaldoximes. OSCAR LISLE BRADY and RICHARD TRUSZKOWSKI (T., 1923, 123, 2434—2439).

Certain Salts of Probable *meta*-Quinonoid Structure.

G. RASTELLI (*Gazzetta*, 1923, **53**, 485—486).—The investigations previously described (A., 1922, i, 1073) have now been extended to the *m*-nitrophenylhydrazones of benzaldehyde and tribromo-*m*-benzoquinone.

The pale yellow acetone solution of benzaldehyde *m*-nitrophenylhydrazone immediately becomes deep green on addition of sodium ethoxide; in presence of a large excess of the latter, these saline compounds decompose and, if the solutions are dilute, the green colour disappears in the course of a few hours. Under similar conditions, pyruvic acid *m*-nitrophenylhydrazone exhibits only a slight green coloration which disappears almost immediately. Like many quinones and also the salts of the corresponding para- and ortho-derivatives, the alkali salt of benzaldehyde-*m*-nitrophenylhydrazone exhibits a pronounced absorption band at about $N=2000$. The same position is occupied by the principal band for tribromo-*m*-benzoquinone *m*-nitrophenylhydrazone, which is, however, dimeric. A quinonoid structure must be assumed for the alkali salts of these hydrazones.

T. H. P.

Synthesis of an Aldehyde having an Odour of Vervain : isoPropyl-*p*-ethanalbenzene [*p*-Cymylacetaldehyde]. L. BERT (*Compt. rend.*, 1923, **177**, 550—551).—*p*-Cymylacetaldehyde, $C_6H_4Pr\cdot CH_2\cdot CHO$, was prepared by condensing magnesium cymyl chloride with ethyl orthoformate and hydrolysis of the resulting product with sulphuric acid, the aldehyde being separated by means of its bisulphite compound. It is a pale yellow liquid, less dense than water, b. p. 243° , and has a strong odour of vervain. Although a reducing agent, it is without action on Fehling's solution. The semicarbazone, m. p. 181° , forms white spangles.

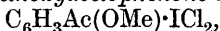
H. J. E.

Condensation of Diphenylformamidine with Phenols. I. A New Synthesis of β -Resorcyraldehyde. JOHN BALDWIN SHOESMITH and JOHN HALDANE (*T.*, 1923, **123**, 2704—2707).

The Relation between Molecular Structure and Odour in Trisubstituted Benzenes. I. Derivatives of *p*-Methoxyacetophenone. MARSTON TAYLOR BOGERT and LEO PATRICK CURTIN (*J. Amer. Chem. Soc.*, 1923, **45**, 2161—2167).—A number of derivatives of *p*-methoxyacetophenone, containing a substituent ortho to the methoxyl radicle, have been synthesised, and shown to be odourless. Thus a trisubstituted benzene carrying osmophores in the positions 1:3:4 is not always odorous, even if sufficiently volatile.

Sodium *p*-methoxyacetophenonesulphonate, large, snow-white, fatty leaflets, is obtained from the product of the action of cold fuming sulphuric acid (30% SO_3) on *p*-methoxyacetophenone; it reacts with methyl sulphate to give the *methyl* ester, a colourless liquid. *m*-Nitro-*p*-methoxyacetophenone may be obtained in 95% yield by the action of a cold (0°) mixture of concentrated nitric and sulphuric acids on *p*-methoxyacetophenone; it is reduced by means of tin and hydrochloric acid to *m*-amino-*p*-methoxyacetophenone,

large, flat, colourless, odourless, hexagonal prisms, m. p. 102° (corr.), yield 74%, *acetyl* derivative, colourless, rhombic prisms, m. p. 122.5° (corr.), *benzylidene* derivative, a solid which easily liquefies, *p-nitrobenzylidene* derivative, an amorphous solid, deep red to yellow, softens 135°, m. p. indefinite, about 160°. *m-Iodo-p-methoxyacetophenone*, yellow, feathery, odourless needles, m. p. 103.6° (corr.), is obtained from the amine by the aid of the diazo-reaction; it is converted by the action of dry chlorine, in chloroform solution, into *p-methoxyacetophenone-m-iodochloride*,



small, bright yellow crystals, which is unstable, but reacts, when freshly precipitated, with 5*M*-potassium hydroxide solution to give *m-iodoso-p-methoxyacetophenone*, a greyish-white, amorphous mass (decomp. suddenly when heated), and *m-iodoso-p-hydroxyacetophenone*, long, pale yellow needles, m. p. 243° (but decomp. suddenly when rapidly heated). *m-Cyano-p-methoxyacetophenone*, slender, pale yellow, odourless needles, m. p. 159.5° (corr.), is prepared in the usual way from the amine, yield 70%; it cannot be hydrolysed to the corresponding amide or acid, and is not converted into the iminochloride by means of anhydrous methyl-alcoholic hydrogen chloride. *5-Acetyl-2-methoxydiazobenzene perbromide*, pale yellow, flat needles, m. p. 68–70°, is immediately precipitated in almost the theoretical yield when bromine in hydrobromic acid solution is added to the diazonium chloride; it gradually decomposes on keeping. The action of ammonium hydroxide solution on an aqueous suspension of the perbromide gives *5-acetyl-2-methoxy-azidobenzene*, $\text{OMe}\cdot\text{C}_6\text{H}_3\text{Ac}\cdot\text{N}_3$, faintly pinkish-buff, long, delicate needles, m. p. 87° (decomp. corr.) (explodes if heated rapidly). *5 : 5'-Diacetyl-2 : 2'-dimethoxydiazoaminobenzene*, small, pale yellow needles, m. p. 178° (corr.), yield 95%, is obtained by diazotising the amine (above), and treating the product with the amine hydrochloride. When it is kept in an aqueous solution containing an equivalent quantity of hydrochloric acid, it is partly converted into *4-amino-5 : 5'-diacetyl-2 : 2'-dimethoxyazobenzene*, dark red, microscopic crystals, m. p. 198–200° (corr.).

From observations on the properties and reactions of the above-mentioned compounds, the following clauses are added to V. Meyer's laws governing steric hindrance. (1) The hindering effect of an interfering group diminishes as the molecular weight of the reacting group in the ortho-position increases. (2) It also diminishes with increasing molecular weight of the foreign reacting molecule.

W. S. N.

Derivatives of Dihydroxydiphenylsulphone. O. HINSBERG (*Ber.*, 1923, 56, [B], 2008–2012).—A further instance of stereoisomerism analogous to that of the β -naphthol sulphide is described (cf. Hinsberg, A., 1919, i, 202). *p*-Dihydroxydiphenylsulphone, $\text{C}_6\text{H}_5\cdot\text{SO}_2\cdot\text{C}_6\text{H}_3(\text{OH})_2$, loses one molecular proportion of water when heated at 250–270° and yields a mixture of *isophenyl-p-benzoquinonylsulphoxide*, $\text{C}_6\text{H}_5\cdot\text{SO}\cdot\text{C}_6\text{H}_3\text{O}_2$, and *isodiphenylene-sulphidoquinone*, $\text{C}_6\text{H}_4\text{—}\overset{\text{S}}{\text{—}}\text{C}_6\text{H}_2\text{O}_2$, slender, yellowish-brown

needles, m. p. 80—85°, which has not been separated completely into its components. The quinonoid nature of the product is established by its reaction with very approximately one molecular proportion of *p*-nitrophenylhydrazine. Treatment of the mixture with acetic anhydride and zinc dust yields *isodiacetoxydiphenyl sulphide*, $\text{SPh} \cdot \text{C}_6\text{H}_3(\text{OAc})_2$, small, yellow needles, m. p. 65°, and *isodiacetoxydiphenylene sulphide*, $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{S} \diagdown \end{array} \text{C}_6\text{H}_2(\text{OAc})_2$, small, yellow crystals, m. p. 126°, which can be separated from one another by taking advantage of the difference in solubility in methyl alcohol; if the reduction is effected at the atmospheric temperature, *isodiacetoxydiphenyl sulphoxide*, $\text{SOPh} \cdot \text{C}_6\text{H}_3(\text{OAc})_2$, colourless crystals, m. p. 95°, can be isolated, which is also produced by the careful oxidation of the sulphide dissolved in glacial acetic acid by means of hydrogen peroxide. *isoDiacetoxydiphenylene sulphoxide* crystallises in small, yellow needles, m. p. 185°. More energetic oxidation of *isodiacetoxydiphenyl sulphide* or of the corresponding sulphoxide with hydrogen peroxide leads to the production of *isodiacetoxydiphenylsulphone*, which has not been isolated in the homogeneous condition; it is, however, shown to be distinct from the normal *diacetoxydiphenylsulphone*, leaflets or pointed prisms, m. p. 129°. H. W.

Preparation of 1-Phenylimino-2-naphthaquinone. SOCIÉTÉ ANONYME DES MATIÈRES COLORANTES ET PRODUITS CHIMIQUES DE ST. DENIS, ANDRÉ RAOUL WAHL, and ROBERT LINTZ (Brit. Pat. 191064).—2-Hydroxy-1-phenylnaphthylamine (this vol., i, 674) is readily oxidised in alkaline solution by air or other oxidising agents to 1-phenylimino-2-naphthaquinone, a green, crystalline, very unstable substance which dissolves in solvents such as acetone or ether with a blue colour. In sulphuric acid the solution is reddish-brown. For example, 94 g. of 2-hydroxy-1-phenylnaphthylamine are dissolved in a warm mixture of 80 c.c. of sodium hydroxide solution (40° Bé.) and 700 to 800 c.c. of alcohol and the solution poured into 14 litres of ice-water and filtered. A concentrated solution of sodium hypochlorite containing the theoretical quantity of chlorine in 8—10 litres of water is then added with vigorous stirring, keeping the temperature at 5°, and controlling the reaction with starch-iodide paper. The crystalline precipitate can be purified by recrystallisation from diluted acetone or a mixture of ether and light petroleum. P. M.

Anthraquinone as a Catalyst in the Discharge of α -Naphthylamine-claret. Sodium β -anthranolsulphonate. M. BATTEGAY and PH. BRANDT (*Bull. Soc. Ind. Mulhouse*, 1923, 89, 365—375).—Reduction of anthraquinone- β -sulphonic acid by means of sodium formaldehyde-sulphoxylate under conditions similar to those employed in textile printing for the discharge of insoluble azo-dyes, results in the formation of anthranol- and anthrone- β -sulphonic acids which are stable and therefore do not assist the discharge process. Derivatives of anthracene- β -sulphonic acid are not formed simultaneously. The pure sodium salts of anthranol-

and anthrone- β -sulphonic acids were prepared, the former as yellow and the latter as almost colourless, crystalline spangles, both being stable at 130°. Sodium β -anthranol-sulphonate is more stable than the free acid. It yields a yellow solution in concentrated sulphuric acid and readily decolorises solutions of iodine and bromine, thereby forming anthraquinone- β -sulphonic acid. When dissolved in warm 60% alcohol, it is partly converted into the isomeric anthrone, the conversion being completed by addition of hydrochloric acid. Sodium anthranolsulphonate readily forms a violet condensation product with *p*-nitrosodimethylaniline. It is decomposed by acids, thereby forming sodium anthraquinone- β -sulphonate and dimethyl-*p*-phenylenediamine. Sodium anthranol- β -sulphonate couples with diazotised *p*-nitroaniline in neutral solution, forming a simple azo-compound, orange needles. The corresponding anthrone compound couples with diazo-compounds only in the presence of sodium acetate. Sodium anthrone- β -sulphonate is less soluble than the anthranol compound in water.

A. J. H.

Reduction in the Anthraquinone Series. M. BATTEGAY and HUEBER (*Bull. Soc. chim.*, 1923, [iv], **33**, 1094—1098).—Anthraquinone- β -sulphonic acid is reduced in alkaline solution by means of sodium hyposulphite to anthranol- β -sulphonic acid, and further, to anthrone- β -sulphonic acid. It is found that both anthraquinone itself and anthraquinone- α -sulphonic acid behave in a similar manner, and the authors suggest that this may be a general reaction. H. H.

Reduction Products of Hydroxyanthraquinones. III. ARNOLD BREARE and ARTHUR GEORGE PERKIN (*T.*, 1923, **123**, 2603—2611).

Occurrence of *l*-Menthone in Pine Oil. A. H. GILL (*Ind. Eng. Chem.*, 1923, **15**, 887).—A commercial sample of pine oil known as "apinol" was distilled under 4 mm. pressure. About 60% distilled over between 74° and 79°, and 10% between 79° and 100°. By repeated fractionation of the first fraction at atmospheric pressure two distinct fractions were isolated, one boiling at 202—203°, constituting 8% of the original oil, which was identified as optically inactive fenchyl alcohol, and the other at 208.5—209.5°, which constituted 20% of the original oil, and had an optical rotation of $-20^{\circ} 28'$. The latter fraction was identified as *l*-menthone by converting it into its semicarbazone (m. p. 184°). This is the first time *l*-menthone has been isolated from oils from the *Pinus* family of trees.

H. C. R.

Camphor and Nitrophenols. N. N. EFREMOV (*Bull. acad. Sci. Russie*, 1919, 255—286).—Nitrophenols do not form molecular compounds, as do phenols, with camphor. Photomicrographs are given for mixtures containing 20 and 70% of picric acid, styphnic acid, and nitroresorcinol, respectively. The eutectic composition, eutectic temperature, and limits of solid solution, respectively, are: *o*-nitrophenol, 45%, 11.8°, 100—92%; *m*-nitrophenol, 41.5%, 16°, 100—65% (approx.); *p*-nitrophenol, 36%, -2° , 0—13

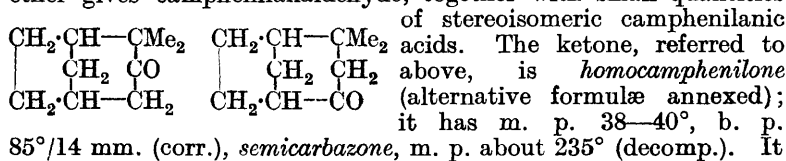
and 70—100% (approx.); 2:4-dinitrophenol, 30.7%, 69.3°, 93—100%; picric acid, 30.5%, 66.4°, 96—100%; 2-nitroresorcinol, 39.3%, 4.6°, 90—100%; 2:4-dinitroresorcinol, 29%, 47.2°, 0—15 and 68—100% (approx.); styphnic acid, 25.3%, 82.6°, 89—100%; " $C_8H_3(OH)_2NO_2$," 33.2%, 26.4°, 0—23 and 73—100% (approx.); 4-nitropyrocatechol, 38%, 25.8°, 0—8 and 86—100% (approx.).

CHEMICAL ABSTRACTS.

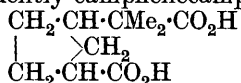
Some New Constituents of Camphor Oil. F. ROCHUSSEN (*J. pr. Chem.*, 1922, [ii], 105, 120—136).—Ethylguaiaicol, $C_8H_3Et(OMe) \cdot OH$, b. p. 94—95°/5 mm., d^{15}_4 1.0473, n^{20}_D 1.53340, has been isolated from the phenol fraction of camphor oil; its crystalline *benzoate* has m. p. 59°. The acid fraction contains *n*-hexoic acid, which is isolated as its ethyl ester, b. p. 55—56°/10 mm., and *r*-citronellic acid. The latter has b. p. 116—118°/3 mm., 121°/3.5 mm., or 126°/4 mm., d^{15}_4 0.9557, $\alpha_D +0^\circ 51'$, 200 mm. (? due to impurity), n^{15}_D 1.46231, n^{20}_D 1.46062, amide, m. p. 88—90°, ethyl ester, b. p. 86°/3 mm. On oxidation by means of potassium dichromate in boiling sulphuric acid solution it gives acetone and β -methyladipic acid, whilst β -methylhexoic acid is formed by fusion at 250—300° with potassium hydroxide and a little water. *r*-Citronellic acid is converted by the action of boiling dilute sulphuric acid into a *lactone*, b. p. 102—103°/4.5 mm., which gives, on hydrolysis, a mixture of unsaturated and hydroxy-acids, as shown by analysis of a silver salt. The formation of this lactone is presumably preceded by a migration of the double bond.

W. S. N.

The Bromination of Camphene ; Dicumphenyl Ether and a Ring-Homologue of Camphenilone. P. LIPP (*J. pr. Chem.*, 1922, [ii], 105, 50—64).—The action of anhydrous potassium hydroxide on boiling ω -bromocamphene leads to the formation of a ketone (below), which may be removed in a current of steam, and of *dicumphenyl ether*, $(C_{10}H_{15})_2O$, a colourless oil, b. p. 182°/9.5 mm. (corr.), having a slight odour of geranium. This ether is unattacked by metallic sodium in boiling xylene solution, but immediately decolorises alkaline potassium permanganate solution or bromine in chloroform solution. In the latter reaction, approximately 4 atoms of halogen are absorbed. No pure product could be isolated by reducing the compound in anhydrous ethereal solution by means of hydrogen and platinum black, or by oxidation by means of potassium permanganate, but the action of chromium trioxide in cold, glacial acetic acid solution gives a ketone of the C_{10} series, the *semicarbazone* of which decomposes at 227—228° (corr.). The action of warm, 50% sulphuric acid on dicumphenyl ether gives camphenilanaldehyde, together with small quantities of stereoisomeric camphenilanic acids. The ketone, referred to above, is *homocamphenilone* (alternative formulæ annexed); it has m. p. 38—40°, b. p. 85°/14 mm. (corr.), *semicarbazone*, m. p. about 235° (decomp.). It



closely resembles camphenilone, but is readily attacked by alkaline potassium permanganate at 100°, with formation of an acid, m. p. 136—138° (corr.), evidently camphenecamphoric acid,



W. S. N.

The Constituents of some Indian Essential Oils. XI. The Essential Oil from the Leaves of *Cupressus torulosa*, Don.

JOHN LIONEL SIMONSEN (*Indian For. Rec.*, 1923, 10, 1—10).—The leaves of *Cupressus torulosa*, the Himalayan cypress, yield, on distillation in steam, 0.5 to 0.8% of a pale brown oil with d_{40}^{30} 0.87, n_D^{30} 1.479, and $[\alpha]_D^{30} +41.72^\circ$. This oil has been found to contain *d*-sabinene, α -pinene, dipentene, and terpinene, together with propionic, *n*-octoic, and *n*-dodecoic acids in the free or combined state. Treatment with sulphuric acid gave, amongst other products, *trans*-terpin, from which the presence of γ -terpineol in the original oil is inferred. This compound has not hitherto been found in any naturally occurring essential oil, but, unfortunately, was not present in this one in sufficient quantity to permit of its isolation. In addition to the above compounds, two sesquiterpene fractions were isolated, having b. p. 195—200°/100 mm., d_{30}^{30} 0.9162, n_D^{30} 1.507, $[\alpha]_D^{30} -15.9^\circ$, empirical formula $\text{C}_{15}\text{H}_{24}$, and b. p. 205—220°/100 mm., d_{30}^{30} 0.9419, n_D^{30} 1.506, $[\alpha]_D^{30} -19.2^\circ$, and empirical formula $\text{C}_{15}\text{H}_{26}\text{O}$.
H. H.

The Constituents of Indian Turpentine from *Pinus longifolia*, Roxb. III. JOHN LIONEL SIMONSEN (*T.*, 1923, 123, 2642—2666).

Swelling of Caoutchouc. M. LE BLANC and M. KRÖGER (*Kolloid Z.*, 1923, 23, 168—176).—The swelling of caoutchouc in a number of organic solvents has been investigated. It is shown that the maximum swelling in a series (27) of organic solvents increases with increasing dielectric constant. Compounds containing halogens or sulphur have an increased swelling power. The velocity of vulcanisation of caoutchouc sols in different solvents shows very marked differences. With the exception of carbon tetrachloride, it is greatest in solvents containing chlorine, following these come the bromine derivatives and finally the hydrocarbons. Carbon disulphide and carbon tetrachloride solutions have the smallest velocity. At the commencement the velocity of the swelling is strongly dependent on the viscosity of the solvent, and because of this, the weakly swelling liquids have a swelling velocity many times as great as that of the strongly swelling liquids at the commencement. Carbon disulphide and mercaptan have the greatest swelling velocity; this is due largely to their strong swelling property and their low viscosity, but not entirely, for benzene at 60°, when its viscosity is much reduced, does not reach the swelling velocity of carbon disulphide. The various varieties of caoutchouc take up the solvent more rapidly the smaller the value of their maximum swelling. Many exceptions to this statement are found,

but it is strictly true in the case of bromine. The outstanding position of carbon disulphide in cold vulcanisation is due to its unusually large swelling velocity, and to the fact that every vulcanising agent is active slowly in it. Its swelling properties are inferior only to those of mercaptan; carbon tetrachloride is inferior to it in this respect, but this solvent has the advantage that vulcanisation takes place slowly in it.

J. F. S.

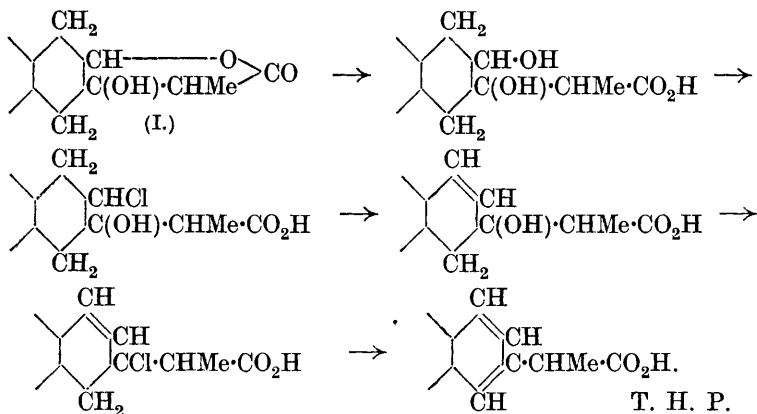
Relation between Ability to form Resins and Chemical Constitution. IV. W. HERZOG and J. KREIDL (*Z. angew. Chem.*, 1923, **36**, [64], 471—473; cf. A., 1922, i, 1168).—Further instances are given of the formation of resins from substances containing the "resinophore" group $-C:C-CO-$. For example, citraconic anhydride heated at 200° in an inert gas gives a resin, and in the same way cinnamylidenemalononic acid, $CHPh:CH:CH:C(CO_2H)_2$, when heated, gives a resin believed to be the anhydride of the mono-carboxylic acid, $(CHPh:CH:CH:CH-CO)_2O$. Numerous other examples are quoted from the literature of the formation of resins from compounds containing this group. The formation of a resin from phenylketimine, $NPh:C:CH_2$, leads to the inclusion of $-N:C:C<$ as a "resinophore" group. The conjugated double linking, $-C:C-C:C-$, is also regarded as a "resinophore" group, as exemplified by the Δ^{γ} -butadienes, etc., and so also is the group, $>C:C:C:N-$, as shown by the formation of a rubber-like substance by the polymerisation of methylallylideneamine, $CH_2:CH:CH:NMe$. P. M.

Digitalinum Verum. A. WINDAUS and G. BANDTE (*Ber.*, 1923, **56**, [B], 2001—2007).—The authors have commenced a systematic study of the chemistry of the cardiac poisons. The present communication is devoted to an account of digitaligenin which has been largely examined by Kiliani (A., 1914, i, 856).

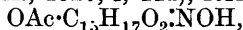
The seeds of *Digitalis purpurea* are extracted with absolute alcohol and the concentrated extracts are treated with dry ether until a distinct precipitate is no longer produced. The precipitations are repeated several times and the solid is worked up for digitonin and gitonin. Digitalinum verum is isolated from the solutions by Kiliani's method and is converted into digitaligenin, needles, m. p. $211-212^\circ$ (Kiliani, m. p. $201-202^\circ$), to which the composition, $C_{24}H_{32}O_3$, is assigned. Acetyldigitaligenin has m. p. 208° (Kiliani, m. p. $201-202^\circ$). Catalytic hydrogenation of digitaligenin in methyl-alcoholic solution in the presence of spongy palladium leads ultimately to the production of hexahydrodigitaligenin, $C_{24}H_{38}O_3$, leaflets, m. p. $186-187^\circ$. Acetylhexahydrodigitaligenin, long, rhombic crystals, m. p. $154-155^\circ$, is obtained by treating the hexahydro-compound with acetic anhydride and sodium acetate or by exhaustive hydrogenation of acetyldigitaligenin. Hexahydrodigitaligenin is oxidised by chromic acid to hexahydrodigitaligenone, $C_{24}H_{36}O_3$, slender needles, m. p. $205-207^\circ$ (oxime, needles, m. p. $205-206^\circ$), and therefore contains a secondary alcoholic group. It is reduced by amalgamated zinc and concentrated hydrochloric acid in the presence of glacial acetic acid to the lactone, $C_{24}H_{38}O_2$, long, lustrous needles, m. p. $168-169^\circ$.

During the hydrogenation of digitaligenin a sudden drop in the rate of absorption of the gas is observed after the absorption of two molecular proportions; if the reaction is interrupted at this stage, *tetrahydrodigitaligenin*, m. p. 194°, can be isolated; the corresponding *acetate*, slender needles, has m. p. 167—168°. Kiliani's "hydrodigitaligenin" is a mixture of much tetra- and little hexa-hydrodigitaligenin. H. W.

Chemical Constitution of Artemisin. P. BERTOLO (*Atti R. Accad. Lincei*, 1923, [v], 32, i, 618—622; cf. this vol., i, 1013).—The properties of artemisin are not in accord with Rimini's supposition that the oxygen atom present in addition to those of santonin occurs in the dimethylated ring as a hydroxyl group united to the carbon atom adjacent to the ketonic carbonyl of the santonin, thus: $\cdot\text{CH}_3\cdot\text{C}(\text{OH})\cdot\text{CO}\cdot$ (A., 1909, i, 115). It is certain that this oxygen atom is situated in the tetrahydrogenated ring, the most probable formula for artemisin being (I), which readily explains the formation of artemisic acid by the action of hydrochloric acid in the following manner:



Acetyl Compound of Artemisin. P. BERTOLO (*Atti R. Accad. Lincei*, 1923, [v], 32, ii, 76—79).—The acetyl compound of artemisin, m. p. 200° (A., 1920, i, 444), forms an *oxime*,



crystallising in white needles, arranged radially, m. p. 188—189°, and a *phenylhydrazone*, $\text{C}_{23}\text{H}_{26}\text{O}_4\text{N}_2$, crystallising in pink, silky needles, m. p. 145°. When hydrolysed with alcoholic potassium hydroxide, the acetyl derivative yields, not artemisin, but a crystalline compound, m. p. 220°, exhibiting acid properties.

T. H. P.

The Constitution of Capsaicin, the Pungent Principle of Capsicum. III. E. K. NELSON and L. E. DAWSON (*J. Amer. Chem. Soc.*, 1923, 45, 217°—2181; cf. A., 1919, i, 543; 1920, i, 380).—Capsaicin is proved to be η -methyl- Δ^6 -nonenylvanillyl-amide, $\text{CHMe}_2\cdot\text{CH}\cdot\text{CH}\cdot[\text{CH}_2]_4\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{OMe}$, by the

following reactions. It is reduced, in absolute alcoholic solution by means of palladium and hydrogen, to *dihydrocapsaicin*, m. p. 65° , n_D^{20} 1.510, n_D^{20} 1.520, n_D^{20} 1.555, which is also produced by condensing vanillylamine with η -methylnonenyl chloride; this demonstrates the position of the methyl group in the unsaturated acid part of the molecule. The location of the double bond is decided by the production of adipic acid and isobutyric acid, when the decenoic acid isolated by hydrolysing capsaicin is oxidised by means of cold 5% potassium permanganate solution. Dihydrocapsaicin is as pungent as capsaicin; the view of Ott and Zimmermann (A., 1922, i, 137), that this property in capsaicin and similar compounds is dependent on unsaturation in the side chain, is therefore incorrect.

W. S. N.

A Tannin which is apparently Free from Sugar. M. NIERENSTEIN (*Ber.*, 1923, 56, [B], 1876).—Mitchell (this vol., ii, 188) has described a commercial specimen of tannin which is optically active but does not appear to yield a sugar when hydrolysed or fermented. Further experiments have shown that the amount of dextrose produced is very slight and quite inadequate to account for the optical activity of the material which is possibly due to the presence of active leucodigallic acid.

H. W.

[The State of Methyl-orange and Methyl-red at the Transition Point.] A. THIEL and A. DASSLER (*Ber.*, 1923, 56, [B], 2082).—The absorption curve of methyl-red is displaced by increase in the hydrogen-ion concentration about $10\ \mu\mu$ towards the region of shorter and not of longer wave-lengths as incorrectly stated in the earlier communication (this vol., i, 937).

H. W.

Furfurylidene and Furfuryl Compounds of Camphor and of some cycloHexanones. (MLLE) NELLIE WOLFF (*Ann. Chim.*, 1923, [ix], 20, 82—130).—A continuation of work previously published (cf. A., 1921, i, 514; 1922, i, 668; this vol., i, 937). The following compounds are described: *Furfurylcamphor*, colourless crystals, m. p. 65° , R_a 65.45, R_D 65.88, R_B 66.80, prepared by the action of sodium amalgam on furfurylidenecamphor and only clearly distinguishable from the latter by its optical properties; *monofurfurylcyclohexanone*, a pale yellow liquid, b. p. $136^{\circ}/17\ \text{mm.}$, $n_D^{22.9}$ 1.49896, $n_D^{22.9}$ 1.50244, $n_D^{22.9}$ 1.51139, *difurfurylcyclohexanone*, colourless leaves, m. p. 53° , R_a 70.14, R_D 70.62, R_B 73.54, obtained by reduction of the corresponding mono- and di-furfurylidene compounds, respectively; *2-furfuryl-4-methylcyclohexanone*, a yellow oil, b. p. $148\text{—}150^{\circ}/20\ \text{mm.}$, $n_D^{24.6}$ 1.49464, $n_D^{24.6}$ 1.49812, $n_D^{24.6}$ 1.50762; *2:6-difurfuryl-4-methylcyclohexanone*, colourless needles, m. p. 52° , R_a 74.48, R_D 75.09, R_B 76.69, by reduction of the furfurylidene derivatives *2-furfurylidene-5-methylcyclohexanone*, yellow crystals, m. p. 43° , R_a 57.30, R_D 58.93, R_B 61.51; *2:6-difurfurylidene-5-methylcyclohexanone*, yellow crystals, m. p. 68° , R_a 89.97, R_D 92.65, R_B 99.84. Optically active isomerides of the two last-named substances were prepared as condensation products of active 5-methylcyclohexanone, but these derivatives are of opposite sign to that of

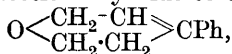
the hexanone used. *Active 2-furfurylidene-5-methylcyclohexanone* forms yellow crystals, m. p. 43° , R_a 58.23, R_D 58.95, R_β 60.89, $[\alpha]_D^{15} -11^\circ 47'$; *active 2:6-difurfurylidene-5-methylcyclohexanone*, yellow crystals, m. p. 68° , R_a 92.46, R_D 93.93, R_β 103.17, $[\alpha]_D^{18} -172^\circ 38'$. Active and inactive isomerides of both substances yield the furfuryl derivative on reduction; *2-furfuryl-5-methylcyclohexanone* is a yellow oil, b. p. $142-143^\circ/17$ mm., $d_4^{25.1}$ 1.0419, $n_D^{25.1}$ 1.49530, $n_D^{25.1}$ 1.49897, $n_\beta^{25.1}$ 1.50876, the constants for the active form being $d_4^{26.1}$ 1.0370, $[\alpha]_D^{18} -5^\circ 13'$, $n_a^{26.1}$ 1.48864, $n_D^{26.1}$ 1.49290, $n_\beta^{26.1}$ 1.50069; *2:6-difurfuryl-5-methylcyclohexanone*, a yellow liquid, b. p. $196-200^\circ/16$ mm., R_a 74.70, R_D 75.10, R_β 76.98; the active form has b. p. $202-204^\circ/16$ mm., $[\alpha]_D^{18} -6^\circ 37'$, R_a 74.66, R_D 75.17, R_β 76.44.

A study of the optical properties of the substances prepared in the course of the work shows that those in which a double bond occurs between the two rings give unusually high values for molecular refraction and dispersion, the values given by the substances obtained on hydrogenation of the double bond being normal.

H. J. E.

Tetrahydro- γ -pyrones. II. W. BORSCHKE and K. THIELE (*Ber.*, 1923, **56**, [B], 2012—2015; cf. Borsche and Mehner, A., 1915, i, 574).—The hydrogenation of 4-pyrone and 2:6-dimethyl-4-pyrone is effected as described in the previous communication: the operation is particularly tedious in the case of the dimethyl derivative.

The following compounds are prepared from tetrahydro-4-pyrone: the *oxime*, long, colourless needles, m. p. $87-88^\circ$, which is reduced by aluminium amalgam in the presence of moist ether to the corresponding *amine*, a colourless liquid without a definite boiling point (the very hygroscopic *hydrochloride*, the *benzoyl* derivative, prisms, m. p. 172° , and the *carbamate*, $C_6H_{12}O_2N_2$, colourless leaflets, m. p. $226-227^\circ$, are described). With magnesium phenyl bromide, tetrahydro-4-pyrone gives the compound, $O\langle\begin{smallmatrix} CH_2\cdot CH_2 \\ CH_2\cdot CH_2 \end{smallmatrix}\rangle CPh\cdot OH$, colourless, lustrous needles, m. p. $103-104^\circ$, which is smoothly dehydrated by boiling acetic anhydride to the substance,



colourless leaflets, m. p. $61-62^\circ$, which rapidly becomes converted into a colourless resin when preserved. Tetrahydro-4-pyrone is oxidised by potassium permanganate in alkaline solution to the *dicarboxylic acid*, $CO_2H\cdot CH_2\cdot O\cdot CH_2\cdot CH_2\cdot CO_2H$, colourless needles, m. p. $93-94^\circ$ (*di-ethyl* ester, a colourless, mobile liquid, b. p. $247-249^\circ$).

2:6-Dimethyltetrahydro-4-pyrone gives an *oxime*, colourless needles, m. p. $82-83^\circ$, b. p. $210-220^\circ/760$ mm. (*benzoyl* derivative, coarse, colourless prisms, m. p. 93°); it is reduced by aluminium amalgam to the corresponding amine, which is isolated as the very hygroscopic *hydrochloride* and the *benzoyl* derivative, small, colourless needles, m. p. $189-190^\circ$. Unlike tetrahydro-4-pyrone, the dimethyl derivative is readily reduced to 2:6-dimethyl-

tetrahydropyran-4-ol, $O<\begin{smallmatrix} \text{CHMe}\cdot\text{CH}_2 \\ \text{CHMe}\cdot\text{CH}_2 \end{smallmatrix}>\text{CH}\cdot\text{OH}$, colourless needles, m. p. 48—49°, b. p. 190°/atmospheric pressure. 2 : 6-Dimethyl-tetrahydro-4-pyrene is converted by magnesium methyl iodide into 2 : 4 : 6-trimethyltetrahydropyran-4-ol, $O<\begin{smallmatrix} \text{CHMe}\cdot\text{CH}_2 \\ \text{CHMe}\cdot\text{CH}_2 \end{smallmatrix}>\text{CMe}\cdot\text{OH}$, b. p. 86—88°/18 mm., which is transformed by boiling acetic anhydride into the corresponding *acetate*, a pale yellow liquid, b. p. 95—100°/16 mm.; with magnesium phenyl bromide it yields 4-phenyl-2 : 6-dimethyltetrahydropyran-4-ol, $O<\begin{smallmatrix} \text{CHMe}\cdot\text{CH}_2 \\ \text{CHMe}\cdot\text{CH}_2 \end{smallmatrix}>\text{CPh}\cdot\text{OH}$, colourless prisms, m. p. 101—102°, b. p. 152—156°/14 mm., which is dehydrated by boiling acetic anhydride to the *compound*, $O<\begin{smallmatrix} \text{CHMe}\cdot\text{CH} \\ \text{CHMe}\cdot\text{CH}_2 \end{smallmatrix}>\text{CPh}$, a colourless liquid, b. p. 133—136°/12 mm. The latter compound is rapidly hydrogenated in the presence of colloidal palladium to the saturated *substance*, $O<\begin{smallmatrix} \text{CHMe}\cdot\text{CH}_2 \\ \text{CHMe}\cdot\text{CH}_2 \end{smallmatrix}>\text{CHPh}$, a colourless liquid, b. p. 125—127°/13 mm. H. W.

Pyranhydrones. IV. WILHELM SCHNEIDER (*Annalen*, 1923, 432, 297—318).—[With ALBERT ROSS.]—The dull red precipitate, obtained by the action of sodium acetate solution on 2 : 6-diphenyl-4-methylpyrylium bromide in faintly acid solution (Schneider and Ross, A., 1922, i, 1171), is 2 : 6-diphenyl-4-methylpyranhydron; it is prepared in a granular, bluish-red, somewhat purer form, m. p. 90—105° (sinters about 55°), by the addition of saturated sodium acetate solution to a solution of the bromide in glacial acetic acid. The more pure product loses, when heated in a vacuum, approximately 1 mol. of water, whilst the less pure material, which is already partly dehydrated, loses about half that amount; in either case a methylenepyran, $\text{C}_{18}\text{H}_{14}\text{O}$, is obtained. Further, the fission of the pyranhydron, by solution in glacial acetic acid (cf. Schneider and Meyer, A., 1921, i, 680), leads to two products, one of which gives a perchlorate, whilst the other does not form salts.

[With HANS JACOBI.]—It is not possible to obtain a pyranhydron by the action of concentrated sodium acetate solution on 2 : 4 : 6-trimethylpyrylium perchlorate, or on a cold ethereal solution of the chloride.

4-Phenyl-2 : 6-dimethylpyrylium iodide (cf. Baeyer and Piccard, A., 1911, i, 901) is obtained by the action of potassium iodide in concentrated hydrochloric acid solution on a cold solution, obtained from the action of dimethylpyrone in anisole solution on an ethereal solution of magnesium phenyl bromide. The iodide exists in two forms, (a) ciliate clusters of slender, yellow needles, (b) red rhombs, of which the latter is the more stable; either form has m. p. 203°. A *periodide*, $\text{C}_{13}\text{H}_{13}\text{OI}_3$, m. p. 126—128°, is also formed, and separates in dark brown flocks. When saturated sodium acetate solution is added to a well-cooled solution of the iodide in dilute acetic acid, and the mixture kept at -10°, 4-phenyl-2 : 6-dimethylpyranhydron gradually separates in dirty violet-red flocks; it passes on drying to

a vitreous, violet mass, which may be ground to a chocolate-coloured powder, m. p. about 80°, sinters at 60°, decomp. 140°. The colour of this compound in alcoholic solution disappears on warming, and deepens on cooling.

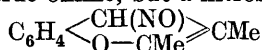
4-*p*-Anisyl-2 : 6-dimethylpyrylium iodide is prepared in the usual way from dimethylpyrone and the Grignard reagent from *p*-bromoanisole; it forms compact, brown crystals having a violet, metallic lustre, m. p. 215°; a yellow modification appears when a hot, saturated, alcoholic solution is suddenly cooled, this being only slowly reconverted into the more stable form. The *picrate* forms small, slender, yellow needles, m. p. 186°. The corresponding *pyranhydron*e is a reddish-brown, violet-tinted, resinous mass, which cannot be purified.

[With GOTTHARD TREBITZ.]—The condensation of acetophenone, or of dypnone, with propionic anhydride in the presence of sulphopropionic acid leads to the formation of 4 : 6-diphenyl-2-ethylpyrylium sulphopropionate, small, yellow crystals, or thin reddish-yellow plates, m. p. 163°. The corresponding *iodide* forms blood-red needles, m. p. 236–237°. These pyrylium salts are converted by the action of sodium acetate solution, or of other weak alkalis, into an amorphous, brownish-red *substance*, which very readily resinifies, does not lose water when heated in a vacuum, and is apparently 4 : 6-diphenyl-2-ethylidenepyran.

[With HELENE NITZSCHE.]—4 : 6-Diphenyl-2-styrylpyrylium chloride, m. p. 115°, or with 2H₂O, intensely red crystals, m. p. 105°, is obtained by warming 4 : 6-diphenyl-2-methylpyrylium chloride (+ 2H₂O) and benzaldehyde at 100°. The *iodide* forms small, dark brownish-red needles, m. p. 183–184°. The action of dilute sodium hydroxide or sodium acetate solution on an aqueous solution of either of these salts gives an amorphous, flocculent, orange-red precipitate, which has m. p. 120°, and does not resinify on drying. It is apparently the pseudo-base, 4 : 6-diphenyl-2-styrylpyranol.

W. S. N.

The Beckmann Conversion of Oximes into Amides. ERNST BECKMANN and ERICH BARK (*J. pr. Chem.*, 1923, [ii], 105, 327–349).—The oxime of 1 : 2-dimethylchromone (Petschek and Simonis, A., 1913, i, 890) is not a true oxime, but a nitroso-derivative,



(Simonis and Elias, A., 1916, i, 499), since it does not undergo the Beckmann transformation. It is, in fact, unaffected by treatment with phosphorus pentachloride, anhydrous hydrogen chloride, acetyl chloride, glacial acetic acid, or acetic anhydride; the action of concentrated sulphuric acid gives a *sulphonic acid*, C₁₁H₁₂O₅NS, m. p. 225°, *silver* salt, m. p. above 280°. The nitrogen cannot be removed from the oxime by boiling it with hydrochloric acid, sulphuric acid, sulphurous acid, sodium hydroxide solution, or formaldehyde solution; a semicarbazone or phenylhydrazone of dimethylchromone cannot be prepared.

The oxime of 1-thio-2 : 3-dimethylchromone (Simonis and Elias,

loc. cit.) is a true oxime, but passes into gummy products when an attempt is made to effect its transformation by means of the usual reagents.

Isatinoxime is unaffected by treatment with sulphuric acid, gaseous hydrogen chloride, acetyl chloride, or acetic anhydride. The use of a mixture of phosphoryl chloride and phosphorus pentachloride leads to the formation of *o*-cyanophenylcarbimide, which Borsche and Jacobs obtained (A., 1914, i, 322) by the use of phosphorus pentachloride alone. Under no conditions is a rearrangement with formation of a six-membered ring brought about. The action of benzenesulphonyl chloride on isatinoxime in cold or boiling pyridine solution gives a *sulphonic acid*, $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{C}(\text{NOH}) \\ \text{N}(\text{SO}_3\text{H}) \end{smallmatrix}\rangle\text{CO}$, ivory-coloured leaflets, m. p. 130–131° (insoluble mercuric salt).

The latter is likewise produced in attempting to prepare isatin-dioxime by the action of the same reagents on its *N*-acetyl derivative; this is not affected by treatment with pyridine alone, or with piperidine, but is converted into isatinoxime by the use of potassium hydroxide. The action of aqueous sodium hydroxide and benzoyl chloride on acetylisatin-dioxime gives isatinoxime benzoate, whilst *o*-cyanophenylcarbimide is obtained by the use of a mixture of phosphoryl chloride and phosphorus pentachloride.

The conversion of benzophenoneoxime into benzanilide is accomplished by fusion with the following chlorides: potassium, magnesium, calcium, aluminium, zinc, ferrous, ferric, mercuric, antimonious, antimonic, and phosphoryl chlorides. Benzophenoneoxime is unaffected by fusion with sodium chloride; by the action of carbonyl chloride in ethereal solution, or of nitrosyl chloride in chloroform solution, it is converted into benzophenone. The presence or absence of atmospheric oxygen apparently makes no difference. Antimony pentachloride and the trichloride effect this transformation with remarkable ease, the former even in cold chloroform solution. Conversion of the oxime into the ketone is also brought about by fusion with calcium, zinc, ferric, mercuric, or antimonic oxides, aluminium hydroxide, copper bronze, or anhydrous zinc sulphate, but hydrated zinc sulphate has no action. Benzanilide is quite unaffected by fusion with mercuric oxide, or by treatment with carbonyl chloride in chloroform solution. W. S. N.

Chemical Reactivity and Conjugation: the Reactivity of the 2-Methyl Group in 2:3-Dimethylchromone. ISIDOR MORRIS HEILBRON, HARRY BARNES, and RICHARD ALAN MORTON (T., 1923, 123, 2559–2570).

Styrylbenzopyrylium Salts. III. The γ -Styryl Derivatives of 7-Hydroxy-2-phenyl-4-methylbenzopyrylium Chloride. JOHANNES SYBRANDT BUCK and ISIDOR MORRIS HEILBRON (T., 1923, 123, 2521–2531).

Thiochromanones and the Products of their Transformations. F. KROLLPFEIFFER and H. SCHULTZE (*Ber.*, 1923, 56, [B], 1819–1824; cf. Krollpfeiffer and Schäfer, this vol., i, 343).—A VOL. CXXIV. i.

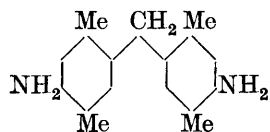
preliminary communication induced by the recent publication of Arndt (this vol., i, 826).

β -Arylthiolpropionic acids are conveniently prepared by the action of an aqueous solution of sodium β -bromopropionate on the requisite mercaptan dissolved in 2*N*-sodium hydroxide solution. β -Phenylthiolpropionic acid, $\text{SPh}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, colourless leaflets, m. p. 59°, b. p. 184°/10 mm., β -*p*-tolylthiolpropionic acid, m. p. 70° (cf. Arndt, *loc. cit.*), β -*m*-xylylthiolpropionic acid, colourless leaflets, m. p. 84–85° after previous softening, b. p. 196–197°/12 mm., β -1-naphthylthiolpropionic acid, m. p. 89–90°, β -2-naphthylthiolpropionic acid, m. p. 104–105°, b. p. 232°/12 mm., and β -2-tetrahydronaphthylthiolpropionic acid, m. p. 76°, after previous softening, b. p. 237°/12 mm., are described. Ring closure of the β -arylthiolpropionic acids to thiochromanones is readily effected by cold, concentrated sulphuric acid. Thiochromanone, colourless leaflets, m. p. 29–30°, b. p. 154°/12 mm. (*semicarbazone*, slender, colourless needles, m. p. 219–220°), 6-methylthiochromanone, colourless plates, m. p. 41–42°, b. p. 174°/10 mm. (*semicarbazone*, colourless leaflets, m. p. 235°, when rapidly heated), 6:8-dimethylthiochromanone, $\text{C}_6\text{H}_2\text{Me}_2\text{S} \begin{smallmatrix} \text{CO}\cdot\text{CH}_2 \\ | \\ \text{CH}_2 \end{smallmatrix}$, large, colourless plates, m. p.

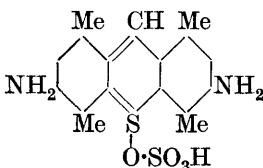
38–39° (*semicarbazone*, colourless needles, m. p. 236–237°, when rapidly heated), 7:8-benzothiochromanone, coarse, yellowish-green prisms, m. p. 107°, and 5:6-benzothiochromanone, m. p. 68–69° (*semicarbazone*, m. p. 241–242°, when rapidly heated), are described.

Ring closure of β -2-tetrahydronaphthylthiolpropionic acid appears to yield a mixture of the two thiochromanones theoretically possible; the crude product of the reaction gives two *semicarbazones*, m. p. 255° and 224°, respectively, the former of which yields a *thiochromanone*, small, colourless platelets, m. p. 60–61°. H. W.

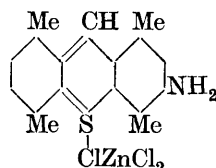
Thiopyronines. M. BATTEGAY and P. FRIES (*Bull. Soc. chim.*, 1923, [iv], 33, 1098–1103).—*p*-Xylidine does not behave in the normal manner with formaldehyde, but 2 mols. of the former condense with 1 mol. of the latter to give a substituted methane (I).



(I.)



(II.)



(III.)

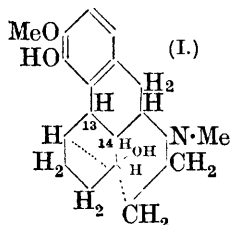
If this base be acetylated and dropped in small quantities with vigorous stirring into fuming sulphuric acid at 20°, condensation occurs, and the sulphate (II) of the substituted thiopyronine may be obtained, after removal of the acetyl groups, as small, green needles. This salt forms a *monodiaz*o-derivative, indigo-blue in solution, and a *bisdiaz*o-derivative, greenish-yellow in solution. On boiling the monodiazo-compound with alcohol and precipitating with zinc chloride, a salt of *apothio-pyronine* (III) is obtained. H. H.

Selenopyronines. M. BATTEGAY and G. HUGEL (*Bull. Soc. chim.*, 1923, [iv], 33, 1103—1106; cf. A., 1920, i, 629).—Two rules governing the formation of selenopyronines are enunciated. First, the diphenylmethane used as parent substance must give a colour reaction with lead peroxide in acetic acid solution. Secondly, the substituents in the benzene nuclei must be such as will exert in fuming sulphuric acid solution a directing influence sufficient to cause the new substituent to enter in the ortho-position to the methane bridge. Examples are given to illustrate these rules and it is pointed out that the presence of nitro- or amino-groups is not in general conducive to successful condensation, although alkylation of the amino-group by removing its tendency to form an ammonium salt is distinctly advantageous. H. H.

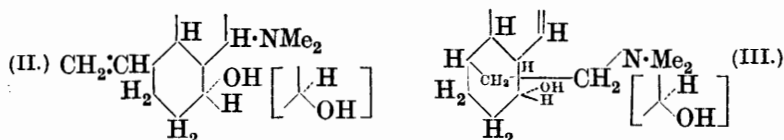
Codeine and its Isomerides. EDMUND SPEYER and WILHELM KRAUSS (*Annalen*, 1923, 432, 233—265).—A simplification is described of Knorr's method (A., 1907, i, 151; 1908, i, 361) for separating the isomerides of codeine. *allo-ψ*-Codeine is obtained from its hydride by the action of ammonia as needles, m. p. 116—117°, $[\alpha]_D^{25} -235.4^\circ$.

In accordance with Knorr's views (A., 1908, i, 42, 956) on the structure of codeine, *isocodeine*, *ψ-codeine*, and *allo-ψ-codeine*, the latter behaves, when treated in dilute acetic acid solution with palladium black and hydrogen, like *ψ-codeine* (A., 1922, i, 47), giving *tetrahydroallo-ψ-codeine* (I), leaflets, m. p. 137—138°, $[\alpha]_D^{25} -75.0^\circ$, in which the oxygen bridge is broken, since it gives a *diacetate*, small needles, m. p. 115°. It is evident that fission of the oxygen—carbon linking precedes the saturation of the bond 13—14, since *dihydro-ψ-codeine*, long needles, m. p. 128° (*methiodide*, leaflets, decomp. 275°) is phenolic (soluble in alkali hydroxide solution); it is obtained by reducing *ψ-codeine*, either by means of sodium and alcohol, or electrolytically in 25% sulphuric acid solution, using lead electrodes. On further reduction by means of palladium-hydrogen, *dihydro-ψ-codeine* gives *tetrahydro-ψ-codeine*; the latter gives a *diacetate*, leaflets, m. p. 137—138°. *Dihydroisocodeine* (*loc. cit.*) gives a *monoacetate*, rods, m. p. 166°, *methiodide*, hexagonal tablets, m. p. 268—269°. The double compound, m. p. 147.5°, described by Lees (A., 1908, i, 42), consists of equal quantities of *isocodeine* and *allo-ψ-codeine*, since it gives equivalent quantities of *dihydroisocodeine* and *tetrahydroallo-ψ-codeine* when reduced in dilute acetic acid solution by means of palladium-hydrogen.

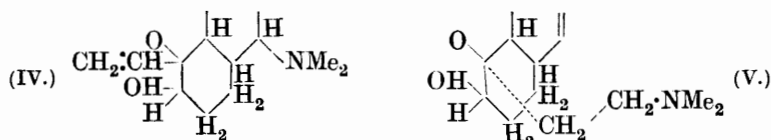
The *methiodide*, needles, m. p. 252°, of *tetrahydroallo-ψ-codeine* is converted by the action of hot, concentrated potassium hydroxide solution into des-N-methyl*tetrahydroallo-ψ-codeine*, an oil, *hydriodide*, rectangular leaflets, m. p. 236°. This base forms an oily *methiodide*, from which an oily, nitrogen-free product is obtained by heating with 50% potassium hydroxide solution. The same behaviour is shown



by *de-N-methyltetrahydro-ψ-codeine*, prisms, m. p. 162—163°, which is derived from tetrahydro-ψ-codeine methiodide. For these *de*-bases the alternative formulæ (II) and (III) present themselves;



whichever is correct, the *ψ*- and *allo-ψ*-bases differ only in the configuration of the secondary alcohol grouping. The action of methyl sulphate and 10% sodium hydroxide solution, followed by treatment with sodium iodide, converts tetrahydro-ψ-codeine into



its *methyl ether methiodide*, leaflets, m. p. 247°, from which, however, defined degradation products are not obtained. Better results attend the use of dihydroisocodeine methiodide, which is converted by means of hot, concentrated potassium hydroxide solution into *des-N-methyldihydroisocodeine* (IV) or (V), small rods, m. p. 151°; this gives a *methiodide*, needles, m. p. 269°, from which, by the using of boiling, concentrated potassium hydroxide solution, the nitrogen-free *compound* (VI), small needles, m. p. 75—76°, is obtained. An *isomeride* of (VI), m. p. 115°, is similarly prepared from *de-N-methyldihydrocodeine* (cf. Freund, A., 1921, i, 125).

The action of phosphorus pentachloride in chloroform solution on *allo-ψ*-codeine gives *allo-ψ-chlorocodide*, hexagonal leaflets, m. p. 154—155°, the amorphous *hydrochloride* of which is reduced in aqueous solution by means of palladium-hydrogen to *α*-deoxytetrahydro*allo-ψ*-codeine (methyl ether methiodide) (Freund, *loc. cit.*). Tetrahydro-ψ-codeine is similarly converted into *tetrahydro-ψ-chlorocodide*, leaflets, m. p. 103°, which is reduced by means of sodium and alcohol to *α*-deoxytetrahydrocodeine.

allo-ψ-Codeine is converted by the action of warm hydrogen peroxide solution into *allo-ψ-codeine N-oxide*, small rods, m. p. 212° (decomp.), which is converted by the action of a mixture of acetic anhydride and concentrated sulphuric acid into its *sulphonic acid*; the latter exists in two forms, (a) the usual, less soluble modification, quadratic tablets, decomp. 280°, (b) the more soluble, or *α*-form, m. p. 271°. *isoCodeine N-oxide*, prismatic rods, m. p. 219° (decomp.), *isocodeine-N-oxide-sulphonic acid*, (a) decomp. 300°, and (b) decomp. 290°, are obtained in a similar manner. A second *modification*, octahedra, decomp. above 300°, of *ψ*-codeine-*N*-oxide-sulphonic acid

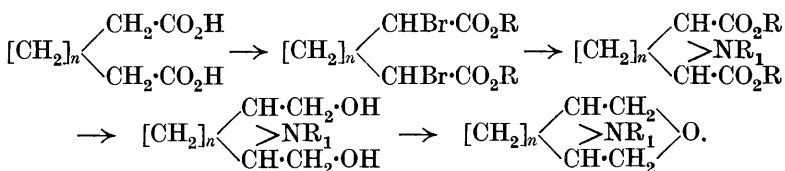
(Speyer and Wieters, *loc. cit.*) is described, which is converted into the usual form by keeping its solution in concentrated sulphuric acid.

The action of cold bromine water on the less soluble form of *allo-ψ-codeine-N-oxide-sulphonic acid* gives a perbromide, which is decomposed by the action of sulphurous acid, giving *bromoallo-ψ-codeine dibromide*, small rods, m. p. 206—207°. *Bromo-ψ-codeine dibromide*, prisms, m. p. 220°, gives tetrahydro-ψ-codeine when reduced in dilute acetic acid solution by means of palladium-hydrogen. An *isomeride*, prisms, decomp. 235°, is obtained by using the α- or more soluble acid. *Bromoisocodeine dibromide* forms hexahedral aggregates, m. p. 212°; *bromocodeine dibromide*, m. p. 200°, is reduced in dilute acetic acid solution to dihydrocodeine by the action of palladium-hydrogen. The action of bromine water on dihydrocodeine-*N-oxide-sulphonic acid* gives a perbromide from which sulphurous acid liberates an oily compound, $C_{18}H_{22}O_3NBr$, which forms a crystalline *methiodide*, m. p. 230° (decomp.).

W. S. N.

Dicyclic Morpholines. I. JULIUS VON BRAUN and JON

SEEMAN (*Ber.*, 1923, 56, [B], 1840—1845).—The authors have commenced a series of attempts to obtain compounds containing the morphopyrrolidine (I) and the morphopiperidine (II) rings. The synthesis proceeds along the lines indicated by the formulæ:



Up to the present it has only been effected with complete success when R^1 is the benzyl group. Since, however, an unexpected stability is conferred on the morpholine ring by association with the pyrrolidine complex, the removal of the benzyl radicle can be effected by means of cyanogen bromide with formation of the parent secondary base from which further *N*-alkyl derivatives can be prepared.

Benzyl meso-αδ-dibromoadipate, $C_{18}H_{20}O_4Br_2$, forms slender crystals, m. p. 83°, b. p. about 280°/15 mm. (slight decomp.).

Ethyl *meso-αα-dibromoadipate* is converted by methylamine in the presence of benzene into a mixture of *αδ-dibromoadipomethylamide*, m. p. 214—215°, *ethyl cis-1-methylpyrrolidine-2:5-dicarbonylate*, $\begin{array}{c} \text{CH}_2 \cdot \text{CH}(\text{CO}_2\text{Et}) \\ \text{CH}_2 \cdot \text{CH}(\text{CO}_2\text{Et}) \end{array} > \text{NMe}$, a colourless liquid, b. p. 142—146°/11 mm. (the *picrate* and *methiodide* are not crystalline; the

hygroscopic *hydrochloride*, m. p. 126—128°, and the *chloroplatinate*,

pale yellow leaflets, m. p. 180° , are described) and pyrrolidine-dicarboxylamide. The ester is reduced by sodium and alcohol to *cis*-1-methyl-2:5-dihydroxymethylpyrrolidine, b. p. $120\text{--}130^{\circ}/12$ mm. (the *hydrochloride*, *chloroaurate*, and *methiodide* are non-crystalline), but the yields are minimal by reason of the ready hydrolysis which occurs.

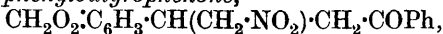
Ethyl *cis*-1-phenylpyrrolidine-2:5-dicarboxylate, b. p. $205^{\circ}/13$ mm. (cf. Le Sueur, T., 1909, **95**, 273), is readily obtained from the dibromo-ester and aniline. It is reduced by sodium and alcohol to *cis*-1-phenyl-2:5-dihydroxymethylpyrrolidine, a colourless, viscous liquid, b. p. $200^{\circ}/11$ mm., which does not yield crystalline salts and is not converted by sulphuric acid into a homogeneous, dihydrated substance.

Ethyl *cis*-1-benzylpyrrolidine-2:5-dicarboxylate, b. p. $205\text{--}207^{\circ}/12$ mm., yields a non-crystalline *picrate* and *methiodide*, a very hygroscopic *hydrochloride*, m. p. 128° , and a *chloroplatinate*, m. p. 158° . It is reduced by sodium and alcohol to *cis*-1-benzyl-2:5-dihydroxymethylpyrrolidine, a somewhat viscous, odourless liquid, b. p. $210\text{--}211^{\circ}/13$ mm., which gives a non-crystalline *hydrochloride*, a *picrate*, m. p. 139° , and a *chloroplatinate*, m. p. 177° . The hydroxymethyl derivative is converted by sulphuric acid (70%) at 175° into 1-benzylmorphopyrrolidine, m. p. 46° (*hydrochloride*, m. p. 255° ; *chloroplatinate*, m. p. 134° ; *picrate*, m. p. 164° ; *methiodide*, m. p. 249°). It is converted by cyanogen bromide into the *product*, $\text{C}_{20}\text{H}_{24}\text{ONBr}$, m. p. 258° , and a compound which appears to be essentially 1-cyanomorphopyrrolidine. H. W.

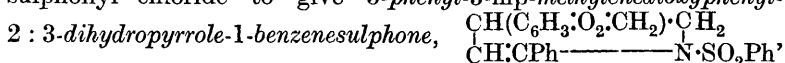
The Catalytic Reduction of Nitro-compounds. II. γ -Nitro-ketones. E. P. KOHLER and N. L. DRAKE (*J. Amer. Chem. Soc.*, 1923, **45**, 2144—2150; cf. this vol., i, 666).—The reduction of three nitro-ketones, in which the nitro-radicle is in the γ -position to the carbonyl group, has been investigated, in the hope that ring formation between the carbonyl radicle and the partly reduced nitro-group might aid in elucidating the obscure mechanism of the reduction. Unfortunately, although cyclic compounds are formed, they are themselves so readily reduced that the process cannot be confined to a single step. Moreover, different products are formed by concurrent, as well as by consecutive reactions, and it is therefore impossible to deduce the course of the reaction.

ϵ -Nitro- δ -phenylpentan- β -one, lustrous needles, m. p. $99\text{--}100^{\circ}$, is prepared by the action of sodionitromethane on styryl methyl ketone in hot, methyl-alcoholic solution. It is reduced in methyl-alcoholic suspension, by means of platinum black and hydrogen, to 4-phenyl-2-methylpyrrolidine, a colourless liquid, b. p. $112^{\circ}/10$ mm., which turns yellow when exposed to the air; it gives an *N*-benzoyl derivative, large prisms, m. p. $82\text{--}83^{\circ}$, and is converted by means of methyl sulphate and ice-cold 10% potassium hydroxide solution into 4-phenyl-1:2-dimethylpyrrolidine, isolated as its *hydrobromide*, slender, colourless needles, m. p. $144\text{--}146^{\circ}$ (probably with decomp.). The condensation of piperonyl-

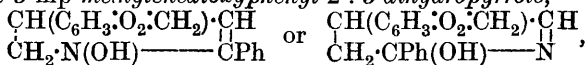
ideneacetophenone with sodionitromethane gives γ -nitro- β -mp-methylenedioxyphenylbutyrophenone,



slender needles, m. p. 95—96°. The reduction of this compound gives γ -amino- β -mp-methylenedioxyphenylbutyrophenone, colourless needles, or plates, m. p. 129—130°, which becomes gummy and discoloured when kept moist or in solution, and gives a hydrochloride which cannot be purified. The amine reacts with benzenesulphonyl chloride to give 5-phenyl-3-mp-methylenedioxyphenyl-



minute plates, m. p. 225—227° (decomp.), after turning brown at 220°. Other products of the reduction are 2-phenyl-4-mp-methylene-dioxyphenyltetrahydropyrrole, isolated as its hydrochloride, long, thin, white needles, m. p. about 208° (decomp.), and 1-hydroxy-5-phenyl-3-mp-methylenedioxyphenyl-2 : 3-dihydropyrrole,



colourless needles, m. p. 144—145°. The former is not produced by reduction of the dihydro-derivative, since the latter is present in the reduction mixture after all absorption of hydrogen has ceased. Moreover, the amino-ketone is stable in neutral, or weakly alkaline solution, and is therefore not the source of the pyrrole derivatives. The three products must consequently be formed by different paths. The reduction of γ -nitro- β -phenylbutyrophenone gives an oily product which cannot be distilled, but from which the following compounds are isolated. The benzoate,
$$\begin{array}{c} \text{CHPh} \text{-----} \text{CH} > \text{CPh} \text{ or } \begin{array}{c} \text{CHPh}\cdot\text{CH}_2 \\ | \\ \text{CH} \end{array} > \text{CPh}\cdot\text{OBz}, \end{array}$$
 colourless needles, m. p. 179—180°, of a hydroxydiphenyldihydropyrrole; 2 : 4-diphenyltetrahydropyrrole hydrochloride, thin, colourless needles, m. p. 171—172°, and the corresponding oxalate, a colourless solid. W. S. N.

Synthesis of Methyl and Ethyl 1 : 2 : 3 : 5-Tetramethylpyrrole-4-carboxylate. G. KORSCHUN and (MME) C. ROLL (*Bull. Soc. chim.*, 1923, [iv], **33**, 1107—1108).—Methyl 1 : 2 : 3 : 5-tetramethylpyrrole-4-carboxylate is prepared by heating a mixture of methyl acetoacetate, methyl α -chloroethyl ketone, and 33% aqueous methylamine in a sealed flask for several hours. The ester crystallises from petroleum, and melts at 101°. The ethyl ester is prepared by agitation of ethyl diacetylbutyrate with excess of 33% aqueous methylamine in the cold. H. H.

Complex Salts of Sexavalent Osmium. G. SCAGLIARINI and A. MASETTI ZANNINI (*Gazzetta*, 1923, **53**, 504—507).—Compounds analogous to the oxyosmyl compounds (cf. Wintrebert, A., 1903, ii, 219) are not, so far as is known, formed by other metals of the platinum family, and the only salts which can be regarded as approaching them are the complex oxalates of tungsten and molybdenum, $\text{WO}_3(\text{C}_2\text{O}_4)\text{K}_2\cdot\text{H}_2\text{O}$ and $\text{MoO}_3(\text{C}_2\text{O}_4)\text{K}_2\cdot\text{H}_2\text{O}$ (cf. Rosenheim, 1893, i, 457). In view of the results obtained by Gibbs (A., 1882,

144), the authors have investigated the action of pyridine hydrochloride on potassium osmate. In strongly acid solution this action yields a *compound*, $\text{OsO}_4\text{H}_4\text{Cl}_2(\text{C}_5\text{H}_5\text{N})_2$, which crystallises in yellowish-brown, fusiform needles, yields potassium osmate when treated with concentrated potassium hydroxide, and is probably pyridine trioxodichloro-osmonate, $\left[\begin{smallmatrix} \text{OsO}_3\text{Cl}_2 \\ \text{H}_2\text{O} \end{smallmatrix} \right] \text{H}_2\cdot\text{Py}_2$. T. P. H.

Complexes with Co-ordination Number Five. A. SCHLEICHER, H. HENKEL, and L. SPIES (*J. pr. Chem.*, 1922, [ii], **105**, 31—38).—The action of aniline on *trans*- $\text{Pt}(\text{NH}_3)_2\text{I}_2$ gives a small quantity of *trans*- $[\text{Pt}(\text{NH}_3)_2(\text{NH}_2\text{Ph})_2]\text{I}_2$, together with an amorphous violet powder and a good yield of *trans*- $\text{Pt}(\text{NH}_2\text{Ph})_2\text{I}_2$. An attempt to prepare the latter from aniline and platinumous iodide gave *cis*- $\text{Pt}(\text{NH}_2\text{Ph})_2\text{I}_2$, pale yellow crystals, which is also formed from aniline and *cis*- $\text{Pt}(\text{NH}_3)_2\text{I}_2$. The latter is obtained by the action of potassium iodide on the salt *cis*- $\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$, which is made by the action of silver nitrate on *cis*- $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$, an 80% yield of which is obtained, together with $[\text{Pt}(\text{NH}_3)_3\text{Cl}_2][\text{PtCl}_4]$ and $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$, when ammonia reacts with potassium chloroplatinite. The *cis*- and *trans*-forms of the compound $\text{Pt}(\text{NH}_2\text{Ph})_2\text{I}_2$ give, on treatment with pyridine, respectively, the *cis*- and *trans*-forms of the compound $[\text{Pt}(\text{NH}_3)_2(\text{C}_5\text{H}_5\text{N})_2]\text{I}_2$, in both of which the iodine atoms are ionisable. The action of concentrated hydrochloric acid on the *trans*-salt gives a mixture of yellow *trans*- $\text{Pt}(\text{NH}_3)_2\text{I}_2$ and white *trans*- $\text{Pt}(\text{C}_5\text{H}_5\text{N})_2\text{I}_2$, whilst the *cis*-salt gives solely *trans*- $\text{Pt}(\text{NH}_3)(\text{C}_5\text{H}_5\text{N})\text{I}_2$. *cis*- $\text{Pt}(\text{NH}_3)_2\text{I}_2$ is easily soluble in aqueous ethylenediamine solution, whilst the *trans*-salt is soluble with difficulty. The product from the *cis*-salt is not the expected *cis*- $[\text{Pt}(\text{NH}_3)_2\text{en}]\text{I}_2$, but the white compound, $[\text{Pt en}_2]\text{I}_2$, which is also formed from the *trans*-salt, or, together with Pt en I_2 (glistening, yellow needles), by treatment of platinumous iodide with aqueous ethylenediamine solution. The action of dilute sulphuric acid on an aqueous solution of the salt, $[\text{Pt en}_2]\text{I}_2$, causes separation of platinumous iodide, with formation of a yellow solution from which a golden-coloured compound of unknown constitution is isolated. The action of chlorine on diethylenediamineplatinous chloride gives the yellow *monohydrate*, the white *dihydrate*, and the *trihydrate* of the compound $\text{Pt en}_2\text{Cl}_4$, from which, by the action of potassium chloroplatinate, a compound, probably $[\text{Pt en}_2\text{Cl}_2]\text{PtCl}_4$, is produced. Two of the chlorine atoms in the compound $\text{Pt en}_2\text{Cl}_4$ are evidently in the *trans*-position with relation to the plane containing the ethylenediamine molecules, since they cannot be replaced by a further ethylenediamine molecule. Chlorination of the compound Pt en Cl_2 gives the *compound*, $[\text{PtCl}_2\text{en}]\text{Cl}_2$, yellow crystals, from which the isomeric *cis*-form of the compound, $\text{Pt en}_2\text{Cl}_4$, should be obtainable by boiling with ethylenediamine. The product is, however, triethylenediamineplatinic chloride. The action of cold pyridine on the compound $[\text{Pt en Cl}_4]\text{Cl}$ gives a *salt*, $\text{Pt en}(\text{C}_5\text{H}_5\text{N})_2\text{Cl}_4$, which is converted by means of ethylenediamine into dichlorodiethylenediamineplatinic chloride. Two of the chlorine atoms

in the dipyridino-derivative are therefore considered to be in the *trans*-position with respect to the plane containing the ethylenediamine and pyridine molecules. The action of alcoholic bromine solution on an aqueous solution of diethylenediamineplatinous chloride gives a yellow compound, $[\text{Pt en}_2\text{Br}_2]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$, which gradually turns green on exposure to the air, gives a white, caseous precipitate with silver nitrate, and a yellow salt with potassium chloroplatinate.

W. S. N.

A New Method for the Preparation of Hydroxy-derivatives of Pyridine, Quinoline, and their Homologues. A. E. TSCHITSCHIBABIN (*Ber.*, 1923, **56**, [B], 1879—1885).—In analogy with the amination of the pyridine nucleus by means of sodamide (cf. Tschitschibabin and Zeide, *A.*, 1915, i, 590), the hydroxylation can be effected with potassium hydroxide.

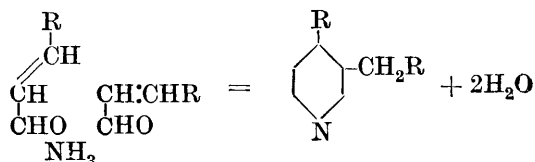
Quinoline reacts readily with potassium hydroxide at 225° with evolution of hydrogen and formation of the potassium derivative of 2-hydroxyquinoline; the success of the operation depends greatly on the care expended in the desiccation of the alkali and to some extent on its state of division. The yield of pure 2-hydroxyquinoline is not less than 80% of that theoretically possible. Small amounts of indole and, possibly, of 4-hydroxyquinoline, appear to be produced simultaneously. 2-Methylquinoline does not evolve hydrogen when treated with potassium hydroxide; it is, however, evolved from lepidine. The analogous reaction with sodium hydroxide can be observed only at temperatures above the boiling point of quinoline. Pyridine is attacked less readily by alkali hydroxides; it is, however, transformed by potassium hydroxide at 320° into 2-hydroxypyridine.

The course of the interaction between quinoline and barium oxide depends greatly on the content of the latter of barium hydroxide; it leads to the production of derivatives of indole and quinoline, but the change appears to be very complicated. H. W.

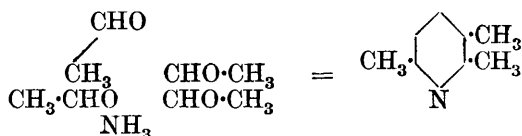
The Synthesis of Pyridine Bases from Aldehydes and Ammonia. A. E. TSCHITSCHIBABIN (*J. Russ. Phys. Chem. Soc.*, 1923, **54**, 402—411).—The condensation of aldehydes with ammonia can follow several courses with the production of a variety of bases. One of the fundamental types is the condensation of three molecules of aldehyde with a molecule of ammonia previously studied in the case of acetaldehyde, butaldehyde, and valeraldehyde and leading to 2 : 3 : 5-trialkylpyridines (*A.*, 1906, i, 451), this reaction is limited to saturated aldehydes of the general formula $\text{CH}_3\text{R}\cdot\text{CHO}$, whilst unsaturated aldehydes of the general formula $\text{CHR}\cdot\text{CH}\cdot\text{CHO}$ follow the scheme given by Baeyer (*Annalen*, 1870, **155**, 981) and by Dürkopff and Schlaugk (*A.*, 1888, 607), in which only 2 mols. of aldehyde take part. The condensation of 3 mols. of a saturated aldehyde with 1 mol. of ammonia can, however, follow an alternative scheme (Tschitschibabin, *loc. cit.*) leading to 3 : 4 : 5-trialkylpyridines, and it is now pointed out that such a reaction actually does take place in some cases. Thus, γ -picoline is formed in addition to α -picoline from acetaldehyde (see following abstracts)

r r*

and ammonia and 2- and 4-phenylpyridines are produced in a similar way (Tschitschibabin, A., 1915, i, 638). It is now suggested that a fourth type of condensation, leading to 3-substituted pyridines, occurs to a limited extent and can be represented as the condensation of ammonia with two molecules of an unsaturated aldehyde (or four molecules of a corresponding saturated one), thus :



This reaction accounts for the isolation of 4-methyl-3-ethylpyridine from the reaction product of acetaldehyde and ammonia (following abstracts), whilst the formation of a new trimethylpyridine, which must be the 2 : 3 : 6-compound, is explained by the condensation of 4 mols. of acetaldehyde with ammonia, thus :



An alternative scheme is possible, but this would lead to the known 2 : 3 : 4-compound (Guareschi, A., 1900, i, 558). A scheme is also given by which 2- or 4-propylpyridines might be produced in the same reaction.

G. A. R. K.

The Condensation of Aldehydes with Ammonia in the Presence of Alumina. A. E. TSCHITSCHIBABIN (*J. Russ. Phys. Chem. Soc.*, 1923, **54**, 411—413).—The reaction between aldehydes and ammonia takes place readily and with satisfactory yield on passing the gaseous mixture of the reacting substances over granular alumina at 200—350°; the optimum temperature depends on the aldehyde used. The apparatus used is similar to that commonly employed for the Sabatier reaction and is described in detail.

G. A. R. K.

The Condensation of Acetaldehyde with Ammonia in the Presence of Alumina. A. E. TSCHITSCHIBABIN, P. A. MOSCOWSKIN, and (MLLE) L. S. TIASHELOVA (*J. Russ. Phys. Chem. Soc.*, 1923, **54**, 413—420).—The reaction was carried out using the method described in the preceding abstract, the temperature being maintained at about 300°. The crude mixture of tertiary bases was obtained in 60% yield and was subjected to fractionation, followed by fractional precipitation by means of picric acid; 60% of the mixture was finally separated in the form of pure compounds. Of these, α - and γ -picoline constitute about 28% and 30%, respectively; 2-methyl-5-ethylpyridine 33%, and 4-methyl-3-ethyl pyridine, about 6%. In addition to these bases, the highest boiling fraction contains two bases, one of which (b. p. 185.5—186.5°, *picrate*, m. p. 133°) is identical with the collidine obtained from acetylene

and ammonia in the presence of alumina (A., 1915, i, 638); the other forms a picrate crystallising in needles, m. p. 164—165°. The products of the reaction are thus essentially the same as those obtained from acetylene and ammonia and also from acetaldehyde and ammonia by the older method.

G. A. R. K.

Products obtained on Heating Paracetaldehyde with Ammonia in Sealed Tubes. A. E. TSCHITSCHIBABIN and (MLLE)

M. P. OPARINA (*J. Russ. Phys. Chem. Soc.*, 1923, 54, 420—427).—It is shown that the compounds produced under the conditions originally used by Dürkopf and Schlaugk (A., 1888, 607) are essentially the same as those obtained from acetaldehyde and ammonia by the catalytic process (preceding abstract). By far the greatest percentage of the pyridine bases which were obtained in 30% yield consisted of 2-methyl-5-ethylpyridine, characterised by its picrate melting at 164·5°; α -picoline was also isolated in quantity in addition to small amounts of γ -picoline and 4-methyl-3-ethylpyridine; a *picrate* melting at 139° and belonging to an unknown base (*chloroplatinate*, m. p. 190°) having the composition of a trimethylpyridine was also isolated. This picrate was not identical with that of Guareschi's 2:3:4-trimethylpyridine or the picrates obtained by Tschitschibabin (A., 1915, i, 638). Neither the trimethylpyridine prepared by Auerbach (A., 1893, i, 175) and by Knudsen (A., 1895, i, 562) nor any trace of lutidines could be found in the reaction product.

G. A. R. K.

The Condensation of Propaldehyde with Ammonia. A. E. TSCHITSCHIBABIN and (MLLE) M. P. OPARINA (*J. Russ. Phys. Chem. Soc.*, 1923, 54, 428—446).—The condensation of propaldehyde with ammonia proceeds satisfactorily in the presence of alumina at 310—320°, the yield of tertiary bases being about 40%. These were subjected to separation through their picrates after a preliminary fractionation. The substances isolated consisted of the picrate of 3:5-dimethyl-2-ethylpyridine (parvoline) which constituted about 60% of the total, the picrate of 3:5-dimethylpyridine 18% and that of another parvoline, melting at 155—156° and crystallising in prisms. This parvoline appears to be identical with a compound obtained in addition to the first two by Dürkopf and Göttisch (A., 1890, 794, 1002); it has b. p. 219—220° (corr.)/748 mm., d_4^{20} 0·9672, d_4^{20} 0·9516, $d_4^{26·7}$ 0·9464, n_D 1·5064, and gives a chloroaurate, m. p. 138°. On oxidation the base yields a dibasic acid, m. p. 261°, identical with that obtained by Dürkopf (*loc. cit.*) which this author wrongly believed to be dimethylpyridinedicarboxylic acid and is now proved to be 4-ethylpyridine-3:5-dicarboxylic acid by its conversion into 4-ethylpyridine (*picrate*, m. p. 169°, *chloroplatinate*, m. p. 108°); the structure of this base is confirmed by its synthesis from pyridine and ethyl iodide. From these facts, it is concluded that the second parvoline obtained by Dürkopf and Göttisch and in the present research must be 3:5-dimethyl-4-ethyl pyridine. The formation of the two parvolines as well as of lutidine from propaldehyde and ammonia is in complete agreement with the authors' views (preceding abstracts)

as to the mechanism of such reactions. It is suggested that the formation of Schiff's paraconiine (*Annalen*, 1873, **166**, 88) which does not fall into line with these views was due to the presence of acetaldehyde in the butaldehyde used and that the product itself was a mixture composed chiefly of 2-propylpyridine and *i*-coniine (2-propylpiperidine); such condensations of mixtures of aldehydes with ammonia have already been observed (Stöhr, A., 1891, 579; 1892, 628) and it has now been found that mixtures of acetaldehyde with acraldehyde or ethylal and ammonia yield, in the presence of alumina, considerable quantities of pyridine. The possible synthesis of pyridine bases in plant organisms is also discussed. G. A. R. K.

The Spontaneous Decomposition of Cyanoacetyl Chloride.

G. SCHROETER and CHR. SEIDLER (*J. pr. Chem.*, 1922, [ii], **105**, 165—176).—The spontaneous decomposition of cyanoacetyl chloride, which proceeds with violence and evolution of much hydrogen chloride when distillation under reduced pressure is attempted, takes place gradually at the ordinary temperature, or, better, at 0°, very little hydrogen chloride being formed. Together with other substances, which are soluble in water but do not crystallise readily, the chief product of the reaction is 5-chloro-1:3-dihydroxynicotinonitrile, slender, colourless needles, which turn yellowish-brown at 187—190°, and decompose at a higher temperature; the disodium salt, with 6H₂O, is described. The constitution of this nitrile follows from its reactions. Although a disodium salt is formed by the action of concentrated alkali hydroxide solution, towards dilute (N/10) solutions the compound behaves as a monobasic acid. The chlorine atom is very firmly held; the action of 20% aqueous sodium hydroxide solution at 170—180° is required to eliminate the chlorine atom, one nitrogen atom being simultaneously removed, giving 1:3:5-trihydroxypyridine or 1:3:5-trihydroxynicotinic acid. The action of concentrated sulphuric acid on the nitrile gives 5-chloro-1:3-dihydroxynicotinamide, decomp. 220°, which, like the nitrile, gives a deep red coloration with ferric chloride in alcoholic solution, and behaves as an acid towards dilute alkali solutions. The prolonged action of alkali hydroxides causes almost complete elimination of the chlorine. The nitrile may be methylated by means of methyl sulphate in sodium hydroxide solution, giving a monomethyl ether, colourless crystals, m. p. 250° (decomp.), which is a monobasic acid, and gives a red coloration with ferric chloride; it forms a white, crystalline sodium salt, which reacts in boiling xylene solution with methyl sulphate, with formation of 5-chloro-1:3-dimethoxynicotinonitrile, m. p. 239—240° (decomp.). The latter is neutral towards cold sodium hydroxide solution, and does not give a coloration with ferric chloride. The chlorine is displaced by the action of boiling sodium hydroxide solution, or of boiling methyl-alcoholic potassium methoxide solution; the product of the latter reaction is 1:3:5-trimethoxynicotinonitrile, m. p. 260—261° (decomp.). The cyano-group in this compound is not converted into the amido-group, even when the action of cold concentrated sulphuric acid is prolonged during twenty-four hours.

W. S. N.

Substituted Indole Derivatives. I. REINHARD SEKA (*Ber.*, 1923, 56, [B], 2058—2062).—The application of the Gattermann and Hoesch syntheses to 2-methylindole is described.

3-Aldehyde-2-methylindole, $C_6H_4 \begin{smallmatrix} C(CHO) \\ \text{NH} \end{smallmatrix} > CMe$, m. p. 198—199°, is obtained in 87% yield by the action of dry hydrogen chloride on 2-methylindole and anhydrous hydrocyanic acid dissolved in ether. 3-Acetyl-2-methylindole, m. p. 195—196°, is prepared by the action of dry hydrogen chloride on an ethereal solution of 2-methylindole and acetonitrile and decomposition of the ketimine hydrochloride by hot water; the yield is 33% of that theoretically possible. Under similar conditions, 2-methylindole and benzonitrile give a well-crystallised *ketimine hydrochloride* which is decomposed by boiling water into 3-benzoyl-2-methylindole, colourless needles, m. p. 181—182° (yield about 75%). 3-Phenylacetyl-2-methylindole, prepared in about 80% yield from phenylacetonitrile and 2-methylindole, crystallises in pale yellow needles, m. p. 196—197°. Ethyl cyanoacetate and 2-methylindole yield (?) *ethyl 2-methylindyl-3-β-aminoacrylate*, $NH \begin{smallmatrix} C_6H_4 \\ CMe \end{smallmatrix} > C(NH_2):CH \cdot CO_2Et$, yellowish-green needles, m. p. 135°. H. W.

N-Substituted Oxindoles and Isatins. R. STOLLÉ [with R. BERGDOLL, M. LUTHER, A. AUERHAHN, and W. WACKER] (*J. pr. Chem.*, 1922, [ii], 105, 137—148).—A preliminary account of a lengthy research on the preparation and reactions of *N*-substituted oxindoles and isatins.

The reactivity of the methylene group in *N*-substituted oxindoles is evidenced by numerous reactions. Thus 1-ethyloxindole and 1-ethylisatin, or the 1-phenyl derivatives, condense in the presence of piperidine to give the 3-hydroxy-3':3'-dihydroisoindigotin derivative, which may be dehydrated to the isoindigotin derivative. The condensation of phenylisatin (1 mol.) and phenyloxindole (2 mols.) is effected by the use of sodium ethoxide. Ethyl- or phenyl-oxindole can be condensed with phthalic anhydride, or with nitrosodimethylaniline. The anil formed in the latter reaction can react with a further molecule of oxindole in boiling acetic acid solution, giving the isoindigotin derivative.

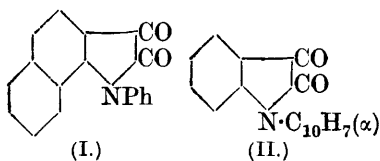
The isatins may be prepared from the oxindoles as follows. The action of ethyl nitrite in the presence of sodium ethoxide gives the isonitroso-derivative, which may then be hydrolysed, using mineral acids; or the 3:3-dihalogenated oxindole is prepared by means of hypochlorous or hypobromous acid, chlorine or bromine, or of phosphorus pentahalide, the dihalide being then hydrolysed to the isatin or isatinic acid (salt).

Hydrogen bromide in aqueous-alcoholic or carbon tetrachloride solution attacks the nucleus, giving, for example, 5-bromo-1-methyloxindole, 5:7-dibromo-1-methyloxindole, 5-bromo-1-ethyloxindole, or 5-bromo-1-phenyloxindole, the constitutions of which are proved by conversion into the isatin or isoindigotin derivatives. Hydrogen bromide in carbon tetrachloride solution acts on phenyloxindole, and moisture acts on the unstable additive compound of bromine

and phenyloxindole, to give 3:5-dibromo-1-phenyloxindole and 3:3:5-tribromo-1-phenyloxindole. The latter is also produced from 3:3-dibromo-1-phenyloxindole by the action of bromine in the presence of iron. 3-Bromo-1-phenyl-1-oxindole, which passes at 280° into diphenylisindigotin, can only be prepared by warming molecular quantities of 3:3-dibromo-1-phenyloxindole and phenyloxindole in carbon tetrachloride solution. The additive product from bromine and ethyloxindole reacts with a further 2 mols. of bromine in carbon tetrachloride solution, giving 3:3:5-tribromo-1-ethyloxindole.

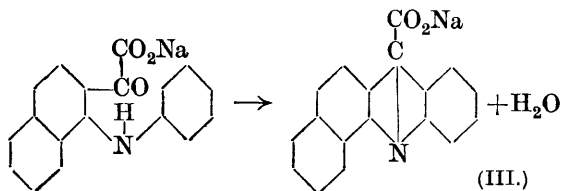
1-Methyloxindole is oxidised to dimethylisindigotin by means of sodium hyposulfite. 1-Phenyloxindole undergoes hydrolytic fission when warmed with aqueous alkali hydroxide solution at 100° ; the reverse change occurs when *o*-anilinophenylacetic acid is fused, or warmed in ethereal or alcoholic solution.

The action of oxalyl chloride on secondary anilines or naphthylamines gives oxamidyl chlorides, tetra-substituted oxamides occurring as by-products. Ring formation from oxamidyl chlorides frequently occurs in the absence of aluminium chloride, simply by heating, or even by warming in ethereal solution. Isatinic acids are oxidised to anthranilic acids by means of alkaline hydrogen peroxide. Most *N*-arylisatinic acids are converted by warming in alkaline solution into salts of acridinecarboxylic acid or its derivatives. Acridinecarboxylic acid is obtained in attempting to prepare phenylisatin by the action of oxalyl chloride on diphenylamine in the presence of aluminium chloride, the intermediate product being presumably *o*-anilinobenzoylformyl chloride. The action of oxalyl chloride on ditolylamine gives di-*p*-tolylamido-oxalyl chloride and 2:7-dimethylacridine hydrochloride; but sodium 5-methyl-1-*p*-tolylisatinate shows no tendency to pass into an acridine derivative. α -Naphthyloxanilyl chloride, α -C₁₀H₇-NPh·CO·COCl, passes, on being heated alone or with aluminium chloride, into



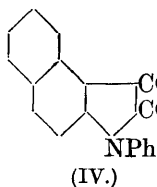
1-phenyl-6:7-benzoisatin, m. p. 217° , (I), and 1- α -naphthylisatin, (II), m. p. 176° . The latter gives α -naphthylanthranilic acid, C₆H₄·CO₂H(NH·C₁₀H₇), when oxidised in alkaline solution by means of hydrogen peroxide.

1-Phenyl-6:7-benzoisatin (I), passes into the salt of 5:6-benzacridine-9-carboxylic acid (III), when warmed in a strongly alkaline



solution; the salt of the isatinic acid is formed immediately. The compound (III), as the free acid, loses carbon dioxide on being heated, giving the known 5:6-benzacridine. Elimination of hydrogen chloride occurs when β -naphthyloxanilyl chloride is

heated alone, or in solution, with formation of 1-phenyl-4 : 5-benzoisatin (IV), which gives, on oxidation, 2-phenylaminonaphthalene-1-carboxylic acid. The compound (IV) passes, on treatment with an excess of alkali, into the salt of 7 : 8-benzo-acridine-9-carboxylic acid, from which the known 7 : 8-benzoacridine is obtained by elimination of carbon dioxide. 1-β-Naphthyl-4 : 5-benzoisatin is readily formed from di-β-naphthylamidoxalyl chloride, even by the action of boiling water; it is converted on treatment with concentrated alkali

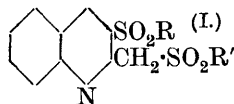


into the salt of 1 : 2 : 7 : 8-dibenzoacridine-9-carboxylic acid, from which elimination of carbon dioxide gives 1 : 2 : 7 : 8-dibenzoacridine.

Phenylisatin is reduced by means of sodium hyposulphite to 1 : 1'-diphenylisatide, $\text{NPh} \langle \text{C}_6\text{H}_4 \rangle \text{C}(\text{OH}) \cdot \text{C}(\text{OH}) \langle \text{C}_6\text{H}_4 \rangle \text{NPh}$, and 1-phenyldioxindole. The latter is coloured a deep indigo blue on addition of barium hydroxide solution to its pyridine solution; although dioxindole itself does not give any coloration (Hantzsch, A., 1921, i, 598). W. S. N.

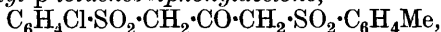
A New Illustrative Synthesis of Quinoline. W. KÖNIG [with K. SEIFERT] (*Ber.*, 1923, 56, [B], 1853—1855).—Quinoline is produced when the substance $\text{NPh} \cdot \text{CH} : \text{CH} \cdot \text{CH} : \text{NPh} \cdot \text{HCl}$ is cautiously heated with fused zinc chloride. The observation confirms the theory, advanced by Beyer in 1886, that the primary product in Skraup's synthesis of quinoline is a substance of the type $\text{C}_6\text{H}_5 \cdot \text{NH} \cdot \text{CHR} \cdot \text{CH}_2 \cdot \text{CHO}$, which passes successively into a dihydroquinoline and a quinoline derivative. H. W.

Syntheses of 3-Arylsulphonyl-2-arylsulphonylmethylquinolines, and of 3-arylsulphonyl-2-phenylquinolines. J. TRÖGER and K. VON SEELEN (*J. pr. Chem.*, 1923, [ii], 105, 208—231).—The action of an excess of *o*-aminobenzaldehyde at 160° for two



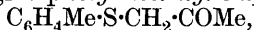
and a half hours on diphenylsulphonylacetone gives 3-benzenesulphonyl-2-benzenesulphonylmethylquinoline (I; R and R' = Ph), white needles, m. p. 168°, which is not a base, and is unaffected by fusion with potassium hydroxide. By the action of hot, concentrated hydrochloric acid under pressure, the $\alpha\text{-Ph} \cdot \text{SO}_2\text{-}$ radicle is replaced by hydrogen. 3-*p*-Toluenesulphonyl-2-*p*-toluenesulphonylmethylquinoline, yellowish-green, prismatic needles, m. p. 202°, is obtained by heating a mixture of *o*-aminobenzaldehyde and di-*p*-toluenesulphonylacetone at 155° for fifteen minutes. *p*-Chlorobenzenesulphonylacetone, white crystals, m. p. 83°, is formed by heating monochloroacetone and sodium *p*-chlorobenzenesulphinate in alcoholic solution at 100° for about an hour; its phenylhydrazone forms colourless, four-sided leaflets, m. p. 161°. The action of bromine (1 mol.) in glacial acetic acid solution on the sulphonylacetone gives ω -bromo-*p*-chlorobenzenesulphonylacetone, white, stellate clusters, m. p. 142°, which reacts with sodium *p*-chlorobenzene-

sulphinate in boiling alcoholic solution to give *di-p-chlorobenzene sulphonylacetone*, large, yellowish-white plates, m. p. 166°. When the latter is heated at 165° for fifteen minutes with *o*-aminobenzaldehyde, the product is *3-p-chlorobenzenesulphonyl-2-p-chlorobenzenesulphonylmethylquinoline*, yellow plates, m. p. 197°. *p-Chlorobenzenesulphonyl-p-toluenesulphonylacetone*,



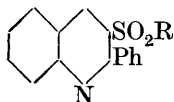
pale yellow needles, m. p. 163° (*oxime*, m. p. 214°), is prepared by heating equivalent quantities of sodium *p*-chlorobenzenesulphinate and ω -bromo-*p*-toluenesulphonylacetone in alcoholic solution for about two hours. When this sulphonylacetone is heated for ten minutes at 165° with *o*-aminobenzaldehyde, it gives *3-p-chlorobenzenesulphonyl-2-p-toluenesulphonylmethylquinoline*, white plates, m. p. 199—200°. The constitution of this compound (cf. I) is proved by heating it with concentrated hydrochloric acid at 240° for a long time, whereby the $-\text{SO}_2\cdot\text{R}'$ radicle is eliminated, giving *3-p-chlorobenzenesulphonyl-2-methylquinoline*. The interaction of sodium *p*-chlorobenzenesulphinate and ω -bromobenzene-sulphonylacetone in boiling alcoholic solution gives *benzenesulphonyl-p-chlorobenzenesulphonylacetone*, yellow needles, m. p. 129—130° [*semicarbazone*, yellow plates, m. p. 231° (decomp.)], which, when perfectly pure, reacts at 130—150° with *o*-aminobenzaldehyde during the course of about twenty minutes, to give *3-p-chlorobenzenesulphonyl-2-benzenesulphonylmethylquinoline*, greyish-white prisms, m. p. 157°. The constitution of the latter follows from the production of *3-p-chlorobenzenesulphonyl-2-methylquinoline*, by the action of concentrated hydrochloric acid at 240° for six to seven hours. *p-Chlorobenzenesulphonyl-3-naphthalenesulphonylacetone*, $\text{C}_{10}\text{H}_7\cdot\text{SO}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{SO}_2\cdot\text{C}_6\text{H}_4\text{Cl}$, long, yellow needles, m. p. 167°, is produced by heating sodium β -naphthalenesulphinate and ω -bromo-*p*-chlorobenzenesulphonylacetone for two to three hours in alcoholic solution; when heated for twenty minutes at 170° with *o*-aminobenzaldehyde, it gives *3-p-chlorobenzenesulphonyl-2- β -naphthalenesulphonylmethylquinoline*, white clusters of needles, m. p. 163°, which is converted into *3-chlorobenzenesulphonyl-2-methylquinoline* by the action of concentrated hydrochloric acid at 240° for five hours.

p-Tolylmercaptan reacts with absolute alcoholic sodium ethoxide and chloroacetone to give *p-tolyl acetonyl sulphide*,



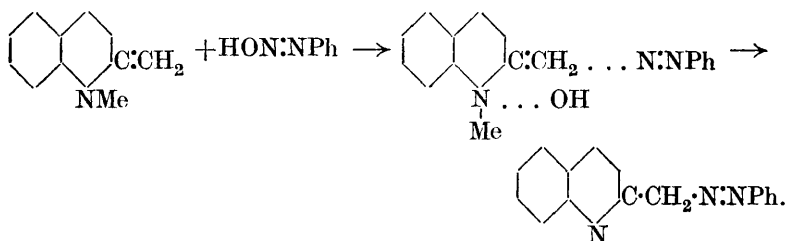
an oil, which gives a crystalline *sodium hydrogen sulphite* additive compound, and an oily *phenylhydrazone*. It has not been found possible in any way to prepare a quinoline derivative by condensing this acetone derivative with *o*-aminobenzaldehyde.

A series of 3-arylsulphonyl-2-phenylquinolines (formula annexed) is obtained by condensing *o*-aminobenzaldehyde with an arylsulphonylacetophenone, by heating at 200—240° for one and a half to two hours. *3-Benzenesulphonyl-2-phenylquinoline* forms pale yellow prisms, m. p. 208.5—209°, *hydrochloride*,



prisms, *nitrate*, *hydrogen sulphate*, *perchlorate*, white plates, *chloroplatinate*, yellow needles. 3-*p-Toluenesulphonyl-2-phenylquinoline* forms white plates, m. p. 243°, *perchlorate*, large, white plates, *nitrate*, clusters of small, white needles, *chloroplatinate*, orange needles. 3-*p-Chlorobenzene-sulphonyl-2-phenylquinoline* forms small, yellow needles, m. p. 237°, *nitrate*, white, hexagonal leaflets, *perchlorate*, slender, yellow needles, *chloroplatinate*, orange-red, flattened prisms, in clusters. W. S. N.

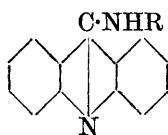
The Anhydro-base of 2-Methylquinoline. ALFRED ADAM (*Wissensch. Ind.*, 1923, 2, 2—8; from *Chem. Zentr.*, 1923, i, 1591—1592).—The methiodide of the anhydro-base of 2-methylquinoline reacts with diazotised aniline or *p*-nitroaniline in the presence of potassium hydroxide with formation of red or violet colouring matters. The reaction takes place with elimination of methyl alcohol, probably according to the following scheme :



The *p*-nitroaniline derivative shows halochromism with alkali hydroxides, changing from reddish-yellow to violet. The violet colouring matter is probably an inner complex salt formed by ring closure with the auxiliary valencies of nitrogen. The hydrazone and its hydrochloride also show halochromism. *Anilinodiazot-2-methylquinoline hydrochloride*, $\text{C}_{16}\text{H}_{14}\text{N}_3\text{Cl}$, obtained by simultaneous addition of potassium hydroxide solution and diazotised aniline to an aqueous solution of 2-methylquinoline methiodide, forms reddish-yellow needles, m. p. 211—212°. An *acetyl* compound, corresponding with three molecules of acetic acid, forms ruby-red crystals, m. p. 202—203°. *p-Nitroanilinodiazot-2-methylquinoline hydrochloride*, $\text{C}_6\text{H}_{13}\text{O}_2\text{N}_4\text{Cl}$, forms dark red needles, m. p. 240—241°. The *inner complex* salt formed from the last compound by the action of potassium hydroxide forms dark violet needles, m. p. 171°. The same compounds are obtained when the ethiodide or amyl iodide is used in the place of the methiodide. *Quinoline-acrylic acid* is obtained as its *barium* salt, m. p. 197°, after discoloration at 165°, by the action of potassium carbonate on chloral-2-methylquinoline and subsequent addition of barium chloride. The *hydrochloride* forms needles, m. p. 184—185°. *2-Methylquinoline-p-nitrophenylhydrazone*, $\text{C}_{16}\text{H}_{12}\text{O}_2\text{N}_4$, forms yellowish-brown needles, m. p. 244—245°. The *hydrochloride*, $\text{C}_{16}\text{H}_{13}\text{O}_2\text{N}_4\text{Cl}$, red crystals, has m. p. 257—258°. G. W. R.

Preparation of Derivatives of Acridine. FARBERWERKE VORM.

MEISTER, LUCIUS, & BRÜNING (D.R.-PP. 360421, 364034, 364032, 367084, and Swiss Pat. 94950; from *Chem. Zentr.*, 1923, ii, 1249—1250).—9-Halogenacridines are treated with ammonia or primary aryl amines, or with secondary aliphatic amines in the presence of catalysts such as copper salts, or 5-alkoxyacridine or 5-aryloxyacridine derivatives are heated with ammonia, or primary or secondary



aliphatic amines. The compounds obtained are of the composition indicated by the annexed formula, where alkyl-, amino-, or alkoxy-groups may enter the acridine group. 5-Ethanolamino-3-ethoxyacridine is obtained by heating 5-chloro-3-ethoxyacridine (crystals, m. p. 144) with ethanolamine at 100°. It

forms yellow crystals, m. p. 146°. 5-Chloro-3-ethoxyacridine is prepared by ethylation of 3-hydroxyacridone to 3-ethoxyacridone, m. p. 259—260°, and treatment of the latter compound with phosphorus pentachloride. 5-Chloro-3-ethoxyacridine and ethylamine give 5-ethylamino-3-ethoxyacridine, yellow crystals, m. p. 131—132°. 5-p-Hydroxyphenylethylamino-3-ethoxyacridine forms yellow crystals, m. p. 233°. The glycollate has m. p. 208°. 4-Aminoantipyrine and 5-chloro-3-ethoxyacridine give 5-antipyrilamino-3-ethoxyacridine, yellowish-red prisms, m. p. 257°. 5-Ethanolaminoacridine from 5-chloroacridine and ethanolamine forms long, yellow needles, m. p. 206°. 5-Aminoacridine forms yellow needles, m. p. 232°. 5-Diethylamino-3-ethoxyacridine is a thick oil; its hydrochloride forms red crystals, m. p. 177° after sintering. 5-Piperidino-3-ethoxyacridine is crystalline, m. p. 122°; the hydrochloride has m. p. 252°. 5-Ethoxyacridine is prepared by the action of sodium ethoxide on 5-chloroacridine; it has m. p. 83° and is easily changed by the action of mineral acids into acridone. With ethylamine it gives 5-ethylaminoacridine, crystals, m. p. 129°. 3:5-Diethoxyacridine obtained from 5-chloro-3-ethoxyacridine and sodium ethoxide forms needles, m. p. 83°. 5-Phenoxyacridine, from 5-chloroacridine and sodium phenoxide, has m. p. 112°. 5-Chloro-3-ethoxyacridine and sodium phenoxide give 5-phenoxy-3-ethoxyacridine, m. p. 85°, which with ammonia under pressure yields 5-amino-3-ethoxyacridine, m. p. 221°. Reduction of 5-chloro-2-nitro-8-ethoxyacridine gives 5-chloro-2-amino-8-ethoxyacridine, m. p. 192°, which with sodium ethoxide yields 2-amino-5:8-diethoxyacridine, and with sodium phenoxide, 2-amino-5-phenoxy-8-ethoxyacridine, m. p. about 100°. The three compounds last mentioned give with ammonia under pressure 2:5-diamino-8-ethoxyacridine, m. p. 124°. G. W. R.

Preparation of Acridine Derivatives. FARBERWERKE VORM.

MEISTER, LUCIUS, & BRÜNING (D.R.-PP. 364031, 364033, 364037; Swiss Pats. 93439, 93752, 93753, 94363, 94625, 94626, 94982, 96608, 96609; from *Chem. Zentr.*, 1923, ii, 1250—1251; cf. preceding abstract).—5-Hydrazinoacridine derivatives, nitro-5-aminoacridine derivatives, or nitro-5-hydrazinoacridine derivatives are submitted to reduction. For example, 5-phenylthylhydrazinoacridine, orange-yellow crystals, m. p. 173—174°, from phenylhydrazine and 9-chloro-

acridine, by reduction gives 5-aminoacridine, which can also be obtained by reduction of 5-hydrazinoacridine, orange needles, m. p. 169°, or of hydrazino-5 : 5-bisacridine, $(C_{13}H_{18}N) \cdot NH \cdot NH(C_{13}H_{18}N)$, dark red crystals, m. p. 265°. Reduction of 5-phenylhydrazino-3-ethoxyacridine, a light yellow powder, m. p. 232—234°, yields 5-amino-3-ethoxyacridine. By nitration of 5-aminoacridine in the presence of strong sulphuric acid, dinitro-5-aminoacridine, red flakes, m. p. above 300° (decomp.), is formed. The sulphate gives by reduction a triaminoacridine which forms dark red leaflets; the hydrochloride forms long, yellow needles. From 2-chloro-4-nitrobenzoic acid and aniline, 5-nitrodiphenylamine-2-carboxylic acid is obtained which by elimination of water yields 2-nitroacridine. The latter, with phosphorus pentachloride, gives 5-chloro-2-nitroacridine, yellow leaflets, m. p. 214°, which with ethyl alcoholic ammonia yields 2-nitro-5-aminoacridine, m. p. above 300° (decomp.). By reduction of this compound, 2 : 5-diaminoacridine is obtained; it forms yellow needles, m. p. 146°; the hydrochloride forms yellow crystals. 5-Nitro-4'-ethoxydiphenylamino-2-carboxylic acid, from 2-chloro-4-nitrobenzoic acid and *p*-phenetidine, is crystalline and has m. p. 233—234°. By elimination of water and subsequent treatment with phosphorus pentachloride, it gives 5-chloro-2-nitro-8-ethoxyacridine, crystals, m. p. 186—187°, which with ammonia yields 2-nitro-5-amino-8-ethoxyacridine, crystals, m. p. 310°, with yellow and red modifications. By reduction of the last compound, 2 : 5-diamino-8-ethoxyacridine is obtained. 2-Nitro-5-phenylhydrazinoacridine forms dark red crystals; the hydrochloride is an orange-red powder which gives by reduction 2 : 5-diaminoacridine. 2-Nitro-5-phenylhydrazino-8-ethoxyacridine is a red mass from which 2 : 5-diamino-8-ethoxyacridine is obtained by reduction. The last compound is also obtainable by reduction of 2-amino-5-phenylhydrazino-8-ethoxyacridine. 2 : 5-Diamino-8-methoxyacridine forms yellow crystals, m. p. 240—242°. The hydrochloride, yellow needles, is obtained by reduction of 2-nitro-5-amino-8-methoxyacridine. The last compound is obtained from 3-nitro-4'-methoxydiphenylamine-6-carboxylic acid, red needles, m. p. 235°, by way of 5-chloro-2-nitro-8-methoxyacridine, yellow needles, m. p. 216—218°. 2-Nitro-5-phenylhydrazino-8-methoxyacridine is a red substance, m. p. above 300°; its hydrochloride is obtained by treatment of the corresponding chloro-derivative with phenylhydrazine. Reduction of 2-nitro-5-amino-8-isoamyloxyacridine, red needles, m. p. 272°, or of 2-nitro-5-phenylhydrazino-8-isoamyloxyacridine, red crystals, yields 2 : 5-diamino-8-isoamyloxyacridine, which forms yellow needles, m. p. 205—206°; the hydrochloride has m. p. above 300°.

G. W. R.

Preparation of Acridine Derivatives. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-PP. 364035, 364036; from *Chem. Zentr.*, 1923, ii, 1251—1252; cf. preceding abstracts).—Acridine-5-carboxylazides are decomposed with elimination of nitrogen, and the intermediate products obtained are hydrolysed, or acridine-5-carboxylamides are treated with hypohalogenites.

Acridine-5-carboxylazide is prepared by esterification of acridine-5-carboxylic acid, treatment of the ester with hydrazine, whereby *acridine-5-carboxylhydrazide*, m. p. 244°, is obtained, and treatment of the last compound with sodium nitrite in acetic acid solution. The azide, which decomposes at the ordinary temperature, on being heated with sulphuric acid gives *5-aminoacridine sulphate*, needles, from which the free base is obtained. By heating the azide with ethyl alcohol, *5-urethanoacridine*, $C_{13}H_8N \cdot NH \cdot CO_2Et$, is obtained: it forms needles, m. p. 188—194°, and on being heated with 2*N*-sulphuric acid gives *5-aminoacridine sulphate*. *Acridine-5-carboxylamide*, m. p. 260°, yields on treatment with potassium hypobromite *5-aminoacridine*. In the same way, *3-chloroacridine-5-carboxylamide*, m. p. 243°, yields with potassium hypobromite *3-chloro-5-aminoacridine*, m. p. 273—274°. G. W. R.

Preparation of Acridine Derivatives. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (Brit. Pat. 176038; from *Chem. Zentr.*, 1923, ii, 1252; cf. preceding abstracts).—*3-Chloroacridine-5-carboxylic acid*, m. p. 264°, is prepared in the following way. *o*-Chlorobenzaldehyde, by treatment with magnesium ethyl iodide, gives *o-chlorophenylethyl alcohol*, which by oxidation with chromium trioxide yields *o-chloroacetophenone*, b. p. 98°/6 mm. By condensation of the last compound with *p*-chloroaniline, *3-chloro-5-methylacridine* is obtained, from which, by Kaufmann and Valette's reaction (A., 1912, i, 655), *3-chloro-5-aldehydoacridine*, m. p. 171—172°, is prepared. Oxidation of the last compound with chromium trioxide yields the carboxylic acid. *Ethyl 3-chloroacridine-5-carboxylate* has m. p. 71—72°. It gives with hydrazine the corresponding *hydrazide*, m. p. 210—211°, which by the action on it of sodium nitrite in acetic acid solution yields *3-chloroacridine-5-carboxylazide*. The last compound, on being heated with ethyl alcohol, gives *3-chloro-5-urethanoacridine*, $C_{13}H_7NCl \cdot NH \cdot CO_2Et$, m. p. 205°, from which by heating with dilute sulphuric acid *3-chloro-5-aminoacridine* is obtained. G. W. R.

***N*-Diphenylglycine-*o*-carboxylic Acid and its Derivatives.** MARTIN FREUND and ADOLF SCHWARZ (*Ber.*, 1923, 56, [B], 1828—1831).—*Diphenylglycine-*o*-carboxylic acid*,



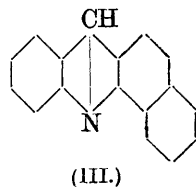
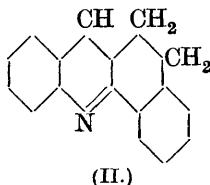
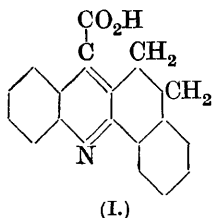
m. p. 165—167°, is conveniently prepared by the interaction of potassium *o*-chlorobenzoate, potassium phenylaminoacetate, and potassium hydroxide in the presence of copper powder and water at 130—160°; the *potassium* salt is described. The acid is transformed by concentrated sulphuric acid into *acridone-10-acetic acid*, $CO < \begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix} > N \cdot CH_2 \cdot CO_2H$, a colourless, crystalline powder which gradually loses carbon dioxide when heated and forms *N*-methylacridone. *Acridoneacetanilide*, a colourless, crystalline powder, and *methyl acridoneacetate*, yellow octahedra, m. p. 178—179°, are described. The presence of the ketonic group in acridoneacetic acid cannot be established by means of the customary reagents, since it does not react with hydroxylamine hydrochloride and with

phenylhydrazine yields the *phenylhydrazine* salt, m. p. 126°. Bromination of the acid in hot glacial acetic acid solution leads to the production of *dibromoacridoneacetic acid*, yellow octahedra, whereas nitric and sulphuric acids transform it into *dinitroacridoneacetic acid*, a yellow, crystalline powder, decomp. 169—170° (the *sodium* salt, red leaflets, is described).

Diphenylglycine-*o*-carboxylic acid is usually converted into indigotin by fusion with potassium hydroxide, but, under certain conditions, 1:1'-diphenylindigotin (cf. Friedländer and Kunz, A., 1922, i, 765) is obtained in small yield. H. W.

Derivatives of Tetrahydrocarbazole. IV. WILLIAM HENRY PERKIN, jun., and GEORGE CLIFFORD RILEY (T., 1923, 123, 2399—2408).

Preparation of Polycyclic Derivatives of 2-Phenylquinoline-4-carboxylic Acid and Products Substituted in the Benzene Nucleus of the Quinoline Group. TETRALIN G. M. B. H. (D.R.-P. 362539; from *Chem. Zentr.*, 1923, ii, 1248—1249).—1-Ketotetrahydronaphthalene or similar polycyclic ketones are condensed with isatin or its substitution products in alkaline solution. Isatin and 1-ketotetrahydronaphthalene give on heating at 100° in ethyl-alcoholic aqueous solution of potassium hydroxide and acidifying the products of reaction *dihydronaphthacridine-7-carboxylic acid* (I), needles, having m. p. 249°. On heating above the m. p. the last compound gives *dihydronaphthacridine* (II), with evolution of carbon dioxide. It is an almost colourless oil with b. p. 248—249°/12 mm. The *hydrochloride* has m. p. 228°, and the methiodide, m. p. 190°. By treating dihydronaphthacridinecarboxylic acid or dihydronaphthacridine with dehydrogenating reagents such as lead oxide, α -naphthacridine (III), (cf. Ullmann and La Torre, A., 1904, i, 929), m. p. 108°, is obtained.



The isomeric *dihydronaphthacridinecarboxylic acid* obtained from 2-ketotetrahydronaphthalene and isatin is a colourless powder, m. p. 255°. 4-Keto-*s*-octahydroanthracene (Schroeter and Tetralin G. m. b. H., A., 1922, i, 1136), gives with isatin a light yellow, crystalline *carboxylic acid*, m. p. 210°. *p*-Bromodihydronaphthacridinecarboxylic acid forms crystals, m. p. 262° (decomp.).

G. W. R.

Phenylmethylooxazolecarboxylic Acids. MARIO BETTI and GUGLIELMO SENSI (*Atti R. Accad. Lincei*, 1923, [v], 32, i, 615—618).—The solubilities in water of the two isomeric 5-phenyl-

3-methylisooxazole-4-carboxylic acids, m. p. 189° and 157° (A., 1922, i, 52), per 100 g. of water are, respectively, 0.0133 and 0.3739 g. at 13.5° and 0.0150 and 1.0890 g. at 35°. For the former acid the value of k is 0.02038; for the latter acid considerably higher values are obtained, but these diminish markedly as the dilution increases, probably owing to the ease with which the acid changes in aqueous solution. These results are in accord with the general rule that of two geometrical isomerides, that with the lower melting point is the more soluble and the more energetic. T. H. P.

Quinhydrone-like Compounds of 1 : 1'-Dialkyldihydro-4 : 4'-dipyridyls. BRUNO EMMERT and VALENTIN DÖLLEIN (*Ber.*, 1923, 56, [B], 2068—2071).—A solution of dipyridyl diisoamyl iodide in water is treated with silver oxide and filtered. The filtrate, when heated in an atmosphere of hydrogen at 95°, gradually becomes intensely blue and deposits resinous matter. If the solution is now treated with hydriodic acid or with dipyridyl diisoamyl iodide the separation of tetraisoamyl dipyridyl violet iodide is observed. This may be regarded as a simple ionic reaction if it is admitted that the solution contains tetraisoamyl dipyridyl violet hydroxide. The formation of the latter can be explained by the hypothesis that a portion of the molecule of diisoamyl dipyridylum hydroxide or of its pseudo-base becomes oxidised at the expense of other molecules. The quinonoid component of the dye is thus produced which combines with unchanged diisoamyl dipyridylum hydroxide.

A similar series of experiments with dibenzyl dipyridylum hydroxide is recorded; in this case the violet coloration is developed without warming. The products formed by the addition of hydriodic or hydrobromic acids of dipyridyl dibenzyl iodide or -bromide are identified as tetrabenzyl dipyridyl violet iodide and -bromide. The solution therefore contains tetrabenzyl dipyridyl violet hydroxide. H. W.

Complex Metallic Derivatives of Indigotin. II. K. KUNZ and O. GÜNTHER (*Ber.*, 1923, 56, [B], 2027—2034).—In continuation of previous work (this vol., i, 155), it is shown that the formation of complex metallic compounds of indigotin and its derivatives takes place without the evolution of hydrogen; the metal therefore is united in the molecule solely by residual valencies. The indigoid compounds appear to be closely related to the metallic compounds of chlorophyll described by Willstätter.

The sodium derivative of indigotin, $C_{16}H_{10}O_2N_2Na$, blackish-green, multi-sided crystals, is prepared by heating indigotin with metallic sodium at 140—150° in the presence of anhydrous xylene in an atmosphere free from oxygen. It is stable when dry and is not affected by oxygen or concentrated sodium hydroxide solution; it is decomposed by water, alcohol, or acids, with regeneration of indigotin and formation of small amounts of ill-defined resinous compounds. The protracted action of the alkali metals at 150° yields dimetallic derivatives, of which the di-potassium compound is described. Close analogy in appearance and properties is shown

by the mono-sodium derivative and the additive compounds of indigotin with sodium hydroxide and ethoxide; the likeness extends to the additive *compounds* with tin tetrachloride, $C_{16}H_{10}O_2N_2, SnCl_4$, small, blackish-green needles, and with magnesium phenyl bromide, $C_{16}H_{10}O_2N_2, MgPhBr$; the so-called additive product of indigotin and sodium phenoxide is really the ethoxide derivative.

Indigotin reacts with zinc in the presence of boiling naphthalene without marked evolution of hydrogen. Under similar conditions, zinc carbonate yields the *compound* $C_{32}H_{20}O_4N_4, ZnO$.

"Thioindigo" yields the *sodium* derivative, $C_{16}H_{10}O_2S_2, Na$, almost black crystals, with some difficulty; the additive compound with sodium ethoxide, $C_{16}H_{10}O_2S_2, 2NaOEt$, is also described.

The action of the alkali metals on diphenylindigotin can be studied only in the case of potassium at 0° . The unstable *mono-potassium* derivative, $C_{56}H_{36}O_4N_4, K$, and the *di-potassium* compound, $C_{56}H_{36}O_4N_4, K_2$, were analysed. They are decomposed by water into diphenylindigotin and by-products from which *N*-phenylisatin and *N*-phenylanthranilic acid can be isolated. When heated with zinc amalgam in the presence of boiling toluene, diphenylindigotin yields the *compound* $C_{56}H_{36}O_4N_4, Zn$, which is too unstable to permit its isolation in substance. H. W.

4 : 5-Diaminopyrimidines and their Conversion into Purines. WILHELM TRAUBE [with FRIEDRICH SCHOTTLÄNDER, CARL GOSLICH, ROBERT PETER, FRANZ ANDREAS MEYER, HEINRICH SCHLÜTER, WILHELM STEINBACH, and KARL BREDOW] (*Annalen*, 1923, 432, 266—296).—4-Amino-2 : 6-dihydroxypyrimidine (A., 1900, i, 416), from which the 4 : 5-diamino-derivative is obtained (*loc. cit.*), is now prepared by the action of ethyl cyanoacetate on an equivalent quantity of carbamide in the presence of 1—2 equivalents of sodium ethoxide in boiling alcoholic solution. 4-Amino-5-carbamido-2 : 6-dihydroxypyrimidine, slender, white needles, is obtained by boiling the sulphate of the 4 : 5-diamino-compound with potassium cyanate in aqueous solution; it loses ammonia at 230° , with formation of uric acid. The action of phenylcarbimide on 4 : 5-diamino-2 : 6-dihydroxypyrimidine sulphate in the presence of sodium hydroxide solution at 0° leads to the formation of 4-amino-5-phenyl-carbamido-2 : 6-dihydroxypyrimidine, colourless needles, which is converted by boiling with dilute hydrochloric acid into 9-phenyluric acid; the formation of the latter proves that it is the 5-amino-group which is attacked by the phenylcarbimide, since the loss of ammonia from the isomeric 5-amino-4-phenylcarbamido-derivative would give 7-phenyluric acid.

4-Amino-2 : 6-dihydroxy-3-methylpyrimidine is made by boiling methylcarbamide, ethyl cyanoacetate, and sodium ethoxide in alcoholic solution, and is used (*loc. cit.*) in preparing 4 : 5-diamino-2 : 6-dihydroxy-3-methylpyrimidine; the latter is converted by the action of boiling acetic anhydride into 4-amino-5-acetamido-2 : 6-dihydroxy-3-methylpyrimidine, $+2H_2O$, clusters of slender needles, the sodium salt of which passes at 230 — 240° , with loss of water, into the *sodium* salt (slender needles) of 3 : 8-dimethylxanthine,

+H₂O, slender needles. The conversion of 4 : 5-diamino-2 : 6-dihydroxy-3-methylpyrimidine into 3-methyluric acid (A., 1901, i. 52) may be effected by the action of cyanic acid, giving a substituted carbamide, which passes at 240°, with loss of ammonia, into 3-methyluric acid. Similarly, by the use of phenylcarbimide, a carbamide derivative is produced, from which ammonia is eliminated by boiling with hydrochloric acid, giving 9-phenyl-3-methyluric acid (cf. Meyer, *Diss. Berlin*, 1903). The use of phenylthiocarbimide in boiling aqueous-alcoholic solution gives 4-amino-5-phenylthiocarbamido-2 : 6-dihydroxy-3-methylpyrimidine, +1½H₂O, which is converted by boiling with 20% hydrochloric acid into 8-thio-9-phenyl-3-methyluric acid, microscopic leaflets. When the latter is treated in dilute hydrochloric acid (d 1.08) solution with sodium nitrite, 9-phenyl-3-methylxanthine, needles, is obtained. 4-Amino-5-oxalylamido-2 : 6-dihydroxy-3-methylpyrimidine, +H₂O, clusters of long needles, is obtained by fusing diaminodihydroxymethylpyrimidine with an excess of oxalic acid at 160—170° in a vacuum; it forms a crystalline *disodium* salt, which passes at 250—260° into the *disodium* salt of 3-methylxanthine-8-carboxylic acid, +1½H₂O, white leaflets, or clusters of needles, *barium* salt, needles. This acid rapidly loses carbon dioxide at 160° to give 3-methylxanthine. 4-Amino-5-cyanoacetamido-2 : 6-dihydroxy-3-methylpyrimidine, white, glistening, flexible needles, is obtained by fusing diaminodihydroxymethylpyrimidine with cyanoacetic acid at 120—130°. It is converted by the action of sodium hydroxide into 3-methylxanthine-8-acetic acid, +H₂O, clusters of white needles, *methyl* ester, needles. If, instead of cyanoacetic acid, succinic acid is used, first at 150°, finally under reduced pressure at 160—170°, the product is 4-amino-5-succinylamido-2 : 6-dihydroxy-3-methylpyrimidine, needles, the crystalline *disodium* salt of which passes at 250—260° into the *disodium* salt of 3-methylxanthine-8-propionic acid, +H₂O, *methyl* ester, long, flexible needles, *amide*, slender needles.

4 : 5-Diamino-2 : 6-dihydroxy-1 : 3-dimethylpyrimidine (*loc. cit.*) may be conveniently obtained by boiling *s*-dimethylcarbamide, ethyl cyanoacetate, and sodium ethoxide, in alcoholic solution. It is converted by the action of boiling acetic anhydride into 1 : 3 : 8-trimethylxanthine, colourless, rhombic prisms. The action of molten cyanoacetic acid at 120—130° under reduced pressure on diaminodihydroxydimethylpyrimidine gives 4-amino-5-acetamido-2 : 6-dihydroxy-1 : 3-dimethylpyrimidine, needles, which is converted by the action of hot sodium hydroxide solution into *theophyllineacetic acid*.

The action of boiling, glacial acetic acid on 2 : 4 : 5-triamino-6-hydroxypyrimidine gives the 5-acetyl derivative, +H₂O, stellate clusters of colourless needles, the sodium salt of which passes at 220—240° into the sodium salt of 8-methylguanine, colourless prisms, *hydrochloride*, +H₂O, colourless prisms, *sulphate*, elongated, colourless, octagonal tablets, *nitrate*, oval leaflets. 8-Ethylguanine, slender, colourless needles (*hydrochloride*, +H₂O, prisms), is similarly prepared from 2 : 4-diamino-5-propionamido-6-hydroxypyrimidine. Tri-

aminohydroxypyrimidine reacts with fused succinic acid at 160—170° under reduced pressure to give 2 : 4-diamino-5-succinylamido-6-hydroxypyrimidine, yellow needles, from which, by heating the sodium salt at 250—260°, *guanine-8-propionic acid* is obtained; its *methyl ester hydrochloride* forms colourless needles, and has a sweet taste.

4-Amino-6-hydroxy-3-methylpyrimidine, $+2\text{H}_2\text{O}$, glistening, white prisms (*hydrochloride*, small, transparent rods), is obtained by keeping an alcoholic solution containing sodium ethoxide, ethyl cyanoacetate, and acetamide hydrochloride. It is converted by the action of nitrous acid into the 5-oximino-derivative, stellate clusters of large, blackish-green crystals (*sodium salt*, faintly violet needles, violet *potassium salt*), which is reduced in boiling aqueous suspension by means of ammonium sulphide, giving 4 : 5-diamino-6-hydroxy-2-methylpyrimidine, $+\text{H}_2\text{O}$, stellate clusters of transparent prisms, *sulphate*, *hydrochloride*, rhombic tablets. The diamine is converted by the action of boiling concentrated formic acid into 6-hydroxy-2-methylpurine (2-methylhypoxanthine), colourless needles, *hydrochloride*, slender, transparent prisms, *sulphate*, rods, *sodium salt*, long, white, lustrous, monoclinic needles. 2-Methylhypoxanthine is converted by the action of aqueous-alcoholic sodium hydroxide solution and methyl iodide into 6-hydroxy-1 : 2 : 7-trimethylpurine, which forms an *additive* compound, $+3\text{H}_2\text{O}$, with sodium iodide, from which it may be liberated by treating its solution with silver oxide.

The action of benzaldehyde on 4 : 5-diamino-2 : 6-dihydroxypyrimidine (*sulphate*) in hot, aqueous solution, gives 4-amino-5-benzylideneamino-2 : 6-dihydroxypyrimidine, felted needles, which is reduced in aqueous suspension by the aid of sodium amalgam to 4-amino-5-benzylamino-2 : 6-dihydroxypyrimidine, lozenge-shaped leaflets, m. p. 265°, *sulphate*, $+\text{H}_2\text{O}$, prisms or leaflets. The benzylamino-derivative is converted by boiling with formic acid into its *formyl* derivative, a heavy, crystalline powder, which passes at 280° into 7-benzylxanthine, prisms, m. p. 295° (decomp.). The latter is converted by means of aqueous sodium hydroxide solution and methyl iodide at 100° into 7-benzyl-1-methylxanthine, m. p. 250°, whereas the use of methyl sulphate gives 7-benzyl-1 : 3-dimethylxanthine (7-benzyltheophylline). 7-Benzyltheophylline is also obtained by the action of methyl sulphate and sodium hydroxide solution on 7-benzyl-3-methylxanthine, m. p. 273°. This is obtained by heating the *formyl* derivative, m. p. 252°, of 4-amino-5-benzylamino-2 : 6-dihydroxy-3-methylpyrimidine, leaflets, m. p. 226°, which is formed by the reduction of the 5-benzylideneamino-derivative (Traube and Nithack, A., 1906, i, 214). W. S. N.

Dioximes. XII. G. PONZIO (*Gazzetta*, 1923, 53, 507—513).—The author's conclusion that the compound obtained by the action of nitrogen peroxide on α -phenylglyoxime is the oxide of benzoyl cyanide oxime (this vol., i, 1019), and not phenylglyoxime peroxide as suggested by Scholl or phenylfuroxan as proposed by Wieland and Semper, is not in accord with the supposed isomerisation of

this compound by alkaline-earth hydroxides or carbonates into 4-hydroxy-3-phenylfurazan, $O \begin{smallmatrix} \text{N:CPh} \\ \text{N:C}\cdot\text{OH} \end{smallmatrix}$.

The author shows that the latter, although its existence has been recently confirmed by Wieland (A., 1921, i, 605), is merely the original oxide of benzoyl cyanide oxime in slightly impure condition.

When, however, this oxide is either heated with a little xylene or treated at the ordinary temperature in dilute benzene solution with phenylhydrazine, it undergoes isomerisation into 5-hydroxy-3-phenyl-1 : 3 : 4-oxadiazole (cf. Tiemann, A., 1885, 1216; Tiemann and Fock, A., 1886, 797; Falck, A., 1885, 1216; 1886, 797). The sodium salt of the latter, $C_2ON_2Ph\cdot ONa$, and the methyl ether, which crystallises in long, white needles, m. p. 116° , are described. The diazole is also obtained, together with β -anilino- α -phenylglyoxime when the oxide is treated in benzene solution with aniline.

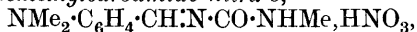
According to Wieland and Semper (A., 1908, i, 108), glyoxime peroxides, termed by them furoxans, do not react with Grignard's reagent. The author finds, however, that the oxide of benzoyl cyanide oxime reacts readily with magnesium methyl iodide, giving phenylmethylglyoxime.

T. H. P.

A Reaction of Carbamide with *p*-Dimethylaminobenzaldehyde. II. H. K. BARRENSCHEEN (*Biochem. Z.*, 1923, 140, 426—434).—In continuation of the author's work (A., 1922, ii, 794), definite derivatives of Ehrlich's aldehyde and carbamide have been prepared. *p*-Dimethylaminobenzylidenecarbamide,



yellow needles, m. p. 188 — 190° , is obtained by adding finely powdered *p*-dimethylaminobenzaldehyde to molten carbamide, but preferably by treating with ammonia the sulphate, lustrous, orange-red crystals of indefinite melting point, prepared by adding carbamide to the aldehyde dissolved in 5% aqueous sulphuric acid. The hydrochloride, orange-red, monoclinic needles, m. p. 196 — 201° , readily hydrolysed in aqueous solution, and *p*-dimethylaminobenzylidenemethylcarbamide nitrate,



rhombohedral, orange crystals, m. p. 165 — 169° , are also described. Phenyl-*p*-dimethylaminobenzylidenecarbamide hydrochloride, $NMe_2\cdot C_6H_4\cdot CH:N\cdot CO\cdot NHPh\cdot HCl$, orange, monoclinic crystals, m. p. 206° , is obtained by passing dry hydrogen chloride into an ethyl-alcoholic solution of phenylcarbamide and the Ehrlich aldehyde. Similar coloured derivatives of thiocarbamide were obtained, but could not be isolated in a pure condition, owing to difficulties in recrystallisation. In an examination of the range of reaction of the Ehrlich aldehyde with substances containing an amino-group, it was found that formamide, acetamide, α -bromodiethylcarbamide, and α -bromo- and α -iodoisovalerylcarbamide gave negative results. Positive reactions of varying intensity were given by biuret, allantoin, and ethylene- ψ -carbamide, whilst parabanic and barbituric acids, the purines, guanidine, creatine, and creatinine gave no reaction. Of the amino-acids positive results were obtained only

in the cases of glycine, alanine, asparagine, glutamine, and glutamic ester. An attempt to make the reaction between carbamide and the aldehyde the basis of a colorimetric method of estimating the former proved unsuccessful.

J. P.

p-Nitrobenzeneazopyrogallol (Chrome Brown P.A.). P. JUILLARD (*Bull. Soc. chim.*, 1923, [iv], **33**, 1084—1089).—An attempt to obtain a dye similar to alizarin, in that it will dye shades fast to washing and to light when mordanted with the sesquioxides of iron, aluminium, or chromium. For this purpose, a compound containing two adjacent hydroxyl groups and the chromophore $-N:N-$ was selected. By coupling *p*-nitrodiazobenzene chloride with pyrogallol in the presence of sodium acetate, a mixture of isomeric *p*-nitrobenzeneazopyrogallols is obtained which may be separated by crystallisation from alcohol. The less soluble and more abundant fraction is thought to be the one in which coupling has taken place in the para-position to the 1- or 3-hydroxyl group of the pyrogallol, and gives an *acetyl* derivative, m. p. 193°. The dye, when chrome-mordanted, gives fast brown shades resembling alizarin. The other isomeride is thought to be the one coupled in the para-position to the 2-hydroxyl group. *Benzene-azopyrogallol*, chrome mordanted on wool, gives yellower shades than alizarin.

H. H.

Reduction of Nitronaphthalenes. I. Reduction of α -Nitronaphthalene. WILLIAM MURDOCH CUMMING and JAMES KING STEEL (T., 1923, **123**, 2464—2470).

Inner Azo-compounds from Azoles. F. ARNDT and F. TSCHENSCHER (*Ber.*, 1923, **56**, [B], 1984—1988).—Triazoles and thiodiazoles which according to their structure may be regarded as cyclic hydrazo-compounds should be capable of oxidation to the corresponding cyclic azo-derivatives. A review of the literature considered in conjunction with the author's own experiments show that intensely coloured solutions are frequently produced from these substances. The conception of the products as azo-compounds must, however, be applied with caution and the simple azo-structure can only be assumed when the oxidised product is more readily soluble in ether and similar solvents than is the initial material and also does not exhibit abnormal acidity.

Phenylguanylthiosemicarbazide, $\text{NHPh}\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}_2$, colourless, crystalline granules, m. p. 146—148° (decomp.), is prepared by the action of thiosemicarbazide hydrochloride on phenylcyanamide in boiling aqueous solution; the *hydrochloride* is sparingly soluble in water. It is converted by methyl sulphate in alkaline solution into the corresponding *S-methyl ether*, colourless, lustrous needles which soften at about 115°, and become converted into phenylguanazole. The ether is oxidised by potassium ferricyanide in dilute acetic acid solution to the corresponding azo-compound, $\text{C}_9\text{H}_{11}\text{N}_5\text{S}$, small, red needles, m. p. 110°, and is converted by boiling water into methyl mercaptan and *phenylguanazole*, coarse, colourless prisms ($+\text{H}_2\text{O}$), m. p. 226—228°, the *nitrate*,

m. p. 212° (decomp.), is described. The substance is not oxidised by potassium ferricyanide in an aqueous-alkaline medium, but is transformed by lead peroxide in dilute acetic acid solution in the presence of ether into 4-phenyldehydroguanazole, $\begin{smallmatrix} \text{N} \cdot \text{C}(\text{NH}) \\ \text{N} \cdot \text{C}(\text{NH}) \end{smallmatrix} > \text{NPh}$, pale brown platelets, m. p. 122—123°. H. W.

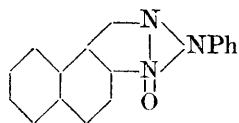
Oxidation of *o*-Aminoazo-compounds in Acetic Acid Solution by Means of Hydrogen Peroxide. G. CHARRIER and G. B. CRIPPA (*Gazzetta*, 1923, **53**, 462—469).—With the view of obtaining better yields of *N*-arylbenz- and naphtha-1 : 2 : 3-triazoles, $\text{Ar}'' < \begin{smallmatrix} \text{N} \\ | \\ \text{N} \end{smallmatrix} > \text{NAr}'$, than are given by the known methods, the authors

have investigated the action of hydrogen peroxide on solutions of certain *o*-aminoazo-compounds in glacial acetic acid. In some cases, the 1 : 2 : 3-triazoles are formed and in others aznitroso-derivatives, but the yields obtained are low and the difficulties of purifying the resultant products great. The results of Angeli and his collaborators (1906—1914) show that oxidation of azo-compounds by means of hydrogen peroxide yields the corresponding azoxy-derivatives which, when the molecule is unsymmetrical, may exist in two structurally isomeric forms. In the present case, it may be assumed that the *o*-aminoazo-compound is first converted into the two azoxyamino-compounds, $\text{NH}_2 \cdot \text{Ar}'' \cdot \text{N} : \text{NAr}' : \text{O}$ and $\text{NH}_2 \cdot \text{Ar}'' \cdot \text{NO} : \text{NAr}'$, in which, by further action of the peroxide, the amino- is transformed into the hydroxylamino-group. Elimination of a molecule of water from these hydroxylamino-derivatives by a reaction similar to that allowing of the passage from *o*-hydroxylaminoazoxybenzene to aznitrosobenzene (cf. Cusmano, A., 1921, i, 132) would then readily yield the corresponding triazole oxides,

$\text{Ar}'' < \begin{smallmatrix} \text{N}=\text{O} \\ | \\ \text{N} \end{smallmatrix} > \text{NAr}'$; if, however, this mechanism resulted in the loss of the oxygen atom of the azoxy-group instead of that of the hydroxylamine radicle, a single aznitroso-derivative should be formed, as is actually found to be the case.

By a similar mechanism, it is easy to explain the formation of triazoles from the two isomeric *o*-aminoazoxy-derivatives, which are assumed to be the initial products of the action of hydrogen peroxide on the aminoazo-compounds. When the para-position of the radicle Ar is occupied, the triazole itself, and not the corresponding oxytriazole, is obtained; the cause of this is not yet ascertained.

The action of hydrogen peroxide on 1-benzeneazo-2-amino-



naphthalene in acetic acid solution yields the first known representative of the aznitroso-derivatives of the naphthalene series, *N*-phenylnaphthatriazole oxide, which, according to the above explanation of the mechanism of the reaction, has the annexed structure. With potassium iodide in acetic acid solution, this compound

behaves similarly to its benzo-analogue, iodine being liberated and *N*-phenyl-1 : 2-naphthatriazole formed.

[With M. AGOSTONI.]—Oxidation of 1-benzeneazo-2-aminobenzene by means of hydrogen peroxide in acetic acid solution gives *N*-phenyl-aznitrosobenzene, together with a compound, m. p. 158—159°, which is probably 2-amino-4'-hydroxyazobenzene, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$ (cf. Cusmano, *loc. cit.*); the formation of the latter indicates that *o*-aminoazoxybenzene is the primary product in this reaction and that Wallach's transposition may occur, not only in concentrated sulphuric acid solution, but also in glacial acetic acid.

N-Phenyl-naphthatriazole oxide (see above) crystallises in colourless leaflets, m. p. 146°, and yields *N*-phenyl-1 : 2-naphthatriazole when reduced by means of zinc dust and acetic acid.

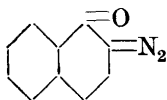
2-*p*-Tolyl- $\alpha\beta$ -naphthatriazole, m. p. 148—149°, prepared by the action of hydrogen peroxide on an acetic acid solution of 1-*p*-tolyl-azo- β -naphthylamine, was previously obtained by heating the latter (cf. Charrier, A., 1910, i, 287). 2-*p*-Acetylphenyl- $\alpha\beta$ -naphthatriazole (Charrier, A., 1922, i, 771) is obtained from 1-*p*-acetylbenzeneazo- β -naphthylamine.

1-*p*-Chlorobenzeneazo- β -naphthylamine, $\text{NH}_2 \cdot \text{C}_{10}\text{H}_6 \cdot \text{N} \cdot \text{N} \cdot \text{C}_6\text{H}_4\text{Cl}$, prepared from *p*-chlorophenyldiazonium chloride on β -naphthylamine, crystallises in slender, orange-red needles, m. p. 116°.

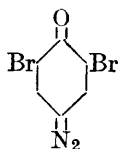
2-*p*-Chlorophenyl- $\alpha\beta$ -naphthatriazole, $\text{C}_{10}\text{H}_6 \begin{smallmatrix} \text{N} \\ | \\ \text{N} \end{smallmatrix} \text{N} \cdot \text{C}_6\text{H}_4\text{Cl}$, prepared by treating the preceding compound in acetic acid solution with either chromic acid or hydrogen peroxide, forms slender, white needles, m. p. 186°. T. H. P.

Diazonium Salts of Anthraquinone (Anthraquinonediazonium Amalgam). BATTEGAY and J. BÉHA (*Bull. Soc. chim.*, 1923, [iv], 33, 1089—1093; cf. this vol., i, 861).— α - and β -Anthraquinonediazonium chlorides were freed from hydrochloric acid and dissolved in distilled water. The solutions were then electrolysed in a cell maintained at 0° and fitted with a mercury cathode and a carbon anode. With a potential difference of 20 volts, gas was evolved and hydroxyanthraquinone formed, presumably by the loss of nitrogen from anthraquinonediazonium hydroxide. At higher voltages, particularly at 60 volts, the formation of a spongy mass on the surface of the cathode was observed. This is supposed to be *anthraquinonediazonium amalgam*, which decomposes to form mercury, nitrogen, and $\alpha\alpha'$ -dianthraquinonyl. H. H.

β -Naphthaquinone- β -diazide and Böhmer's β -Dibromouquinonediazides. E. BAMBERGER, O. BÖCKING, and EMIL KRAUS (*J. pr. Chem.*, 1923, [ii], 105, 251—265).—A detailed account is given of the preparation of β -naphthaquinone- β -diazide (annexed formula), which has already been described under the name naphthalene-2 : 1-diazo-oxide (A., 1894, i, 295). This compound is converted by means of hydrogen chloride in ethereal solution into α -naphthol- β -diazonium chloride, yellow, glistening crystals, which readily loses hydrogen chloride when kept in a vacuum, or in



contact with water. The diazide is reduced by means of tin and fuming hydrochloric acid to α -naphthol, and a greater quantity of β -amino- α -naphthol; the latter is reconverted into the diazide by the action of nitrous acid at 0° . The diazide reacts at 70° with phosphorus pentasulphide to give naphthalene- β -diazosulphide, m. p. $91-91.5^\circ$ (cf. Jacobson, A., 1894, i, 137). The action of a hot, concentrated, aqueous solution of potassium sulphite on the diazide gives *potassium α -naphthol- β -diazosulphonate*, glistening, orange-yellow crystals, which gives, with aqueous ferric chloride, a dark red coloration, and is reducible to β -amino- α -naphthol. The action of warm, dilute sulphuric acid on the diazide causes evolution of nitrogen, with formation of 1:4-naphthaquinol, and not the 1:2-derivative. The isomeric dibromo-*p*-quinonediazides, decomp. 137° and 145° , respectively, described by Böhmer (A., 1882, 396), are identical. The compound, when pure, decomposes between 145° and 154° , according to the rate of heating. It has the annexed formula, since it is converted into *s*-tribromophenol, by the action of hydrobromic acid and copper.



W. S. N.

β -Naphthaquinone- α -diazide. E. BAMBERGER, MARIE BAUM, and LEO SCHLEIN (*J. pr. Chem.*, 1923, [ii], 105, 266—278).—If the action of nitrous acid on α -amino- β -naphthol (Grandmougin and Michel, A., 1892, 861) is conducted at 0° , the product contains, besides β -naphthaquinone, β -naphthaquinone- α -diazide, the preparation of which from α -naphthylnitroamine (Bamberger, this vol., i, 28) is described in detail. β -Naphthaquinone- α -diazide is reduced by means of stannous chloride in concentrated hydrochloric acid solution to α -amino- β -naphthol.

Whereas β -naphthaquinone- β -diazide gives 1:4-dihydroxy-naphthalene when warmed with dilute sulphuric acid (cf. preceding abstract), the α -diazide is converted by means of the boiling acid into 1:2-naphthaquinol, together with small quantities of β -naphthol and β -dinaphthylidiquinol. 1:2-Naphthaquinol (1:2-dihydroxy-naphthalene) has m. p. 102.5° ; the low m. p., about 60° , recorded by Liebermann and Jacobson (A., 1882, 521) was due to the presence of dinaphthylidiquinol.

β -Naphthaquinone- α -diazide reacts with phosphorus pentasulphide in warm benzene solution to give (cf. preceding abstract) 1:2-naphthalenediazosulphide, white needles, m. p. 68.5° .

When a solution of either the α -diazide or the β -diazide in xylene is boiled for three to four hours, nitrogen is evolved, with the formation of *bisnaphthaleneoxide*, $C_{10}H_6 \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} C_{10}H_6$, flat, glistening, white needles, m. p. 256° .

W. S. N.

β -Naphthaquinone- α -diazide and Methyl-alcoholic Potassium Hydroxide. E. BAMBERGER and S. WILDI (*J. pr. Chem.*, 1923, [ii], 105, 278—282; cf. preceding abstract).—The action of boiling methyl-alcoholic potassium hydroxide solution on β -naphthaquinone- α -diazide leads to the formation of α -naphthol, $\beta\beta$ -di-

naphthol, and a *methyl ether*, columnar crystals, m. p. 90·5—91°, of 1 : 2-dihydroxynaphthalene. The action of boiling water on β -methoxynaphthalene- α -diazonium chloride gives β -methoxynaphthalene, and not the expected α -hydroxy- β -methoxynaphthalene, which would be identical or isomeric with the above methyl ether. The structure of the latter remains, therefore, undecided.

W. S. N.

Determination of the Hausmann Numbers of the Proteins.

JOHN KNAGGS (*Biochem. J.*, 1923, **17**, 488—492).—When gelatin is left for some time in the presence of cold acid before being heated, higher diamino-acid figures are obtained than when the hydrolysis by boiling is proceeded with at once. This is due to partial hydrolysis of the protein in the cold and the formation of resistant polypeptides from the products of hydrolysis by polymerisation which are also precipitated by phosphotungstic acid. The fact has to be taken into consideration if a correct value for the percentage of diamino-nitrogen in the hydrolysis of gelatin is to be obtained, and the author has worked out the conditions it is necessary to observe in order to obtain correct results. Brucke's reagent, Mayer's reagent, cadmium iodide, and tannic acid do not precipitate diamino-acids from acid solution. Tannic acid is precipitated only in neutral solution and the precipitate thus obtained gives the same results as the phosphotungstic acid precipitate.

S. S. Z.

The Catalytic Fission of Proteins according to Sadikov and Zelinski. PERCY BRIGL (*Ber.*, 1923, **56**, [B], 1887—1889).—In a recent communication (this vol., i, 867), Zelinski and Sadikov have obtained diketopiperazines in large amount by the hydrolysis of proteins with dilute hydrochloric acid (1—2%) at 180°, and have drawn the conclusion that the protein molecule is largely composed of diketopiperazine rings united by long methylene chains. This conclusion does not appear to be valid, since under the experimental conditions the simplest dipeptide, diglycine, gives a yield of at least 40% of diketopiperazine. It appears, therefore, that the hydrolysis in these circumstances is accompanied by polymerisation.

H. W.

Composition of the Specific Egg-albumin Precipitates.

FRITZ ÖTTENSOOSER (*Kolloid Z.*, 1923, **23**, 176—178).—A number of experiments are described on the precipitate obtained when solutions of egg-albumin are mixed with the immune-serum of rabbits. They were undertaken with the object of confirming Jarisch's statement, ψ -globulin + lipoid substance \rightarrow euglobulin. The experiments show that freshly prepared precipitate from egg-albumin on warming at 55° passed completely and irreversibly into solution.

J. F. S.

Physico-chemical Investigations on Body-fluids. VII.

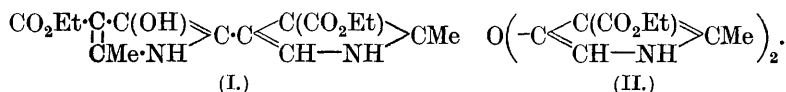
The Change of Albumin into Globulin. STEFAN RUSZNYÁK (*Biochem. Z.*, 1923, **140**, 179—184).—The interconvertibility of serum-albumin and globulin under varying conditions, as shown by nephelometric measurements, is confirmed. Conditions favouring

the conversion of globulin into albumin are: heating at 42°, the addition of dilute alkalis. The reverse change is conditioned by: heating at from 42° to 60°, the addition of dilute acids, concentrated alkalis, alcohol, and a variety of other organic substances. Native serum-globulin is supposed to exist in part as a reversible, and in part as an irreversible modification which last cannot undergo conversion into albumin. J. P.

The Oxygen Content of Methæmoglobin. HERBERT ELDON ROAF and WILLIAM ARTHUR MERRETT SMART (*Biochem. J.*, 1923, **17**, 579—585).—The addition of acid sufficient to convert oxyhæmoglobin into methæmoglobin liberates approximately half the amount of oxygen that would be given off by the same quantity of hæmoglobin when acted on by ferricyanide. S. S. Z.

The Acid Nature of Oxyhæmoglobin. ARCHIBALD VIVIAN HILL (*Biochem. J.*, 1923, **17**, 544—546).—A theoretical contribution in support of Parsons' assertion that oxygenated blood is more acid than reduced blood. S. S. Z.

Constitution of the Bile Pigments. ERICH BENARY (*Z. physiol. Chem.*, 1923, **129**, 304—306).—Fischer and Loy (this vol., i, 718) have expressed some doubt as to the constitution (I) assigned by Benary and Silbermann to the product, $C_{16}H_{20}O_5N_2$, of the condensation of ethyl 4-hydroxy-2-methylpyrrole-3-carboxylate by means of concentrated hydrochloric acid and suggested as probable the constitution (II),



The author reaffirms the correctness of his view, pointing out especially that the reaction with ferric chloride indicates the presence of a hydroxyl group. W. O. K.

Gelatin. II. The Methods of Purifying Gelatin. JOHN KNAGGS, ALEXANDER BERNARD MANNING, and SAMUEL BARNETT SCHRYVER (*Biochem. J.*, 1923, **17**, 473—487).—It is practically impossible to free gelatin from its nitrogenous contaminants, produced mostly by thermal decomposition in the process of its preparation, by washing or dialysis. It is also difficult to free it entirely from electrolytes by washing with acid and water by Loeb's method. Gelatin thus purified can, however, be freed from almost the last traces of electrolytes by electrolysis, which procedure fails to remove substances of colloidal character, non-electrolytes, and weak electrolytes. It is possible to obtain a gelatin free from soluble nitrogenous contaminants by a process of "recrystallisation" in the following manner. When gelatin purified by washing and electrolysis is made up to a less than 2% aqueous solution it separates out as an insoluble hydrate. By repeated "recrystallisation" a supernatant fluid is obtained which contains about 10 mg. of the solute per 100 c.c. of the solvent,

a condition which indicates that the gelatin is free from soluble nitrogenous impurities. This concentration of the supernatant fluid remains constant independently of the strength of the solution from which the gelatin separates. Such a gelatin behaves almost as a pure substance in equilibrium with a saturated solution which contains 0.056% of gelatin. S. S. Z.

Effect of Time on the Physico-chemical Properties of Solutions of Gelatin. R. DE IZAGUIRRE (*Anal. Fís. Quím.*, 1923, 21, 330—354).—The variation with time of the viscosity of gelatin solutions in the presence of increasing concentrations of hydrochloric acid shows a minimum corresponding with a maximum initial viscosity. This occurs at a concentration of 0.00912*N*-hydrochloric acid. Similar results were obtained for osmotic pressure. Gelatinisation is considered as consisting of a dehydration and not of the formation of a new chemical modification. Data are given for the mutarotation of gelatin solutions. The results are in accord with the formula $[\alpha]_D = Kt^n$. G. W. R.

The Action of Pepsin. EML ABDERHALDEN and ANDOR FODOR (*Fermentforsch.*, 1923, 7, 61—67).—Brief acid extraction of the mucous membrane of the pig's stomach gives a pepsin preparation which digests strongly, and also a strong biuret reaction, but not a protein reaction. It is not ultrafiltrable and there is no difference in activity when submitted to dialysis. Its action appears to be composite in nature, as under certain conditions of digestion there is a change of electrical conductivity and other properties, whilst under other conditions digestion proceeds without these changes. H. K.

The Action of Metals on Pepsin. MITSUTARO TSUCHIHASHI (*Biochem. Z.*, 1923, 140, 149—153).—Pepsin is markedly inhibited by contact with powdered metallic copper and zinc, somewhat less by iron and cobalt, and not at all by nickel. Glycine does not protect the enzyme against copper or zinc. J. P.

Nephelometric Investigations on the Enzymatic Hydrolysis of Proteins. P. RONA and H. KLEINMANN (*Biochem. Z.*, 1923, 140, 478—492).—The course of peptic hydrolysis of serum proteins dissolved in physiological salt solution was followed by means of the authors' nephelometric method. Curves plotted from the results show the initial rate of hydrolysis to be linear, but later the curve flattens out as the rate of hydrolysis diminishes. With increasing amounts of pepsin the linear portion of the curve is lessened relatively to the rest. The rate of hydrolysis is proportional to the ferment concentration. The results of varying the amounts of substrate while keeping the amount of enzyme constant revealed no simple proportionality. J. P.

Influence of Various Quinine Derivatives on the Fermentative Function of the Organism. II. The Influence of some Quinine and Urea Derivatives on Ptyalin. I. A. SMORODINCEV and A. S. NOVIKOV (*Biochem. Z.*, 1923, 140, 12—16).—Quinine sulphate and hydrochloride accelerate the action of ptyalin on

starch. The dihydrochloride of quinine and carbamide, and carbamide and its salts inhibit the action of ptyalin, the salts of carbamide being much more active in this respect than is free carbamide. Thus the actions of these compounds noted in the case of trypsin (this vol., i, 412) are reversed in the case of ptyalin.

J. P.

The Secretion and Activity of Ptyalin. HANS PRINGSHEIM and HARALD GORODISKI (*Biochem. Z.*, 1923, **140**, 175—178).—A comparison of the amylolytic activity of human saliva collected under carefully standardised normal conditions and after brushing the teeth with inactive paste and with paste containing different amounts of radioactive substance revealed no differences of a qualitative or quantitative nature.

J. P.

Asymmetric Hydrolysis of Racemic Amino-acid Esters by Esterase. EMIL ABDERHALDEN, HANS SICKEL, and HARUJIRO UEDA (*Fermentforsch.*, 1923, **7**, 91—99).—*r*-Tyrosine ethyl ester was submitted to the action of pancreatic lipase in decinormal sodium hydrogen carbonate solution. There was preferential hydrolysis of the *l*-tyrosine ethyl ester with separation of *l*-tyrosine. The *d*-tyrosine ethyl ester was isolated from the mother-liquors by extraction with chloroform.

H. K.

The Action of Tyrosinase. Experiments with *d*-, *l*-, and *dl*-Tyrosine. EMIL ABDERHALDEN and HANS SICKEL (*Fermentforsch.*, 1923, **7**, 85—90).—Tyrosinase from *Russula delica* added to equally concentrated solutions of *d*-, *l*-, and *dl*-tyrosine produced the red coloration first with *l*-tyrosine, then with *dl*-tyrosine and last with *d*-tyrosine. If examined polarimetrically, inactivation takes place before the development of the red colour and sooner with *l*-tyrosine than *d*-tyrosine. This inactivation occurs in absence of oxygen, but oxygenation of the three solutions after inactivation leads to simultaneous development of the red colour. The process of deamination therefore takes place at different rates in the three cases.

H. K.

The Tyrosinase-Tyrosine Reaction. HENRY STANLEY RAPER and ARTHUR WORMALL (*Biochem. J.*, 1923, **17**, 454—469).—The velocity of the oxidation of tyrosine by tyrosinase is markedly influenced by the hydrogen-ion concentration of the medium. The limits of the reaction between which tyrosinase in potatoes acts are P_H 5— P_H 10. The oxidation of tyrosine by the enzyme in buffered solution has a greater velocity at P_H 8.0 than at P_H 7.0; at the latter hydrogen-ion concentration the velocity is greater than at P_H 6.0. The oxidation proceeds according to the formula of a unimolecular reaction. Tyrosinase produces from tyrosine at first a red substance, which is brought about by the action of the enzyme in the presence of oxygen. The red substance is then converted into a colourless substance. This conversion takes place spontaneously and more rapidly on warming. The colourless substance is eventually oxidised to form melanin. The last two processes take place in the absence of tyrosinase, but may be accelerated by it or by

other oxydases present in potato juice. In neutral and acid solutions the main product during the first six hours is the red substance, but in alkaline media the conversion of it into melanin proceeds so rapidly that solutions darken without any marked preliminary reddening. The authors show that tyrosinase does not contain a hydrolytic oxidation catalyst as suggested by Bach. Haehn's observations that tyrosinase inactivated by dialysis can be reactivated by the addition of certain salts has been confirmed. The acceleration of the enzyme by the addition of boiled potato juice is not due to inorganic constituents, but to some substance or substances present in the juice. This activator is not always present in boiled potato juice but is usually found in the boiled juice of new potatoes.

S. S. Z.

Blood Catalase. MITSUTARO TSUCHIHASHI (*Biochem. Z.*, 1923, **140**, 63—112).—A comparative investigation of different methods of isolating blood catalase in solution. Corpuscles from horse-blood were centrifuged, washed with saline, dialysed against distilled water, and the resulting solution was evaporated. The dry powdered residue was dissolved in water to give a 1% solution, centrifuged, and filtered. This solution was then shaken for five minutes with one-fifth of its volume of chloroform, again centrifuged, and the supernatant light yellow solution separated from the chloroform and from precipitated proteins. This solution possessed from 70—80% of the catalase activity of the original dry powder and when fresh dog-corpuscles were used, without drying, the method gave an 80—90% extraction of catalase. Such purified solutions contain 2% of the nitrogen, and from 3 to 6% of the dry residue of the original watery solution before treatment with chloroform. They may be kept in an ice-box without change for several weeks. An alternative method of purifying the catalase is to adsorb it, together with hæmoglobin, from the centrifuged and filtered solution of the dry powder by means of tricalcium phosphate, and subsequently to wash it out with *M*/150-disodium hydrogen phosphate. Applied to the chloroform purified solution, this method results in a further elimination of nitrogen without corresponding loss of catalase activity. The optimum time of contact with the calcium phosphate is ten minutes, and for the washing out process fifteen minutes. The purified catalase solutions lost 20% of their activity after exposure for thirty minutes to a temperature of 45°, and were rendered inactive at 65°. Very dilute solutions of catalase, even in the presence of phosphate buffers, glycine or alanine, are unstable. Urea has a slight protective action.

J. P.

A Heat-stable Catalyst in Animal Tissues which Destroys the Iminazole Ring and Unmasks Amino-groups. WINIFRED MARY CLIFFORD (*Biochem. J.*, 1923, **17**, 549—555).—The catalytic agent present in beef and cod which destroys carnosine in beef extract also destroys histidine in aqueous solution. Cod, washed beef, or liver added to histidine or muscle extract solutions at 100° decrease the colour obtained on diazotising the solutions which indicates a degradation of the iminazole ring. As the intensity of

the iminazole reaction falls there is a rise in amino-nitrogen which suggests a rupturing of the iminazole ring and a conversion of the ring nitrogen into amino-nitrogen. S. S. Z.

The Importance of Glycine and Potassium Cyanide for the Action of Urease. TETSUGORA TAKAHATA (*Biochem. Z.*, 1923, **140**, 154—157).—Urease in extreme dilution is rendered much more active by the addition of traces of potassium cyanide or glycine. The inactivation of urease by copper sulphate or mercuric chloride is inhibited by potassium cyanide and to a less extent, especially in the latter case, by glycine. Sodium cyanide acts like potassium cyanide, whilst potassium thiocyanate is very much less effective. J. P.

The Purification of Fumarase. MITSUTARO TSUCHIHASHI (*Biochem. Z.*, 1923, **140**, 161—165).—With the object of purifying the fumarase present in the dry powdered residue from a cold aqueous extract of human liver, the aqueous solution was treated with various precipitants. Methyl alcohol proved ineffective, but using various concentrations of ammonium sulphate, it was found that the enzyme was completely precipitated between 30% and 85% saturation. The aqueous solution prepared from this precipitate kept its activity for two weeks, but lost it on drying. J. P.

Sulphatase. I. The Enzymatic Hydrolysis of Phenyl Hydrogen Sulphate. CARL NEUBERG and K. KURONO (*Biochem. Z.*, 1923, **140**, 295—298).—An enzyme, to which the name *sulphatase* has been given, has been found in *Aspergillus oryzae*. Incubated at 37° with solutions of potassium phenyl sulphate, marked hydrolysis was obtained, amounting in sixteen days to 13.6% of the substrate. J. P.

Solubility of Insulin. ERIK MATTEO PROCHET WIDMARK (*Biochem. J.*, 1923, **17**, 668—670).—Insulin is insoluble or very slightly soluble in tetrachloromethane, ethyl acetate, ethyl alcohol, isobutyl alcohol, amyl alcohol, chloroform, acetone, light petroleum, ethyl ether, benzene, xylene, and pyridine. It is easily soluble in methyl alcohol, glacial acetic acid, phenol, and formamide. Several facts argue in favour of its being an albumose. S. S. Z.

Some Derivatives of Arsphenamine [Salvarsan]. WALTER G. CHRISTIANSEN (*J. Amer. Chem. Soc.*, 1923, **45**, 2182—2188).—It is shown that the relation between the mode of synthesis and the toxicity of salvarsan (this vol., i, 723) also holds for the production of salvarsan polyarsenide. The arsenic content of this substance varies between 41.87% and 50.81%; it is, in general, higher when the polyarsenide is produced by the reduction of *m*-amino-*p*-hydroxyphenylarsenious oxide and sodium arsenite by means of hypophosphorous acid (A., 1921, i, 370), than when *m*-nitro-*p*-hydroxyphenylarsinic acid and sodium arsenite are reduced by means of sodium hyposulphite. The toxicity of salvarsan polyarsenide is not very different from that of salvarsan itself.

In the preparation of sulpharsphenamine (this vol., i, 70) the

yield is improved by using 3 mols. of formaldehyde and 3 mols. of sodium hydrogen sulphite, instead of 2 mols. and 4 mols., respectively. It is unnecessary to use pure, freshly prepared sulphite, the commercial material being sufficiently pure. Also, it is unnecessary to start with salvarsan itself (*i.e.*, the hydrochloride); the dry salvarsan base will do equally well. The toxicity of sulpharsphenamine is apparently not increased by using salvarsan, in the preparation of which the nitro-group has been improperly reduced (*loc. cit.*), or by the impurities present in the product.

When salvarsan polyarsenide is subjected to the procedure used in preparing sulpharsphenamine, a very soluble, orange-coloured sodium salt (deep red in solution) is produced, which is described as *sulpharsphenamine polyarsenide*. It is considerably more toxic than sulpharsphenamine, which is tolerated in doses of 400 mg./kg., not being tolerated in doses even as low as 200 mg./kg.

W. S. N.

The Arsination of Phenol. WALTER G. CHRISTIANSEN and ARTHUR J. NORTON (*J. Amer. Chem. Soc.*, 1923, **45**, 2188—2192).—In the arsination of phenol by means of arsenic acid (Conant, A., 1919, i, 230; Jacobs and Heidelberger, A., 1919, i, 604), the yield of anhydrous sodium *p*-hydroxyphenylarsinate may be increased from 20% to 33% by vigorously agitating the reacting substances and allowing part of the water produced to distil off during the first stage of the reaction. It is suggested that a phenyl ester of arsenic acid may be an intermediate product in the formation of hydroxyphenylarsinic acids by this method. By distillation of aqueous solutions of *p*-hydroxyphenylarsinic acid, with steam, and estimation of phenol in the distillate, it is shown that hydrolysis to phenol and arsenic acid scarcely occurs at all at 100° (cf. Schmitz, A., 1914, i, 342).

W. S. N.

As-Methyldihydroarsindole. EUSTACE EBENEZER TURNER and FRANK WARD BURY (T., 1923, **123**, 2489—2492).

Cyanurylphosphinimines and the Pyrogenic Fission of the Methyl and Ethyl Esters of Normal Cyanuric Acid. W. KESTING (*J. pr. Chem.*, 1923, [ii], **105**, 242—250).—*Di(triphenylphosphinimine)cyanuryl azide*, $\text{N}_3 \cdot \text{C} \begin{smallmatrix} \text{N:C(N:PPh}_3\text{)} \\ \text{N:C(N:PPh}_3\text{)} \end{smallmatrix} \text{N}$, a light powder, m. p. 243° (decomp.), is formed by the interaction of triphenylphosphine and cyanuryl triazide in ethereal solution (cf. Staudinger and Meyer, A., 1920, i, 106); during the first stages of the reaction an intense green coloration is developed, which may be due to the intermediately formed phosphazide. This monoazide reacts with a further molecule of triphenylphosphine at 170—180° to give *cyanuryltri-triphenylphosphinimine*, a grey powder, m. p. 239°, which cannot be recrystallised because, apparently, it forms additive compounds with the solvents employed, *e.g.*, benzene. When the vapour of ethyl cyanurate is passed, under reduced pressure, over a glowing platinum wire, it does not give

s s*

ethyl cyanate, but ethylene and cyanic acid. Methyl cyanurate depolymerises with greater difficulty, giving methylcarbimide.

W. S. N.

Organic Derivatives of Silicon. XXVII. A Probable Example of Tervalent Silicon. FREDERIC STANLEY KIPPING (T., 1923, **123**, 2590—2597).

Organic Derivatives of Silicon. XXVIII. Octaphenyldiethylsilicotetrane. FREDERIC STANLEY KIPPING (T., 1923, **123**, 2598—2603).

A New Phenyl Compound of Silver. ERICH KRAUSE and BRUNO WENDT (*Ber.*, 1923, **56**, [B], 2064—2066).—Freshly precipitated silver chloride is converted by an ethereal solution of magnesium phenyl bromide into a brown, granular powder, which readily decomposes when dry with sudden evolution of clouds of diphenyl fumes. It has not yet been possible to isolate the compound in a homogeneous state, but it appears that the ratio of silver to phenyl = 1 : 1. Similar compounds are obtained from magnesium *p*-xylyl bromide, magnesium α -naphthyl bromide, and the magnesium compound of *p*-bromodiphenyl ether. The various colours exhibited by the solutions during the course of the reaction indicate that in each case a series of silver compounds is produced.

H. W.

Physiological Chemistry.

The Chemistry of Respiratory Tetany. P. GYÖRGY and H. VOLLMER (*Biochem. Z.*, 1923, **140**, 391—396).—During respiratory tetany following on forced breathing the blood-sugar diminished slightly whilst the blood salts showed no definite alteration. The urine showed a marked diminution in acidity and ammonia content, confirming the observations of other workers. It is concluded that the tetany is due to the increased alkalinity of the blood owing to elimination of carbon dioxide and does not depend on the action of any specific ion such as phosphate. J. P.

The Diminution of the Blood-sugar in Normal Dogs by Ergotamine. E. J. LESSER and K. ZIPF (*Biochem. Z.*, 1923, **140**, 612—615).—Subcutaneous injection of from 5 to 10 mg. of ergotamine produces in dogs a lowering of blood-sugar of one hour to two hours' duration. In cases of human diabetes similar results were obtained in only one instance. The positive results are taken to indicate a sympathetic control of "sugar tonus." J. P.

The Alkali Reserve of Blood-plasma in Avitaminosis. J. A. COLLAZO (*Biochem. Z.*, 1923, **140**, 254—257).—During the first six weeks of vitamin-free feeding, dogs showed no alteration in the alkali reserve of the blood-plasma, but later, especially during

the two weeks preceding death, a decrease was noted. In guinea pigs a marked decrease set in during the fourth week, but much less decisive results were obtained in the case of pigeons. The alkali reserve of dogs decreased during starvation from the third to the seventh day and subsequently rose slightly. It is concluded that the acidosis accompanying avitaminosis is not characteristic, but of secondary origin. J. P.

The Alteration of the Sugar-content of Blood-serum in Vitro. A. STASIAK (*Biochem. Z.*, 1923, **140**, 420—425).—Blood-serum from normal and pathological cases kept in vitro at 37° for twenty-four hours shows a variable copper reducing value, in some cases increasing, in others decreasing. These alterations also occur in serum which has been kept for one hour at 56°, and are therefore not due to enzyme action. Endocrine extracts added to pure dextrose solutions under the same conditions produce no change. The changes are ascribed in the main to the colloids present in the serum, since similar variable copper reduction results were obtained with pure dextrose-globulin and dextrose-cholesterol solutions. Albumin and lecithin, on the other hand, gave negative results. J. P.

Blood Clotting. VIII. The Prevention of Clotting by Neutral Salts. BERNHARD STUBER and MINORU SANO (*Biochem. Z.*, 1923, **140**, 42—62).—The addition to blood of the sodium salts of cholic, glycocholic, taurocholic, and deoxycholic acids and of magnesium sulphate and sodium chloride prevents the alcohol or heat coagulation of the fibrinogen, and at the same time causes a marked and steady increase in internal friction as determined by the viscostagonometer. The mechanism of the prevention of clotting by these salts is the same as that postulated in the case of oxalated and citrated plasmas—the formation of a highly ionised fibrinogen-salt complex (*A.*, 1923, i, 410, 411). The case of sodium fluoride is different. It has no inhibiting action on fibrinogen-thrombin coagulation, nor does it prevent the alcohol precipitation of fibrinogen, and the washed and hæmolysed corpuscles from fluoride blood are effective coagulants, unlike those from oxalated or citrated blood. Here it is supposed that the corpuscles and not the fibrinogen itself are chiefly concerned. The fluoride so alters their permeability as to prevent the passage of the coagulating substance from corpuscles to plasma. Fibrinogen (fibrinsol) is regarded as a hydrophobe colloid and the whole question of coagulation is one of physico-chemical interaction between lyophile and lyphobe colloids. J. P.

The Isolation of Soja-agglutinin and Anti-agglutinin. KYOYETSURO FUJIWARA (*Biochem. Z.*, 1923, **140**, 113—131).—Soja-agglutinin can be adsorbed by kaolin, aluminium hydroxide, and tricalcium phosphate from all of which it can be subsequently washed out by weak bases such as ammonia or disodium hydrogen phosphate. Weak acids are much less efficient in this respect. Use of excess of adsorbent renders the washing out more difficult.

The activity of soja-agglutinin is destroyed by boiling. Repeated injection of soja-bean extract produces in dog serum a specific anti-substance which inhibits the soja-agglutinin. This inhibition is not shown by normal serum. The anti-agglutinin can be adsorbed by the same substances as the agglutinin, but recovery by washing out is very imperfect. J. P.

The Action of Metallic Copper on Ricin. MITSUTARO TSUCHIHASHI (*Biochem. Z.*, 1923, **140**, 140—148).—The agglutinating action of ricin on red blood-corpuscles is destroyed if the solution be treated with finely divided metallic copper and, in its stead, a hæmolytic action appears, irrespective of whether the ricin solution has been boiled, and so lost its agglutinating action, or otherwise. This hæmolytic action is attributed to the copper and not to any specific property of ricin. Glycine and potassium cyanide have no effect on the agglutinating action of ricin, but they inhibit the hæmolytic action of the copper-treated solution, without regenerating the agglutinating powers. Anti-ricin serum from dogs has no specific action on the hæmolysis produced by copper-treated ricin. The toxicity of ricin to mice is reduced by copper treatment. J. P.

. The Chemical Causes of Normal and Pathological Hæmolytic. R. BRINKMAN and A. VON SZENT-GYÖRGYI (*Proc. K. Akad. Wetensch. Amsterdam*, 1923, **26**, 470—479).—The hæmolytic constituents of normal human blood were extracted by means of boiling acetone or cold light petroleum, and showed the typical reactions of the higher fatty acids. Measurements of surface tension were made, which support the hypothesis that these acids are present in the blood in the form of their calcium salts. Finally, experimental pernicious anæmia was induced in rabbits by intramuscular or intravenous injection of linolenic acid. H. H.

The Isolation of Crotin and Anti-crocin. KYOYETSURO FUJIWARA (*Biochem. Z.*, 1923, **140**, 132—139).—Crotin-hæmolysin can be adsorbed from a 1% solution by means of kaolin, aluminium hydroxide, and tricalcium phosphate, but subsequent recovery by washing out is imperfect. Crocin extract injected into dogs produces an anti-hæmolysin, absent from normal serum, which, like the hæmolysin, can be adsorbed but cannot be subsequently washed out from the adsorbents. J. P.

The Influence of Cell Salts on Protein and Gaseous Metabolism and on Body-weight. KAZUO ASADA (*Biochem. Z.*, 1923, **140**, 326—347).—A dog kept in nitrogen equilibrium on a mixed diet of sufficient heat value and vitamin content, with sodium chloride as the only salt, was given a salt mixture containing calcium, magnesium, iron, potassium, chlorides, phosphates, and iodides. Increases were observed in oxidation, nitrogen retention, and in body-weight. The water excretion in urine and fæces was not definitely altered. The same results were produced by the addition of potassium chloride alone to the original diet. J. P.

Intermediate Carbohydrate Metabolism in Avitaminosis.

I. Glycogen Formation and Exchange in Avitaminosis. P. RUBINO and J. A. COLLAZO (*Biochem. Z.*, 1923, **140**, 258—267).—Administration of dextrose and other carbohydrates to avitaminosed pigeons, guinea pigs, and dogs results in a large and immediate increase in liver- and muscle-glycogen, followed by an equally rapid decline to sub-normal values. The maximum increase of blood-sugar occurs before the maximum rate of formation of glycogen. It is concluded that in avitaminosis the ability to form glycogen is unimpaired, and may even be increased, but that there is marked loss of the glycogen-storing powers. The rapid breakdown of glycogen does not produce an increase of blood-sugar, and is probably accompanied by the formation of toxic products. J. P.

Polarimetric Observations on Solutions of Dextrose Subjected to Contact with Intestinal Mucosa of Rabbit.

DAVID STIVEN and EDWARD WAYMOUTH REID (*Biochem. J.*, 1923, **17**, 556—563).—The experiment of Hewitt and Pryde (*A.*, 1920, i, 648) has been repeated thirty-four times. In eight cases, the solutions obtained from the gut had to be discarded as not clear enough for polarimetric estimations. In the remaining twenty-six experiments, no sign of mutarotation in the earlier minutes after removal of the solution from the gut was observed. S. S. Z.

The Occurrence of Citric Acid in Sweat. C. D. LEAKE (*Amer. J. Physiol.*, 1923, **63**, 540—544).—In twenty-four hours, 72.8 mg. of citric acid would be excreted in heat-sweat, or 60.7 mg. in work-sweat. Human saliva does not contain citric acid.

CHEMICAL ABSTRACTS.

The Hydrogen-ion Concentration, Carbon Dioxide Content, and the Ratio Ionic Calcium to Ionic Potassium, of the Cerebrospinal Fluid of Children. JOACHIM BROCK (*Biochem. Z.*, 1923, **140**, 591—599).—The cerebrospinal fluids of various individuals ranging in age from nine months to ten years were examined with the view of obtaining normal data. The p_H determined by the indicator method was 7.50—7.55, and the carbon dioxide content 52 vol. %. Potassium and calcium were, respectively, 6.9 mg. % and 13.1 mg. %. The ratio of ionic calcium to ionic potassium of the cerebrospinal fluid is the same as that of the blood-serum. J. P.

Colloid Chemistry of Protoplasm. I. General. II. The Electrical Charges of Protoplasm. L. V. HEILBRUNN (*Amer. J. Physiol.*, 1923, **64**, 481—498).—Calcium or magnesium chloride tends to liquefy the protoplasm of sea-urchin eggs, whilst sodium, potassium, or ammonium chloride tends to increase its viscosity. The effects of these salts on the viscosity is thus in the reverse order of the adsorption of the kations by egg-albumin. It is consequently held that the colloids in the interior of the eggs are positively charged, a further increase in positive charge due to adsorption of kations causing decreased viscosity. The effects of various chlorides on the swelling of the vitellin membrane of sea-urchin eggs lead

the author to conclude that the exterior layer of protoplasm is negatively charged.

CHEMICAL ABSTRACTS.

Does Adrenaline Affect the Metabolism of the Surviving Skeletal Muscles of the Frog ? F. R. GRIFFITH, jun. (*Amer. J. Physiol.*, 1923, **65**, 15—29).—Adrenaline has no effect on the carbon dioxide production of surviving frog muscles. A modified Osterhout apparatus (*J. Gen. Physiol.*, 1918, **1**, 17) used in the experiments is described.

CHEMICAL ABSTRACTS.

The Behaviour of the Glycogen of the Frog in Anoxybiosis and Restitution. IV. E. J. LESSER (*Biochem. Z.*, 1923, **140**, 577—582).—The observations of Meyerhof (*Pflüger's Archiv*, 1920, **185**, 20) on the disappearance of glycogen from, and the formation of lactic acid in, excised muscles cannot be extended to the whole animal, nor are his conclusions in agreement with those of the author. A series of investigations on summer and winter frogs is given, in which it is shown that, in the latter, during anoxybiosis, 40% of the total glycogen loss occurs in the liver, while, in the former, only 15% is so lost, in contrast to Meyerhof's findings. During restitution, the resynthesis of glycogen in the muscle is independent of the season, but during the winter it is in part masked by the concurrent diminution of liver glycogen.

J. P.

The Significance of the Xanthidrol Reaction for the Microchemical Demonstration of Uric Acid in the Kidney. K. WALTER (*Pflüger's Archiv*, 1923, **198**, 267—278; from *Physiol. Abstr.*, 1923, **8**, 272).—After injection of xanthidrol into rats, crystals of dioxanthylurea are to be found in both glomeruli and convoluted tubules. This would suggest a process of secretion in both renal elements.

W. O. K.

Blood-sugar Studies. III. **Glycæmia and Glycosuria in Kidney Diseases and Effects of Peroral and Intravenous Administration of Sugar.** MAX ROSENBERG (*Arch. expt. Path. Pharm.*, 1923, **99**, 143—161; cf. *A.*, 1922, **i**, 482, 789).—In bad cases of renal insufficiency, the blood-sugar curve may not be normal, but may resemble that of diabetics, and there may be absence of glycosuria even although the blood-sugar is high. High blood pressure may be associated with a high fasting blood-sugar, but, if the kidney function is normal, with only a normal, or even sub-normal, rise after administration of dextrose.

W. O. K.

The Behaviour of Amino-acids in the System Hide Powder-Tannin. I. W. MOELLER (*Z. Leder. Gerberei Chem.*, 1923, **2**, 212—227). The systems tannin-hide powder, formaldehyde-hide powder, basic chrome alum-hide powder have been studied with and without the addition of glycine. The amount of tannin, formaldehyde, and basic chrome alum adsorbed by the hide powder was diminished by the addition of glycine. The glycine and tanning material (tannin, formaldehyde, or basic chrome alum) resemble the system non-tannin-hydrolysed hide substance in their behaviour, and yield a substance which is not leather [cf. *J.S.C.I.*, 1923, 1083A].

D. W.

The Theory of the Biochemical Degradation of Complex Structures. O. STEPPUHN (*Fermentforsch.*, 1923, 7, 68—76).—A comparison is made of the quantitative distribution of formic acid in the tissues of the rabbit and rat after injection of sodium formylglycine and after sodium formate. In all cases, the formic acid in the formylglycine was more easily destroyed by the tissues than by the free formate. The same results were found in experiments on ox-liver in vitro. H. K.

Isolation and Determination of the Constitution of Tetramine, a Toxin from *Actinia equina*. D. ACKERMANN, F. HOLTZ, and H. REINWEIN (*Z. Biol.*, 1923, 79, 113—120).—The toxin from *Actinia equina* was isolated by way of the picrate. It is shown to be tetramethylammonium hydroxide. G. W. R.

Coagulation of Milk by Acid. LEONARD ANDERSON (*Trans. Faraday Soc.*, 1923, 19, 106—111).—When hydrochloric acid is added to milk of various dilutions, the casein is precipitated to an extent which is greater the larger the amount of acid up to a maximum beyond which the casein redissolves to be again precipitated as chloride by further quantities of acid. The amount of acid required to effect each precipitation is inversely proportional to the dilution of the milk. The fat globules in the milk are carried down mechanically by the casein curd, and when this redissolves in excess of acid they rise to the surface, but remain for many hours without coalescing even in the presence of decinormal sodium hydroxide. Similar effects are observed in the cases of emulsions of benzene and olive oil in casein solution, so that it is probable that the protective agent for the fat globules in milk is a thin film of casein. The fat, benzene, or olive oil droplets may be caused to coalesce by removing the excess of protein by thorough washing with distilled water. A. R. P.

The Action of Polished Metals on some Ferment Reactions of Milk and their Relation to Oligodynamic Phenomena. WALTER WEICHINGER (*Fermentforsch.*, 1923, 7, 110—133).—Contrary to Hildebrandt's observations, metals cannot reactivate the peroxylase of milk. Reductase is influenced in various ways by metallic ions, and this depends apparently on the degree of dissociation of the salt used. Catalase of milk is uninfluenced by metals. The typical oligodynamic inhibition of diastase by copper is also not observed in milk. H. K.

New Picric Acid Compounds (Uropicrates). P. BERGELL (*Z. klin. Med.*, 1922, 95, 63; from *Physiol. Abstr.*, 1923, 8, 274).—A crystalline precipitate produced from urine one-fifth saturated with sodium chloride and treated with Esbach's solution, yields pure uric acid when decomposed by alcoholic hydrochloric acid. The precipitate is almost wholly composed of picric acid and uric acid in equal proportions. W. O. K.

Analysis of Liquid from a Paraovarian Cyst. MARCEL GUERBET (*J. Pharm. Chim.*, 1923, [vii], 28, 177—178).—The liquid

had d^{25}_D 1.005, was alkaline in reaction, and furnished no deposit when kept. Pseudomucin, globulin, urea, and fatty matter were present, together with sodium chloride and traces of sulphates and carbonates. The total solid content per litre was 10.3 g., 8.1 g. of this representing ash. Phosphates were absent. H. J. E.

The Intermediate Fate of Chloral Hydrate in the Organism. MUNEJI AKAMATSU and FERD. WASMUTH (*Arch. exp. Path. Pharm.*, 1923, **99**, 108—116).—If chloral hydrate or trichloroethyl alcohol is administered to guinea pigs, about one-half of the amount given is excreted as urochloralic acid. As urochloralic acid reduces copper there is an increase in the reducing power of the blood after administration of chloral hydrate. W. O. K.

The Fate of some Halogen Derivatives of Benzene and of Benzene in the Animal Body. T. S. HELE and E. H. CALLOW (*J. Physiol.*, 1923, **57**, xliii: from *Physiol. Abstr.*, 1923, **8**, 301).—One mol. of monochlorobenzene administered to dogs corresponds with one atom of sulphur in combination as sulphate (chlorophenyl sulphate) or as mercapturic acid (chlorophenylcystine) in the urine. The sulphur calculated from the output of halogen in organic combination corresponds with the excess of sulphur (ethereal and neutral) over the normal average. The same holds good for *o*-dichlorobenzene, *m*-dichlorobenzene, and *p*-bromoanisole. The administration of benzene, *o*- or *m*-dichlorobenzene, but not of *p*-bromoanisole increases the neutral sulphur (mercapturic acid) in the urine. W. O. K.

The Ethereal Sulphate and Mercapturic Acid Syntheses in the Dog. T. S. HELE (*J. Physiol.*, 1923, **57**, xlv-xlvii; from *Physiol. Abstr.*, 1923, **8**, 301).—It is doubtful whether phenol will combine with sulphate directly in the animal to form ethereal sulphate, but after large doses of the non-toxic guaiacol and sulphate by the mouth, 60—80% of the administered sulphate was excreted as ethereal sulphate. Likewise chlorobenzene, after oxidation to chlorophenol, will unite with sulphate to form ethereal sulphate, as well as with cystine to form mercapturic acid. The rise in neutral sulphur was always about double that in ethereal sulphur. It was found very difficult to upset this quantitative relation by the simultaneous administration of sodium sulphate or of cystine by the mouth. W. O. K.

Chemistry of Vegetable Physiology and Agriculture.

Bacterial Reduction of Organically Combined Phosphoric Acid. H. K. BARRENSCHEEN and H. A. BECKH-WIDMANSTETTER (*Biochem. Z.*, 1923, **140**, 279—283).—Ox-blood inoculated with putrefying blood and kept under anaërobic conditions at 37° gives a positive Blondlot-Dusart reaction (evolution of phosphine in the

presence of nascent hydrogen), from which it is concluded that reduction of the organically combined phosphoric acid has occurred.
J. P.

Detection of Phenols Produced by Bacteria. WILLIAM H. BELL (*J. Infectious Diseases*, 1921, **29**, 424—428).—The acidified medium is distilled with steam, and the distillate is treated with diazotised *p*-nitroaniline in alkaline solution; a yellowish-red colour is developed with concentrations of phenol as small as 1 in 500,000.
CHEMICAL ABSTRACTS.

Urease as a Product of *Bacterium radiculicola*. M. W. BEIJERINCK (*Nature*, 1923, **112**, 439; cf. Werner, this vol., i, 1046).—Urease is produced more profusely by pure cultures of *Bacterium radiculicola* than by the nodules, particularly by *Vicia*, *Trifolii*, and *Pisi* forms. Urease is also, in certain cases, a product of normal papilionaceous plants. Its existence is best demonstrated by a modification of the author's plate-method (*Centr. Bakt.*, 1893, **II**, 5, 323).
A. A. E.

Preparation of a Urease Solution from Bacteria. TETSU-GORA TAKAHATA (*Biochem. Z.*, 1923, **140**, 168—170).—From dried cultures of *Bacillus proteus* a soluble urease has been extracted by the use of various phosphate solutions.
J. P.

Bacterial Catalase. IV. J. HAGIHARA (*Biochem. Z.*, 1923, **140**, 171—174).—By precipitating cultures of *Bacillus proteus* with methyl alcohol and by subsequently extracting the precipitate with water, purified catalase preparations were obtained with from 60 to 80% of the original activity of the culture. The purified solutions, unlike the original cultures, contain only traces of amino- and ammonia nitrogen.
J. P.

The Fermentation of Arabinose and Xylose by certain Aërobic Bacteria. E. B. FRED, W. H. PETERSON, and J. A. ANDERSON (*J. Bact.*, 1923, **8**, 277—286).—The fermentation of pentoses by *Bacillus vulgatus*, *Acetobacter sorbose*, *A. xylinum*, *B. herbicola aureum*, and two yellow coccus forms called A and B are studied. The rates of fermentation of xylose and in certain cases of arabinose were slower than with the facultative anaërobic bacteria. The products of fermentation of the pentoses depend on the kind of organism. The ratio of the products depends on the age of the culture. *B. vulgatus* ferments xylose with the formation of acetone, ethyl alcohol, carbon dioxide, and a small amount of fixed acids. As the culture grows older the ratio of acetone and ethyl alcohol to carbon dioxide decreases. The maximum amount of acetone and ethyl alcohol is found about the sixth day. In the case of *A. xylinum*, an increase in the age of the culture is accompanied by an increase of acetone and ethyl alcohol. Although in different proportions, the substances obtained by the breaking down of xylose are the same as those noted with *B. vulgatus*. The remaining organisms studied ferment the pentoses slowly. They form a trace of acid, but the chief end-product is carbon dioxide.
CHEMICAL ABSTRACTS.

Bacteriophages. II. Concentration of Lysin in its Relation to the Disappearance of the Bacteriophage Reaction.

HANS MEULI (*Z. Hyg. Infekt.-Krankh.*, 1923, **99**, 46—66; from *Chem. Zentr.*, 1923, i, 1600).—Lysin is probably not a protoplasmic poison acting in the manner of chemical disinfectants. It acts by disturbing bacterial exchanges, possibly by means of a membrane effect.
G. W. R.

Bacteriophages. III. Antagonistic Effect of Gelatin and Agar on the Disappearance of the Bacteriophage Reaction.

R. DOERR and W. BERGER (*Z. Hyg. Infekt.-Krankh.*, 1923, **97**, 422—432; from *Chem. Zentr.*, 1923, i, 1600).—Gelatin and other colloids such as gum and starch inhibit the bacteriophagous action of lysin. The protective action of gelatin increases with concentration, but even at the highest concentrations some effect of lysin on bacterial growth is shown.
G. W. R.

Utilisation of Atmospheric Nitrogen by *Saccharomyces cerevisiæ*.

ELLIS I. FULMER (*Science*, 1923, **57**, 645—646).—*Saccharomyces cerevisiæ*, Race F., was sub-cultured for three years at 30° in a medium containing 10 g. of sucrose, 0.188 g. of ammonium chloride, 0.1 g. of dipotassium hydrogen phosphate, and 0.1 g. of calcium chloride in 100 c.c. and then for six months in a medium containing 10 g. of sucrose, 0.188 g. of ammonium chloride, and 0.1 g. of dipotassium phosphate in 100 c.c. It was then inoculated into sterile 10% sucrose solution containing the optimal amount (0.45%) of potassium phosphate, and air free from ammonia or oxides of nitrogen was passed through the mixture. The results show that yeast will grow continuously in a medium composed of sugar and one salt, and that *S. cerevisiæ* will grow in an apparently good state of nutrition, using atmospheric nitrogen as the sole source of that element. It is suggested that the beneficial effect of the aëration of yeast-cultures may be due as much to the addition of nitrogen as to that of oxygen.
A. A. E.

The Mechanism of Autolysis. I. The Influence of Iodine on Yeast Autolysis.

O. STEPPUHN and L. UTKIN-LJUBOVZOV (*Biochem. Z.*, 1923, **140**, 17—27).—Iodine in certain concentrations accelerates the autolysis of the proteins of various yeast preparations. This action is not due to acid formation, nor is it shown by potassium iodide, and it cannot be explained on the basis of the addition of iodine to an unsaturated fatty acid with anti-proteolytic properties. Higher concentrations of iodine have an inhibiting action on the autolysis which is ascribed to the addition of iodine to the substrate.
J. P.

The Balance of Pyruvic Acid Fermentation.

C. NEUBERG and A. VON MAY (*Biochem. Z.*, 1923, **140**, 299—313).—The yeast fermentation of pyruvic acid, both in the presence of yeast-cells and under cell-free conditions, proceeds in accordance with the equations : $\text{COMe}\cdot\text{CO}_2\text{H} \rightarrow \text{CO}_2 + \text{CHMeO}$ and $2\text{COMe}\cdot\text{CO}_2\text{H} \rightarrow 2\text{CO}_2 + \text{COMe}\cdot\text{CHMe}\cdot\text{OH}$, both acetaldehyde and acetylmethylcarbinol being formed along with carbon dioxide. The acetylmethylcarbinol

was isolated as the *p*-nitrophenylosazone and the acetaldehyde as the "dimedon" compound. By quantitative measurements, the accuracy of the above formulation was confirmed. In the presence of sulphites, fermentation proceeds almost wholly as in the first equation, only traces of acetylmethylcarbinol being found. J. P.

The Enzymatic Decarboxylation of Pyruvic Acid in a Current of Oxygen. A. GOTTSCHALK (*Biochem. Z.*, 1923, **140**, 348—352).—By the fermentation with yeast of pyruvic acid in a current of oxygen, acetaldehyde was formed in quantities as great as under anaërobic conditions. The acetaldehyde was carried over in the stream of oxygen and isolated as the bisulphite and "dimedon" compounds. J. P.

The Fermentation of α -Keto-*n*-hexoic Acid. H. K. SEN (*Biochem. Z.*, 1923, **140**, 447—452).— α -Keto-*n*-hexoic acid is fermented by yeast carboxylase in the presence of disodium hydrogen phosphate with the formation of carbon dioxide, *n*-valeraldehyde, and *n*-amyl alcohol. The secondary formation of amyl alcohol is inhibited by the addition of sodium hydrogen sulphite and an acetate buffer solution. J. P.

The Destruction of Pentosans by Moulds and other Micro-organisms. E. G. SCHMIDT, W. H. PETERSON, and E. B. FRED (*Soil Sci.*, 1923, **15**, 479—488).—Studies on the destruction of pentosans in plant materials by moulds. The pentosans of wood are more rapidly destroyed in the soil than cellulose, lignin, and other cell constituents. Pentosans occur as cell constituents in fungi and may serve later as sources of carbohydrate. [See, further, *J.S.C.I.*, 1923, 1041A.] G. W. R.

Mechanism of Oxidation in the Plant. The Oxygenase of Bach and Chodat. Function of Lecithins in Respiration. PATRICK HUGH GALLAGHER (*Biochem. J.*, 1923, **17**, 515—529).—Alcoholic extracts of plants when exposed to the air form peroxides. No evidence can be found that this formation is produced by the action of an enzyme. Minute traces of phenolic substances such as quinol or gallotannic acid usually prevent the fixation of oxygen. An autoxidisable substance of this nature isolated from fresh potato tubers was found to bear a close relation to the lipins, and it is concluded that the so-called oxygenase of the potato is an autoxidisable lecithin-like substance. Terpenes can combine with oxygen, forming a substance which can take the place of the peroxide in the peroxydase system. The blackening of aqueous extracts of the potato and of the mangold is not due to oxidation of a catechol derivative by the action of a peroxydase, but to the action of tyrosinase on tyrosine. The constituent of extract of mangold root which gives a ferric chloride coloration is a tannin. S. S. Z.

Assimilation of Ammonia by Higher Plants. PRIANICHNIKOV (*Compt. rend.*, 1923, **177**, 603—606).—In presence of calcium carbonate, ammonium chloride is a better source of nitrogen than calcium nitrate. Of all the ammonium salts, the hydrogen carbonate is the most favourable for plant growth. E. E. T.

The Absorption and Translocation of Lead by Plants. A Contribution to the Application of the Method of Radioactive Indicators in the Investigation of the Change of Substance in Plants. GEORGE HEVESY (*Biochem. J.*, 1923, 17, 439—445).—The assimilation of lead by *Vicia faba* from lead nitrate solutions was estimated by a method which was based on the principle of mixing the lead solution with a radioactive isotope (thorium-*B*) and determining the radioactivity. The amount of lead taken up was estimated by measuring after incineration the radioactive intensity of the ash. Very small amounts of assimilated lead could be determined in this way, and it was found that whilst from 200 c.c. of a $10^{-1}N$ -lead nitrate solution only 0.3% of the lead was taken up in the course of twenty-four hours, 60% of the lead was assimilated from a $10^{-6}N$ -solution in the same time. The leaves were found to take up only 1% of the lead in the solution. The assimilated radioactive lead could be displaced by inactive lead when the plant was placed in a solution containing the inactive element, from which observation the author concludes that the lead is not combined with carbon in the plant, but that it exists there as a dissociable salt of low solubility. A $10^{-1}N$ -solution of a lead salt produces a toxic effect on the plant, whilst more dilute solutions do not.

S. S. Z.

The Effect of Different Concentrations of Manganese Sulphate on the Growth of Plants in Acid and Neutral Soils and the Necessity of Manganese as a Plant Nutrient. J. S. MCHARGUE (*J. Agric. Res.*, 1923, 24, 781—794).—Plants grown in a carefully prepared manganese-free solution indicate the lack of manganese in the small amount of green matter produced, and in an etiolated condition of the younger leaves and buds. Seeds do not usually contain sufficient manganese to supply the needs of the plant throughout its whole growing period. Leguminous plants suffer from a deficiency of manganese more than the non-legumes. It is possible that the toxicity of acid soils may be associated in part with the presence of soluble manganese salts: but the proportion of soluble to total manganese is always small. The addition of manganese sulphate to acid soils causes a decrease in crop yields but in the presence of calcium carbonate an improved crop is obtained.

A. G. P.

The Iron-chlorosis caused by Manganese in Green Plants. AUGUST RIPPEL (*Biochem. Z.*, 1923, 140, 315—323).—The addition of soluble manganese salts to the cultures in which oats seedlings were growing produced a chlorosis which was remedied by the addition of iron. Since the iron content of the chlorotic and normal seedlings was the same, it is concluded that manganese does not prevent the uptake of iron by the plant, but inhibits its action after absorption.

J. P.

The Influence of Chemical Fertilisers on the Chlorophyll Coefficient. JEAN WLODEK (*Bull. acad. polonaise sci. let. classe sci. math. nat.*, 1920, [B], 19—52).—Determinations were made

of the chlorophyll coefficient, neochlorophyll (*A*): *allochlorophyll* (*B*) (Willstätter's chlorophyll *a* and *b*) by comparing the limits of the absorption bands by means of a Wagner spectrometer (*Z. Instrumentenk.*, 1913, 149). The live leaves of potato and sugar-beet were studied, grown in soils to which various fertilisers were added. It is concluded that after a certain period of development of the plants the relation of the chlorophyll pigments varies during the course of twenty-four hours; *B* increases during the day and *A* during the night. The lack of potassium results in an absolute and relative diminution of *B* and an increase in *A*, as well as a reduction of the daily variation of the two components. Lack of phosphorus also reduces the daily variation of the chlorophyll components and narrows the absorption bands; nitrogen tends to reduce *A* and augment *B*. The action of calcium and magnesium is not definitely established.

CHEMICAL ABSTRACTS.

The Influence of Light and of Chemical Fertilisers on the Chlorophyll Coefficient. JEAN WLODEK (*Bull. acad. polonaise sci. let. classe sci. math. nat.*, 1921, [B], 143—90; cf. preceding abstract).—The variations of the chlorophyll coefficient in *Iris germanica* under the influence of light with attached and excised leaves were studied. During illumination, the absorption bands shift toward the more refrangible portion of the spectrum and in the opposite direction in the dark. In illuminated leaves the absorption band of *allochlorophyll* becomes wider, that of neochlorophyll narrower, whilst the reverse happens in the dark. This change requires three-quarters of an hour to two hours. The shifting of the absorption band is noticeable after fifteen minutes. Leaves which have died through wilting show an increased chlorophyll coefficient and a shifting of the absorption band towards the violet. Ether diminishes the variations in the chlorophyll coefficient. With a lack of potassium the coefficient diminishes at a certain phase of development of oats, barley, and beans. This is due to an increase of the absorption band of neochlorophyll and a decrease in that of *allochlorophyll*, as compared with plants grown under normal conditions. A lack of nitrogen in the soil increases the chlorophyll coefficient. A relation seems to exist between the width of the first absorption band and the nitrogen content in fresh bean leaves, in the straw and harvest of oats and barley. The nitrogen content increases with the width of the band. With a lack of potassium, the chlorophyll coefficient does not change under the influence of light and dark. In leaves which show an abnormal chlorophyll coefficient the production of vegetative material is less.

CHEMICAL ABSTRACTS.

The Physiological Significance of Titanium in the Plant Organism. ANTONÍN NĚMEC and VÁCLAV KÁŠ (*Biochem. Z.*, 1923, 140, 583—590).—By the addition of sodium titanate or sodium titanocitrate ($\text{Na}_2\text{TiO}_3 \cdot \text{C}_6\text{H}_6\text{O}_7 \cdot \text{H}_2\text{O}$) to the earth in which mustard, pea, and lucerne plants were grown, a 30—40% increase in growth over controls was obtained. The magnitude of the increase ran

parallel to the amount of titanium absorbed. The iron content of the plants diminished with increasing uptake of titanium, and the other mineral constituents showed variations more or less marked.
J. P.

Pectin and its Hypothetical Precursor "Protopectin."
FRANK TUTIN (*Biochem. J.*, 1923, **17**, 510—514).—Unripe apple tissue was repeatedly disintegrated and extracted with alcohol and with water in order to remove the pectin. On heating the residual marc in an autoclave at 110° with *N*/20-hydrochloric acid, only an insignificant quantity of pectin was obtained. The author concludes that "protopectin" does not exist, and that all the pectin present in the apple occurs in ordinary soluble form. The persistent retention of pectin in an insoluble form by the tissue of unripe fruit is due partly to the presence in it of a substance insoluble in water but soluble in alcohol and partly to the difficulty of the disintegration by mechanical means of the unripe tissue. Hence "protopectin" is not the cause of the hardness of the tissue of unripe fruit.

S. S. Z.

Presence of Maltase in Germinated and Ungerminated Barley. ARTHUR ROBERT LING and DINSHAW RATTONJI NANJI (*Biochem. J.*, 1923, **17**, 593—596).—Malts, whether green or kilned, obtained by germinating barley hydrolyse maltose (cf. Daish, A., 1916, i, 535). The intensity of the action of the enzyme depends on the temperature and on the way in which the malt has been heated. Ungerminated barley also contains an enzyme capable of producing dextrose from maltose. This reaction can only be obtained by employing ground barley, as the enzyme cannot be extracted with water. This enzyme is also destroyed by alcohol, and therefore diastase preparations obtained by cold water extraction of malt and precipitation of the aqueous extract with alcohol do not hydrolyse maltose.

S. S. Z.

The Hydrogen-ion Concentration of the Soil in Relation to the Flower Colour of *Hydrangea hortensis*, W., and the Availability of Iron. W. R. G. ATKINS (*Sci. Proc. Roy. Dublin Soc.*, 1923, **17**, 201—210).—The flowers of *Hydrangea hortensis* are blue when the plant is grown in acid soil, p_H 5·7 to 6·0 or slightly above, pink with p_H 7·5 or above, whilst if the p_H value of the soil lies between these values, blue and pink flowers may be present on the same plant. The flower pigment is not here acting as an indicator, for the p_H of both kinds of flower is about 4·2. There is strong evidence that blue flowers only occur when ferrous iron is available. Ferrous salts remain in solution after ferric salts are completely precipitated. Precipitation of ferrous hydroxide starts at about p_H 5·1, and is not complete at 7·1. The blue flowers are found to contain considerably more iron than the pink flowers, the proportions being 140 and 60 parts per million of dried flower, respectively. Treatment of soils with alum or aluminium sulphate solution causes the formation of blue hydrangeas. These solutions

have p_H 3.6 to 4.0, and may well increase the availability of iron. It may be, however, that aluminium as well as iron may form a blue complex with the pink anthocyanin. The occurrence of chlorosis in plants grown on alkaline soil may be due to the non-availability of iron.

E. H. R.

Presence of Maltose in *Mercurialis perennis*. P. GILLOT (*J. Pharm. Chim.*, 1923, [vii], 28, 148—154; cf. A., 1922, i, 1101).—The dextrorotatory sugar present, together with sucrose, in the rhizomes of *Mercurialis perennis* is maltose. The amount increases during the summer months to a maximum of about 2% in September and then decreases, the minimum of 0.25% being reached in April.

W. P. S.

Formation of Maltose in Sweet Potatoes on Cooking. H. C. GORE (*Ind. Eng. Chem.*, 1923, 15, 938—940).—The presence of maltose in cooked sweet potatoes is shown by the agreement of the quantity of sugars as determined by copper reduction with the quantities measured by polarisation and by its isolation in crystalline form. Sugar is not formed at the boiling point, but is produced very rapidly, although not instantaneously, by diastatic action during the initial stages of the digestion. The increase in sugar calculated as maltose caused by cooking in steam, baking, or boiling varied from 11.5% to 17%.

H. C. R.

Odorous and Bitter Constituents of Neem Oil. EDWIN ROY WATSON, NITYA GOPAL CHATTERJEE, and KSHITISH CHANDRA MUKERJEE (*J. Soc. Chem. Ind.*, 1923, 42, 387—389T).—By saponification of neem oil (from *Melia azadirachta*) and repeated salting out of the resulting soaps, the bitter constituents are obtained in the lyes, from which they are precipitated as a resin by acidifying. From this resin, after extraction of some free sulphur with benzene, an amorphous bitter substance, $C_{15}H_{20}O_5$, and a crystalline bitter substance, *margosopicrin*, $C_{24}H_{32}O_8$, were obtained. The latter forms rhombic prisms, m. p. 221—222° after swelling at 128°. It has $[\alpha]_D^{25} +163.8^\circ$, and from the properties of its acetyl derivative would appear to be $OH \cdot C_{23}H_{24} \cdot CO_2H, 3H_2O$. *Acetylmargosopicrin*, $OAc \cdot C_{23}H_{24}O_2 \cdot CO_2H$, forms colourless needles, m. p. above 280°; it is devoid of bitterness, which, however, can be regenerated by hydrolysis. The odorous constituent, obtained by steam distillation of the oil (? $C_{21}H_{44}S$), was not obtained in a pure state; it is not a mercaptan. On boiling neem seeds with water, precipitating the extract with basic lead acetate, and concentrating the filtrate, an inodorous substance of composition $C_{13}H_{24}O_7S_2$ is obtained; it forms rectangular prisms, m. p. above 230°, and has $[\alpha]_D^{20} -325^\circ$. On prolonged boiling with dilute hydrochloric acid, hydrogen sulphide is evolved and the solution becomes reducing to Fehling's solution.

G. W. R.

Cultural Experiments in France—Peppermint and Lavender. ERNEST AUTRAN and LOUIS FONDAND (*Perf. Essent. Oil. Rec.*, 1923, 14, 334—335).—Red peppermint oil was obtained

containing 7.07% menthyl acetate and 83.2% menthol. The figures for white peppermint oil were 12.37% and 60.6% respectively. Of the lavender oils, the "blue" showed α $-10^{\circ} 12'$ with 44.4% esters, and the "white" α $-9^{\circ} 5'$ with 58.6% esters. A. G. P.

The Effect of Respiration on the Protein Percentage of Wheat, Oats, and Barley. F. W. MCGINNIS and G. S. TAYLOR (*J. Agric. Res.*, 1923, **24**, 1041—1048).—The loss of carbohydrate material of grain during the ripening stage was measured by the amount of carbon dioxide evolved during respiration. This loss was found to be considerable, the maxima occurring just before the drying off of the grain, *i.e.*, when the moisture content is of the order of 40%. The loss of carbohydrate would appear markedly to influence the protein content of the grain, although other factors were doubtless concerned. Variations in protein were greatest in wheat, followed, in order, by barley and oats. A. G. P.

Factors Affecting the Nitrogen Content of Wheat and the Changes that occur during the Development of Wheat. GEORGE A. OLSON (*J. Agric. Res.*, 1923, **24**, 939—953).—The nitrogen content of wheat was determined during growth under varying conditions. By increasing the width apart of the rows, higher nitrogen contents of wheat were obtained in non-irrigated land. On irrigated land, however, no differences were observed. During the formation and early maturing stages of the grain, the nitrogen of the plant moved upwards. As the grain matured, its nitrogen content decreased. The nitrogen content of wheat was not affected by irrigation, but the placing of the plant in water caused a movement of nitrogen into the grain. The actual grain ceased to increase in weight when the soil moisture content fell below 40%. After the initial stages of growth, the intake curves for nitrogen and phosphorus were almost identical in character. A. G. P.

The Occurrence of Polypeptides and Free Amino-acids in the Ungerminated Wheat Kernel. S. L. JODIDI and K. S. MARKLEY (*J. Amer. Chem. Soc.*, 1923, **45**, 2137—2144).—It is shown that the following varieties of ungerminated wheat kernel, Kanred, Fultz, Marquis, and Kubanka, contain nitrogen as amides, free amino-acids, and polypeptides.

The presence of amino-acids is demonstrated by the following procedure. The clear, filtered extract, obtained by digesting the "whole wheat" flour, ground to pass a 40-mesh sieve, with cold water for two hours, is concentrated on the water-bath. During this process a precipitate, apparently proteins, is formed, and is removed by centrifuging. The liquid is taken to dryness, and the non-protein matter extracted from the residue by means of 70% alcohol, the latter being then removed from the filtered extract. The residue, a yellow syrup, is dissolved in hot water; the total nitrogen is estimated in part of the solution, by Kjeldahl's method, whilst another part of the solution is freed from carbon dioxide, phosphoric

acid, and colouring matter, and titrated with formol (cf. Jodidi, A., 1911, ii, 820; 1912, ii, 292; 1918, ii, 379). Since proteins may not be completely removed by this method, it is modified as follows. The boiling, aqueous solution of the dried alcoholic extract is treated successively with acetic acid, and with freshly prepared lead hydroxide and lead acetate; the liquid is boiled and filtered after each treatment. The clear solution is concentrated, and treated as before. Both these methods are further modified by conducting the evaporations under reduced pressure.

Amides, and other substances containing ammoniacal nitrogen, are estimated by estimating the total nitrogen, by Kjeldahl's method, in the aqueous solution of the dried alcoholic extract, and then estimating the nitrogen evolved as ammonia, when the solution is treated with hydrochloric acid to a final concentration of 20% and boiled for thirty minutes. This corresponds with the amides; the further quantity of ammonia eliminated when the hydrolysis is continued for twelve hours corresponds with the other ammoniacal substances.

Polypeptides present in the wheat kernel must, when hydrolysed long enough, yield free amino-acids. Hence they may be estimated by determining the increase in amino-acid content after hydrolysis. The boiling aqueous solution of the dried alcoholic extract is treated successively, as above, with acetic acid, lead hydroxide, and lead acetate. The nitrogen in the final, clear solution is estimated by Kjeldahl's method. A portion of the solution is then treated with hydrochloric acid, to give a final concentration of 20%, boiled for twelve hours, and taken to dryness. The residue is distilled with a cream made by grinding magnesium oxide with water (Jodidi and Moulton, A., 1919, i, 603). The aqueous extract of the magnesium oxide residue is then analysed by Kjeldahl's method, and by formol titration.

The following method is devised to remove proteoses and peptones, if present. The aqueous solution of the dried alcoholic extract is treated with sulphuric acid and phosphotungstic acid. After keeping for twenty-four hours, the precipitate is removed and washed with a solution of the same reagents. The filtrate is freed from sulphuric and phosphotungstic acids by treatment with barium hydroxide, the excess of which is removed by means of carbon dioxide. The filtered liquid is concentrated, and the peptide nitrogen estimated after hydrolysing with hydrochloric acid.

Kanred, Fultz, Marquis, and Kubanka ungerminated wheat kernels contain peptide nitrogen in the following percentages, respectively: 26.86, 28.09, 32.20, and 37.76%, on the basis of water-soluble nitrogen, or 3.89, 4.67, 4.98, and 5.13%, calculated to the total nitrogen. The figures for amino-acid nitrogen are, approximately, 16, 11, 11, and 10%, calculated to the water-soluble nitrogen, and 2.3, 1.8, 1.8, and 1.4%, calculated to the total nitrogen. Amide nitrogen is present to the following extent: 12.99, 8.76, 12.33, and 12.61%, on the basis of water-soluble nitrogen, or 1.88, 1.46, 1.91, and 1.72%, calculated to the total nitrogen. W. S. N.

The Litmus Paper Method for Detecting the Soil Reaction. EVERETT A. CARLETON (*Soil Sci.*, 1923, **16**, 91—94).—The results of the litmus paper test with soils depend on their hydrogen-ion concentration. The arrangement of a series of soils in order of increasing acidity, using the litmus paper test by two observers, showed a fair agreement with p_H figures, obtained electrometrically. A soil cannot be assumed to be basic if it does not impart the full blue colour to litmus paper. Soils which do not show acidity by the litmus paper test may yet show a lime requirement by the calcium acetate method. G. W. R.

Influence of the Absolute Reaction of a Soil on its *Azotobacter* Flora and Nitrogen-fixing Ability. P. L. GAINNEY (*J. Agric. Res.*, 1923, **24**, 907—938).—The examination is recorded of a large number of soils, for the presence and activity of nitrogen-fixing organisms. The results of previous laboratory researches were confirmed; few soils with p_H lower than 6.0 contained *Azotobacter*, whilst in nearly all soils having p_H greater than 6.0 *Azotobacter* were observed. The possibility is noted that the reaction of the soil may well be the limiting factor governing the growth of *Azotobacter*. Soil reactions determined electrically agreed well with those found by Gillespie's modification of the indicator method. In general, the electrometric method indicated slightly higher hydrogen-ion concentrations on the acid side, and lower on the alkaline side, as the actual values diverged from the neutral point. A. G. P.

Soil Reaction. P. E. KARRAKER (*Soil Sci.*, 1923, **15**, 473—478).—Data are given for soil reaction, determined by the electrometric method, lime requirement by Veitch and Hopkins's methods, and yields of clover hay, for a number of plots with different manurial treatments. The correlations observed are in general agreement with current hypotheses. Similar results were obtained in a series of experiments with sweet clover. G. W. R.

A Modification of the Truog Soil Acidity Test. F. W. PARKER and J. W. TIDMORE (*Soil Sci.*, 1923, **16**, 75—78).—The Truog soil acidity test is modified so that the hydrogen sulphide evolved is collected and estimated volumetrically. [See, further, *J.S.C.I.*, 1923, 1035A.] G. W. R.

Oxygen-supplying Power of the Soil as Indicated by Colour Changes in Alkaline Pyrogallol Solution. LEE M. HUTCHINS and BURTON E. LIVINGSTONE (*J. Agric. Res.*, 1923, **25**, 133—140).—The apparatus consisted of a porous porcelain cylinder soaked in paraffin oil and having a pair of leading-in tubes sealed passing in through a stopper closing the open end of the cylinder. Oxygen from the soil in which the cylinder was buried diffused into the cylinder and was swept out into wash-bottles containing alkaline pyrogallol by a continuous current of inert oxygen-free gas, e.g., coal gas. Experiments with this apparatus indicated that the

oxygen-supplying power of a soil is greater nearer the surface, and is decreased by excessive moisture and close packing. [Cf. *J.S.C.I.*, 1923, Nov.] A. G. P.

Effect of Season on Nitrification (in Soils). BRUNO SCHÖNBRUNN (*Zentr. Bakt. Par.*, 1922, 56, ii, 545—565, from *Chem. Zentr.*, 1923, i, 1606).—From ammonification and nitrification experiments on soils with temperature control, it is concluded that there is no inherent periodicity in these processes in the soil apart from that due to changes in temperature and other factors.

G. W. R.

Effect of Season on Nitrification in Soils. F. LÖHNIS (*Zentr. Bakt. Par.*, 1923, 58, ii, 207—211; from *Chem. Zentr.*, 1923, i, 1606—1607).—Criticism of Schönbrunn's conclusions (see preceding abstract). The author contends that there is a seasonal effect in nitrification.

G. W. R.

The Occurrence and Action of Fungi in Soils. ERNEST V. ABBOTT (*Soil Sci.*, 1923, 16, 207—216).—Twenty-eight species of fungi representing twelve genera were isolated from five Iowa soils of varying lime requirement. With two exceptions all the species showed vigorous ammonifying power.

G. W. R.

Partial Sterilisation of Soil. Microbiological Activities and Soil Fertility. SELMAN A. WAKSMAN and ROBERT L. STARKEY (*Soil Sci.*, 1923, 16, 137—158).—Experiments on the effect of treatment with toluene, and of heat on soils are described. Partial sterilisation affects not only bacteria and protozoa but also fungi and actinomycetes. Whilst protozoa may limit bacterial development in abnormal soils such as greenhouse soils, such an inhibition is held to be improbable in ordinary soils. [See, further, *J.S.C.I.*, 1923, Nov.]

G. W. R.

Distribution of the Phosphorus-ion in the Upper Layers of the Soil in Relation to Vegetation and the Addition of Various Salts. G. LEONCINI and F. A. ROGAI (*Agr. Italiana*, 1922, 45, Nos. 4—6, 109—124).—The effect exerted by vegetation or soluble salts on the known adsorption of added phosphate in the surface layers of irrigated soils is, in general, to render the distribution of the phosphorus-ion more uniform, hence causing deeper penetration, and to increase the soluble phosphate-fixing power of the soil. An attempt to determine the specific effects of anions and kations was unsuccessful.

CHEMICAL ABSTRACTS.

The Fixation of Phosphoric Acid by the Soil. G. S. FRAPS (*Texas Agr. Expt. Sta. Bull.*, 1922, No. 304).—The fixation of phosphoric acid from dilute solutions of dipotassium hydrogen phosphate was usually increased with time of contact, and in some cases by increase of temperature, whereas treatment with acid often caused a decrease. Ignition increased the fixing power. Percolation experiments indicated that, under natural conditions,

heavy rains would be required to cause any loss of phosphoric acid even from soils of low fixing power. The active phosphoric acid was found to increase with the absorbing power until the latter reached 40—60%, and then to decrease. The acid consumed and the calcium oxide increased until the absorption was 60—80% and then decreased. The iron and aluminium oxides, however, increasing with the phosphoric acid fixed, were found to have a much greater influence on the fixation.

CHEMICAL ABSTRACTS.

Comparison of the Jones Calcium Acetate Method for Lime Requirement with the Hydrogen-ion Concentration of some Quebec Soils. EVERETT A. CARLETON (*Soil Sci.*, 1923, **16**, 79—90).—A general correlation was observed between soil reaction, determined electrometrically and colorimetrically, and lime requirement by the Jones calcium acetate method. [See, further, *J.S.C.I.*, 1923, Nov.] G. W. R.

Effect of Addition of Calcium and Magnesium on the Outgo of Sulphates in Leachings from a Loam Soil. W. H. MACINTYRE, W. M. SHAW, and J. B. YOUNG (*Soil Sci.*, 1923, **16**, 1—40).—Applications of the oxides and carbonates of calcium and magnesium, ground limestone, dolomite, and magnesite, all cause an increase in the loss of sulphates by leaching from surface soil. The rate of loss diminishes after the first year. Excessive applications of calcium oxide depress the losses of calcium sulphate. [See, further, *J.S.C.I.*, 1923, 1036A.] G. W. R.

The Transient Nature of Toxicity induced by Magnesium and its Bearing upon Lime-Magnesia Ratio Studies. W. H. MACINTYRE and J. B. YOUNG (*Soil Sci.*, 1923, **15**, 427—461).—Lysimetric studies over a period of years with tall oat grass and cowpeas grown in cylinders of soil with different dressings of calcium and magnesium compounds are reported. An initial toxic effect which subsequently disappeared was observed where precipitated magnesium carbonate was used. Dolomite showed no toxic effect and was as beneficial as limestone. The initial toxicity due to magnesium compounds and its subsequent disappearance are discussed. The authors suggest that the initial reaction whereby magnesium carbonate is rapidly converted into relatively soluble silicate combinations is succeeded by a slow change into more complex and less soluble combinations. Attention is directed to the necessity for using cultures in soil extending over several seasons when studying the effect of magnesium carbonates on plant growth. G. W. R.

Organic Chemistry.

The Extraction of Mineral Oils with Methyl Alcohol. HANS STÄGER (*Helv. Chim. Acta*, 1923, 6, 893—900).—To investigate the cause of sludge formation in transformer oils (cf. this vol., i, 649), the author extracted a number of such oils with methyl alcohol and submitted the extracts and the extracted oil to the usual tests for such oils. The alcohol extracted from the oil the unsaturated cyclic compounds, and the extracts when oxidised with sodium peroxide showed high acidity. The extracted oils, however, still showed considerable sludge formation when heated for a long period at 112° in presence of copper. [Cf. *J.S.C.I.*, 1923, 1117A.]

E. H. R.

Density of Acetylene. JITSUSABURO SAMESHIMA and KOICHI FUKAYA (*J. Chem. Soc. Japan*, 1923, 44, 690—708).—It has been found that acetylene behaved differently from other gases when the velocity of diffusion of methane, ammonia, acetylene, nitrogen, carbon monoxide, air, oxygen, and carbon dioxide through an unglazed porcelain plate, and through a perforated platinum plate, was measured at various pressures. The behaviour of acetylene may be explained by assuming that it undergoes molecular association at high pressure. The density of acetylene was therefore measured at 0° and 25° under pressures from 0.3858 to 2.3764 atmosphere by Dumas' method, and an equilibrium, $(C_2H_2)_3 \rightleftharpoons 3C_2H_2$, was established. The equilibrium constant at 0° is 319.1 and that at 25° 509.7, so the heat of dissociation $(C_2H_2)_3 \rightleftharpoons 3C_2H_2$ —3027 cal.

K. K.

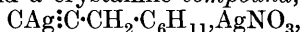
Contact Polymerisation of Acetylene. N. D. ZELINSKI (*Compt. rend.*, 1923, 177, 882—885).—The well-known conversion of acetylene into benzene has hitherto only been effected with very small quantities of material. If, however, acetylene is passed through a tube filled with activated wood-charcoal, and heated at 640—650°, 70—80% of the gas is converted into a tar, of which, by weight, 45% boils at 20—150°, 13.9% at 150—250°, 29% at 104—300°/13 mm., 12% remaining as a residue. Of the lowest fraction, 40% boils at 79—115°, and is mainly benzene, containing toluene and xylene. The fraction boiling at 79—80°/738 mm. has d_4^{20} 0.8857, n_D^{20} 1.504, and after purification with concentrated sulphuric acid gives pure benzene (about 35% of total tar), b. p. 79.6°/747.5, d_4^{20} 0.8790, n_D^{20} 1.49678, n_D^{20} 1.50148, n_F^{20} 1.51350, n_D^{20} 1.52375. Toluene (4%), *p*-xylene (0.4%), styrene, and indene may be isolated in the pure state, whilst naphthalene (6.7%), fluorene (1%), and much anthracene are isolable after repeated recrystallisation.

E. E. T.

Double Decompositions, in Aqueous Media, between Metallic Acetylides and Salts. J. F. DURAND (*Compt. rend.*, 1923, **177**, 693—695).—When calcium carbide is added to an aqueous solution of cupric or mercuric chloride, the corresponding acetylide, CuC_2 or HgC_2 , is precipitated, together with the hydroxide, etc. With silver nitrate, calcium carbide gives an explosive precipitate, presumably of the compound $\text{Ag}_2\text{C}_2\cdot\text{AgNO}_3$, whilst with normal lead acetate it gives a precipitate containing *plumbous acetylide*, PbC_2 , as a grey powder stable to air and water, and giving acetylene when treated with hydrochloric acid. From ferrous, nickelous, cobaltous, and manganous chloride solutions, calcium carbide precipitates the impure *acetylides*, FeC_2 , NiC_2 , CoC_2 , and MnC_2 , respectively. Mercuric acetylide with aqueous silver nitrate gives silver acetylide, but with cupric chloride or nitrate it gives no precipitate. With mercurous nitrate solution, mercurous acetylide is formed. Cuprous acetylide affords an explosive mixture of silver and silver acetylide with aqueous silver nitrate, and a mixture of mercury and mercurous acetylide with aqueous mercurous nitrate. Cupric acetylide with silver nitrate gives silver acetylide, and with mercurous nitrate, mercurous acetylide. Silver acetylide has no action on aqueous solutions of cupric, mercurous, or mercuric nitrates.

E. E. T.

Preparation of True Acetylene Hydrocarbons from $\beta\gamma$ -Dibromopropylene, using Sodamide: True Hexinene and cycloHexylpropinene. BOURGUEL (*Compt. rend.*, 1923, **177**, 688—690; cf. this vol., i, 429, and Lespieau, A., 1921, i, 656, etc.).—The interaction of Grignard reagents and $\beta\gamma$ -dibromopropylene gives better yields of β -bromo- Δ^α -alkylenes if the magnesium derivative is added to excess of the dibromo-compound. Magnesium ethyl and *n*-propyl bromides, respectively, gave β -bromo- Δ^α -pentene and β -bromo- Δ^α -hexene (b. p. $134^\circ/760$ mm., d^{20}_D 1.203, n^{19}_D 1.455), the latter, with sodamide, affording *n*- Δ^α -hexinene, b. p. 70 — 71° . Magnesium phenyl and magnesium cyclohexyl bromides similarly led to the preparation of β -bromo- γ -phenyl- Δ^α -propene and β -bromo- γ -cyclohexyl- Δ^α -propene, the properties of the latter now being determined accurately (b. p. 84 — $85^\circ/10$ — 11 mm., d^{20}_D 1.125, n^{20}_D 1.495), and its conversion into γ -cyclohexyl- Δ^α -propinene (b. p. $48^\circ/12$ mm. or 157° [corr.]/ 760 mm., d^{20}_D 0.836, n^{20}_D 1.459) repeated. This hydrocarbon gives a yellow precipitate with ammoniacal cuprous chloride, and a crystalline compound,



with silver nitrate.

E. E. T.

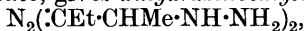
The Action of Aluminium Chloride on Trichloroethylene. FELIX KAUFLEDER (*Annalen*, 1923, **433**, 48—51).—The action of aluminium chloride on boiling trichloroethylene causes condensation, with elimination of hydrogen chloride and the formation of two isomeric *tetrachlorobutadienes*. The first has b. p. 193 — $198^\circ/720$ mm., d^{16}_D 1.622, and the second b. p. 198 — $200^\circ/720$ mm., d^{16}_D 1.634. Their chemical properties are similar. Oxygen at temperatures up to 100° has no action; zinc has no action. Chlorine

is not perceptibly taken up at 60° in the presence of sulphur or iodine, but at 110° in the presence of ferric chloride (10%) an increase in weight of 44% is observed after ten hours. The product is almost entirely hexachloroethane. W. S. N.

The Alkylglycerols. R. DELABY (*Ann. Chim.*, 1923, [ix], 20, 196—232; cf. this vol., i, 993).—The action of industrial (88%) formic acid on ethylglycerol results in the formation of a mixture of mono-, di-, and tri-formins together with unchanged alcohol. If, however, 96% acid is employed, the reaction-mixture yields *ethylglycerol triformin*, needles, m. p. 55—56°, on distillation at 155—158°/20 mm. Addition of a crystal to the mixture of formins causes crystallisation of this substance to take place; further, on heating the mixture at a temperature gradually increasing to 270° and distilling the residue at 136—140°/12 mm., the same substance is obtained. The distillate resulting from the decomposition of the mono- and di-formins contains a mixture of water, β -*ethylallyl formate*, and the formin of vinylethylcarbinol from which the alcohols may be obtained by saponification followed by careful fractionation. A suggestion as to the mechanism of formation of these alcohols and their formins by loss of water and of carbon dioxide from the three isomeric monoformins and the three possible isomeric diformins is made.

Catalytic dehydration of ethylglycerol over anhydrous magnesium sulphate leads to the formation of a complex mixture of substances, among which acraldehyde, ethyl vinyl ketone, and a furan derivative of unknown constitution were identified (cf. following abstract). The following are described: Δ^{β} -*pentene- α -ol*, (β -*ethylallyl alcohol*), b. p. 141—142° (corr.), d_4^{20} 0.8645, d_4^{15} 0.8554, n_D^{15} 1.43787; *allophanate*, crystalline powder, m. p. 157—157.5°. Δ^{β} -*Penten- α -aldehyde* (β -*ethylacraldehyde*), $\text{CHEt}\cdot\text{CH}\cdot\text{CHO}$, a mobile lachrymatory liquid, b. p. 139°, d_4^{20} 0.867, d_4^{15} 0.854, n_D^{15} 1.4387; *semicarbazone*, needles, m. p. 177—178°. H. J. E.

Catalytic Dehydration of Ethylglycerol. RAYMOND DELABY (*Compt. rend.*, 1923, 177, 690—693; cf. this vol., i, 753).—The catalytic dehydration of ethylglycerol (using anhydrous magnesium sulphate at 340—360°), which could theoretically give rise to Δ^{γ} - and Δ^{β} -pentenaldehydes, Δ^{γ} -penten- β -one, Δ^{α} -penten- γ -one (ethyl vinyl ketone), $\Delta^{\beta\gamma}$ -pentadiene- α -ol, and various compounds of lower carbon-content, actually affords a mixture of acraldehyde, furan derivatives, and ethyl vinyl ketone, the latter being detected by its behaviour towards semicarbazide (cf. Maire, A., 1908, i, 290). Thus, whilst the above pentenaldehydes and Δ^{γ} -penten- β -one give crystalline derivatives when treated with semicarbazide, the product of the above dehydration gives sparingly soluble, amorphous derivatives, characteristic of vinyl ketones. The same product, with hydrazine hydrate, gives *dihydrazinoethylvinylketazine*,



volatile, scaly crystals, m. p. 80—81°.

It is thus probable that the homologues of acraldehyde cannot

be prepared by the catalytic dehydration of the homologues of glycerol. E. E. T.

Alkyl Hypochlorites. FREDERICK DANIEL CHATTAWAY and OTTO GUIDO BACKEBERG (T., 1923, **123**, 2999—3003).

Molecular Compounds of Orthophosphoric Acid and Ethyl Ether. MARK RABINOWITSCH and SOPHIE JAKUBSOHN (*Z. anorg. Chem.*, 1923, **129**, 55—59).—The system ortho-phosphoric acid-ethyl ether was investigated between 0.0 and 17.50% ether by the method of thermal analysis. The existence of the following two compounds was indicated: $6\text{H}_3\text{PO}_4\cdot\text{OEt}_2$, m. p. 28.2° , and $4\text{H}_3\text{PO}_4\cdot\text{OEt}_2$, m. p. 30.0° . W. T.

Process for Producing Formic Acid Derivatives. BADISCHE ANILIN- & SODA-FABRIK (Brit. Pat. 203812).—Formamide is obtained by the interaction of carbon monoxide and ammonia at high pressures and temperatures exceeding 100° . In the presence of water, formamide and ammonium formate, or the latter alone, are produced. Catalysts may be employed to accelerate the reaction. [Cf. *J.S.C.I.*, 1923, Dec.] W. T. K. B.

Separation of Octoic and Decoic Acids from Coconut Oil. ERIC EVERARD WALKER (T., 1923, **123**, 2837—2839).

New Method for the Reduction of Esters. H. J. PRINS (*Rec. trav. chim.*, 1923, **42**, 1050—1052).—The ester is dissolved in ether, and saturated sodium acetate is added to form a bottom layer. The temperature is kept at about -5° and sodium and 80% acetic acid are added in sufficient quantity to keep the ether slightly acid. If allowed to become alkaline, the ester is hydrolysed, whilst an acid solution increases the evolution of gaseous hydrogen at the expense of reducing hydrogen. The reaction for 0.5 kg. lots takes from three to five days, and about 30% excess of sodium is required. It is supposed that aldehyde is first formed and then is reduced to alcohol on the surface of the metal. The yield is about 90% with aliphatic acids, but only about 50% with phenyl-acetic acid. H. H.

The Conversion of Paraformaldehyde into Glycollic Acid. DALZIEL LLEWELLYN HAMMICK and ALFRED REGINALD BOEREE (T., 1923, **123**, 2881—2882).

Acetone Compounds of α -Hydroxy-acids. RICHARD WILL-STÄTTER and FRANZ KÖNIGSBERGER (*Ber.*, 1923, **56**, [B], 2107—2109).—The ketonic compounds of α -hydroxy-acids can be obtained directly from their components under the influence of hydrogen chloride, sulphuric acid, or copper sulphate. In the series glycollic, mandelic, benzilic acids, the reactivity towards acetone and the stability of the acetone compounds increases with increasing substitution of the carbinol group.

Acetone-glycollic acid, $\begin{array}{c} \text{CH}_2\cdot\text{CO} \\ | \\ \text{O}\cdot\text{CMe}_2 \end{array} > \text{O}$, is obtained under definite conditions by the addition of concentrated sulphuric acid to a

solution of glycollic acid in acetone at -5° ; it is a colourless liquid, b. p. 41° /about 11 mm., d_4^{20} 1.0857, which is extremely readily hydrolysed by water. *Acetone-r-mandelic acid* form scolorless crystals, m. p. $47.5-48^{\circ}$, b. p. 135° /about 11 mm.; it is decomposed into mandelic acid slowly when preserved in a closed vessel, and moderately rapidly when exposed to the air of the laboratory. *Acetone-d-mandelic acid* has m. p. 73.5° , $[\alpha]_D^{18} +94.41^{\circ}$, when dissolved in ethyl acetate, whereas the *l-isomeride* has m. p. 73.5° , $[\alpha]_D^{18} -94.78^{\circ}$ in ethyl acetate solution. *Acetone-benzilic acid*, $C_{17}H_{16}O_3$, forms cubic crystals, m. p. 48° .
H. W.

Inorganic Complex Salts. III. Racemisation and the Stability of Complex Ions. WILLIAM THOMAS and RONALD FRASER (T., 1923, 123, 2973—2976).

The Dissociation of Certain Oxalato-salts. GEORGE JOSEPH BURROWS and GEORGE WALKER (T., 1923, 123, 2738—2742).

Thermal Decomposition of Ethylene Oxalate. M. TILIT-SCHÉEV (*Ber.*, 1923, 56, [B], 2218—2222).—Ethylene oxalate, $\begin{array}{c} \text{CO} \cdot \text{O} \cdot \text{CH}_2 \\ | \\ \text{CO} \cdot \text{O} \cdot \text{CH}_2 \end{array}$, m. p. $160-162^{\circ}$, b. p. about $175^{\circ}/5$ mm., is prepared from ethylene glycol and methyl oxalate. It decomposes at 241° to the extent of about 40% into ethylene and carbon dioxide, and to about 28% into ethylene carbonate and carbon monoxide. The remainder (about 24%) yields products which are very difficult to identify; it probably contains acetaldehyde in a combined form.

Glycerol and methyl oxalate yield *glyceryl oxalate*,
 $\begin{array}{c} \text{CO} \cdot \text{O} \cdot \text{CH}_2 \\ | \\ \text{CO} \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH} \end{array}$,
a hard, glassy substance, m. p. $220-225^{\circ}$ (decomp.). Allyl alcohol, carbon monoxide, and carbon dioxide are found among the products of its decomposition by heat.
H. W.

Ring-chain Tautomerism. VII. The $\alpha\beta\beta$ -Trisubstituted Glutaric Acid Type. KANTILAL CHHAGANLAL PANDYA and JOCELYN FIELD THORPE (T., 1923, 123, 2352—2865).

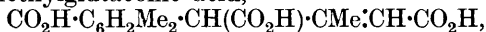
The Formation of Stable β -Lactones. LESLIE BAINS and JOCELYN FIELD THORPE (T., 1923, 123, 2742—2745).

Optical Activation of Racemic Acid by *d*-Malic Acid. ALEX. MCKENZIE, HAROLD JAMES PLENDERLEITH, and NELLIE WALKER (T., 1923, 123, 2875—2880).

A Condensation Product from Four Acetoacetic Ester Molecules, α -(4-Carboxy-3 : 5-dimethylphenyl)- β -methylglutaconic Acid. FRANZ FEIST [with ERICH EGGERT] (*Annalen*, 1923, 433, 51—64).—By the action of concentrated alkali on ethyl isodehydracetate, Anschütz, Bendix, and Kerp (A., 1891, 172) obtained two acids, having m. p., respectively, 149° and 234° . The latter has already been shown to be tribasic, and to have the formula $C_{15}H_{16}O_6$ (Feist and Beyer, A., 1906, i, 334). It is now shown to be α (4-carboxy-3 : 5-dimethylphenyl)- β -methylglutaconic acid.

The formation of this compound proceeds as follows. The lactone ring of *isodehydracetic ester* undergoes fission, and simultaneously the carboxyl group is hydrolysed, with production of the dibasic acid (I), $\text{OH}\cdot\text{CMe}\cdot\text{C}(\text{CO}_2\text{H})\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{H}$; the latter readily loses carbon dioxide (Hantzsch, A., 1883, 1083), giving the monobasic acid (II), $\text{OH}\cdot\text{CMe}\cdot\text{C}(\text{CO}_2\text{H})\cdot\text{CMe}\cdot\text{CH}_2$. Condensation, analogous to the formation of mesityl oxide, now occurs between the methyl group of the acetyl radicle of the acid (I) (keto-form), and the hydroxyl group of the acid (II), a molecule of water being eliminated. A second molecule of water is then lost from the enolic form of the resulting tribasic acid (III),

$\text{CH}_2\cdot\text{CMe}\cdot\text{C}(\text{CO}_2\text{H})\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{H}$, with production of a benzene ring. The product is a substituted α -phenyl- β -methylglutaconic acid,

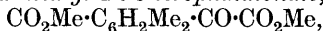


which now, owing to the tendency for the double bond to become conjugated with the phenyl group, undergoes isomerisation to

the acid, $\text{CO}_2\text{H}-\text{C}_6\text{H}(\text{Me})_2-\text{C}(\text{CO}_2\text{H})\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, which is the

“ Anschütz ” acid, m. p. 234°.

This structure is clearly demonstrated by oxidising the trimethyl ester of the acid by means of ozone. Decomposition of the heavy, yellow, oily *ozonide* by means of water gives methyl acetoacetate and *dimethyl 2 : 6-dimethyl-1 : 5-terephthalonate*,



long needles, m. p. 52°, *p-nitrophenylhydrazone*, pale yellow needles, m. p. 166°, *semicarbazone*, glistening prisms and leaflets, m. p. 183—184°. When treated in benzene solution with concentrated sulphuric acid, this ketonic ester gives a deep red coloration, which soon becomes violet. On addition of water, the benzene layer becomes carmine-red. Hydrolysis of the dimethyl ester by means of methyl-alcoholic potassium hydroxide leaves the carbomethoxyl group attached to the benzene nucleus intact. The resulting *monomethyl ester*, $\text{CO}_2\text{Me}\cdot\text{C}_6\text{H}_2\text{Me}_2\cdot\text{CO}\cdot\text{CO}_2\text{H}$, has m. p. 108—109°, or $+\text{H}_2\text{O}$, m. p. 78°, *p-nitrophenylhydrazone*, sinters at 180°; decomp. 210°. Treatment of the free acid, m. p. 234°, with ozone, and decomposition of the ozonide by means of water, give acetone, acetic acid, and 2 : 6-dimethylterephthalic acid; the latter is also produced if potassium permanganate is used for the oxidation. Its calcium salt crystallises with $8\text{H}_2\text{O}$ (cf. Jannasch and Weiler, A., 1895, i, 288). The action of boiling methyl sulphate, under somewhat reduced pressure, on the sodium salt of the known methyl hydrogen dimethylterephthalate (Noyes, A., 1899, i, 284) gives the *dimethyl ester*, leaflets, m. p. 73°, b. p. 165—167°/14 mm., hydrolysis of which by means of aqueous alkali gives the isomeric monomethyl ester, 4-carbomethoxy-3 : 5-dimethylbenzoic acid, long needles, m. p. 154°.

In the preparation of Anschütz's acids, $\beta\beta$ -dimethylacrylic acid and a *monoethyl ester* of the acid, m. p. 234°, are also formed (Feist

and Beyer, *loc. cit.*). The acid ester is an asbestos-like mass, $+H_2O$, m. p. 175° , and forms insoluble *ferric* (brown), *chromium* (green), *lead*, *tin*, and *silver* salts. Conversion of the tribasic acid into its trimethyl ester is most readily accomplished by heating the sodium salt with methyl sulphate under somewhat reduced pressure. The action of 3% methyl-alcoholic hydrogen chloride leads gradually to the formation of a *monomethyl* ester, which has m. p. 171° , but resolidifies on further heating, and then has m. p. 228° . By still more prolonged action of an excess of alcoholic acid, a substance, rods, m. p. $139-140^\circ$, presumably a *dimethyl* ester, is produced.

W. S. N.

Experiments on the Synthesis of the Polyacetic Acids of Methane. VIII. An Improved Synthesis of Methanetriacetic Acid. MARCEL HENRY DREIFUSS and CHRISTOPHER KELK INGOLD (T., 1923, 123, 2964—2967).

The Interaction of $\beta\beta'$ -Dichlorodiethyl Sulphide, Sulphoxide, and Sulphone with Glycine Ester and with Potassium Phthalimide. ALBERT ERIC CASHMORE and HAMILTON MCCOMBIE (T., 1923, 123, 2884—2890).

Oxidation of Hydrocarbons to Formaldehyde. R. SCHÖNFELDER (*Ber. Ges. Kohlentechnik*, 1923, [iv], 247—263; from *Chem. Zentr.*, 1923, [iv], 206—207).—When methane is passed with steam and air over copper or silver heated at 500° , 55 to 58% is oxidised to formaldehyde, 25—40% is unattacked, whilst 10—20% is burnt to carbon monoxide, carbon dioxide, and water. By the use of different catalysts, or activated carbon, or by silent electrical discharge, a certain amount of formaldehyde can always be obtained from methane and air. Better yields are obtained using unsaturated gaseous hydrocarbons.

G. W. R.

The Oxidation of Hydrocarbons, with Special Reference to the Production of Formaldehyde. IV. Some Further Experiments on the Action of Oxygen on Ethylene. E. W. BLAIR and T. SHERLOCK WHEELER (*J. Soc. Chem. Ind.*, 1923, 42, 415—417t).—The authors' experiments on the oxidation of ethylene (A., 1922, i, 917) have been repeated by an improved method and the former results were confirmed. The amount of interaction occurring depends more on the concentration of the interacting gases than in the case of methane; this may be due to the fact that in the ethylene experiments the reaction was less a surface effect than in the methane experiments. A large excess of oxygen, even at 560° , retards the oxidation so much that about 50% of the ethylene consumed appears as acetaldehyde and a further 29% as formaldehyde. The arguments for and against the view that acetaldehyde is an intermediate product in the production of formaldehyde are considered. Possibly in slow oxidations acetaldehyde is difficult to oxidise, and when it does at length oxidise it breaks down to carbon monoxide or carbon dioxide and water. The reason why formaldehyde is oxidised to formic acid rather than decomposed into carbon monoxide and hydrogen may be that

the latter process is endothermic. The ethylene \rightarrow acetaldehyde \rightarrow formaldehyde sequence is sound thermochemically.

E. H. R.

Kinetic Investigation of the Oxidation of Acetaldehyde by Means of Hydrogen Peroxide, which can be regarded as a Partial Autoxidation Reaction. L. REINER (*Z. anorg. Chem.*, 1923, 127, 187—204).—Pure acetaldehyde is oxidised only very slowly by hydrogen peroxide, but the reaction is autocatalysed by the acetic acid formed. It is found, however, that this explanation of the reaction by autocatalysis is not entirely satisfactory, and it is suggested that it is not the aldehyde, but rather the acetic acid, which forms a compound with the hydrogen peroxide present, and that this complex decomposes with relative slowness. H. H.

The Grignard Synthesis of Aldehydes. CHARLES EDMUND WOOD and MERVYN ARTHUR COMLEY (*J. Soc. Chem. Ind.*, 1923, 42, 429—432r).—The preparation of a number of aldehydes, including propaldehyde, *n*-butaldehyde, cyclohexanecarbaldehyde, phenylacetaldehyde and benzaldehyde, from Grignard compounds and ethyl orthoformate are described in detail. To obtain good yields, it is necessary to heat the reaction mixture for some time under a reflux condenser, and it does not seem possible to replace more than one ethoxyl group in the orthoformate by aryl or alkyl groups. After part of the ether has been distilled off, the product is treated with ice-water and the ethereal acetal layer is separated. The acetal is then hydrolysed with 5*N*-sulphuric or hydrochloric acid, preferably in stages, as prolonged heating of the aldehyde with acid causes polymerisation. The aldehyde is removed at the end of each stage with sodium hydrogen sulphite, and the unchanged acetal recovered and treated again with acid. In this manner, high yields of the aldehydes are obtained. A method is described by which a 54% yield of ethyl orthoformate can be obtained by adding sodium and chloroform portion-wise to boiling absolute alcohol. E. H. R.

Action of Sodamide on the Chloro-compounds resulting from the Action of Phosphorus Pentachloride on Aldehydes and Ketones. BOURGUEL (*Compt. rend.*, 1923, 177, 823—825).—The conversion of alkylidene dichlorides into single acetylenic hydrocarbons is difficult to effect, using alcoholic or solid potassium hydroxide. Thus, $\beta\beta$ -dichloropentane (from methyl *n*-propyl ketone), with these reagents, affords a mixture of pentinenes boiling at 45—55°, whereas the two possible individual pentinenes boil, respectively, at 40° and 55°. Similarly, $\beta\beta$ -dichlorohexane gives a mixture of hexinenes, b. p. 80—85°, whereas the individuals present boil at 70° and 83°, respectively. When, however, a dichloro-derivative, dissolved in toluene or xylene, and heated at 100—130°, is treated with sodamide, a 60% yield of the pure normal acetylenic hydrocarbon results.

n-Heptaldehyde gives with phosphorus pentachloride a mixture

of $\alpha\alpha$ -dichloroheptane and α -chloro- Δ^{α} -heptene, which are readily separated. Either compound, on treatment with sodamide, affords *n*-heptinene, b. p. 99—100.5°. Methyl *n*-propyl ketone, on treatment with phosphorus pentachloride, gives a mixture (separable by distillation under diminished pressure, keeping the temperature below 45°), of (1) β -chloro- Δ^{α} -pentene (b. p. 88—89°/760 mm., d^{24}_{20} 0.903, n^{24}_{D} 1.421; formed, presumably, not by loss of hydrogen chloride from the dichloro-compound, but by the action of phosphorus pentachloride on the enol, $\text{OH}\cdot\text{CPr}^{\alpha}\cdot\text{CH}_2$) and (2) $\beta\beta$ -dichloro-pentane, b. p. 36—37°/20 mm., or 128—129°/760 mm., d^{20}_{20} 1.040, n^{20}_{D} 1.434. This substance reacts readily with sodamide, first giving the chloropentene (which reacts less readily with sodamide) and finally pure *n*-pentinene. E. E. T.

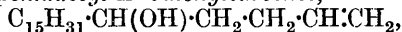
γ -Hydroxyaldehydes. V. Ketocyclic Desmotropy in the Case of γ -Hydroxy-*n*-novadecaldehyde. BURCKHARDT HELFERICH and HANS KÖSTER (*Ber.*, 1923, 56, [B], 2088—2094).—The term ketocyclic desmotropy is applied to the desmotropy between an open and a cyclic form, such as has been assumed in the case of the reducing sugars and established for γ - and δ -hydroxyaldehydes (cf. A., 1920, i, 11; 1922, i, 431). The isolation of the individual desmotropes has not hitherto been possible. Attempts are now described to prepare crystalline compounds of this type. It is shown that a case of desmotropy between two or several forms is presented by γ -hydroxynonadecaldehyde; one of these, possibly one of the two cyclic racemic varieties which are possible by reason of the presence of two dissimilarly situated, asymmetric carbon atoms, has been isolated in the homogeneous condition. Also a diol has been prepared in good yield from solutions of the aldehyde the formation of which can be ascribed only to the presence of the aldehydic variety.

The gradual addition of palmityl chloride to a solution of ethyl sodioacetoacetate in ice-cold, absolute alcohol leads to the formation of *ethyl palmitylacetoacetate*, $\text{COMe}\cdot\text{CH}(\text{CO}\cdot\text{C}_{15}\text{H}_{31})\cdot\text{CO}_2\text{Et}$, m. p. 36—36.5° (the *sodio*-derivative is described). It is converted by cautious hydrolysis with water into *ethyl palmitylacetate*, m. p. 37—38° rising to m. p. 41° after long preservation; the *copper* salt, $\text{C}_{40}\text{H}_{74}\text{O}_5\text{Cu}$, crystallises in pale green needles, m. p. 111°. The constitution of the ester is established by its hydrolysis with aqueous sodium hydroxide solution to methyl pentadecyl ketone, m. p. 48° (semicarbazone, m. p. 127°). Ethyl palmitylacetate is transformed by phenylhydrazine hydrochloride in the presence of a few drops of concentrated hydrochloric acid at 150—160° into 1-phenyl-3-pentadecylpyrazol-5-one, $\text{NPh}\cdot\text{C}(\text{CO}\cdot\text{CH}_2)\cdot\text{C}_{15}\text{H}_{31}$, m. p. 75°,

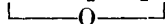
which gives an orange-coloured, crystalline precipitate with nitrous acid and a blue dye with ferric chloride; it is converted by methyl iodide in the presence of methyl alcohol at 100—120° into 1-phenyl-2-methyl-3-pentadecylpyrazol-5-one, needles, m. p. 66°, which yields pale green needles with nitrous acid. When free phenylhydrazine reacts with ethyl palmityl acetate, the compound (?) 4:4'-bis-
t*

1-phenyl-2-pentadecylpyrazol-5-one, colourless crystals, m. p. 238°, is also produced.

The introduction of the allyl group into ethyl palmitylacetoacetate cannot be conveniently effected. On the other hand, palmityl chloride and ethyl sodioallylacetate give ethyl palmitylallylacetate which, without being completely purified, is hydrolysed by aqueous-alcoholic potassium hydroxide solution to palmityl Δ^7 -butenyl ketone, $C_{15}H_{31} \cdot CO \cdot CH_2 \cdot CH_2 \cdot CH : CH_2$, m. p. 52° (semicarbazone, m. p. 80°). The ketone is converted by ozone in glacial acetic acid solution and subsequent reduction of the ozonide and peroxide with zinc dust into γ -keto-n-nonadecaldehyde, $C_{15}H_{31} \cdot CO \cdot CH_2 \cdot CH_2 \cdot CHO$, m. p. 60–65°; it is reduced by sodium and alcohol to pentadecyl- Δ^7 -butenylcarbinol,



m. p. 50°. Ozonisation of the carbinol leads to the production of γ -hydroxynonadecaldehyde, $C_{15}H_{31} \cdot CH \cdot CH_2 \cdot CH_2 \cdot CH(OH)$, or



$C_{15}H_{31} \cdot CH(OH) \cdot CH_2 \cdot CH_2 \cdot CHO$, which, after being purified by distillation under greatly diminished pressure (b. p. 169–173°/0.06 mm.), has m. p. 37°, rising to m. p. 48° in fourteen days; d_4^{20} 0.86986, n_D^{20} 1.4497. When allowed to crystallise slowly from xylene at the atmospheric temperature, it gives flattened prisms, m. p. 64°, whereas the material obtained from the mother-liquor has m. p. (indefinite) 30–40° and 40–49°. A solution of γ -hydroxynonadecaldehyde in ether is transformed by magnesium ethyl bromide into the corresponding diol, $C_{21}H_{44}O_2$, m. p. 95°, which is characterised further by conversion into the diacetate, $C_{25}H_{48}O_4$, m. p. 48°. H. W.

Two Methyl Derivatives of Acetone [*iso*Propylidene] Xylose.

OLAV SVANBERG (*Ber.*, 1923, 56, [B], 2195–2199).—In the preparation of xylose diisopropylidene ether, the neutralisation of the sulphuric acid used as condensing agent is conveniently effected by a slight excess of concentrated sodium hydroxide solution (cf. Freudenberg and Ivers, A., 1922, i, 523). The monoisopropylidene compound is obtained as described previously (this vol., i, 540). It is methylated by silver oxide and methyl iodide in the presence of anhydrous acetone, and the products are separated from one another by fractional distillation in a high vacuum. Monomethylisopropylidene xylose, $C_9H_{16}O_5$, crystallises in needles, m. p. 78°, b. p. 105–107°/0.5 mm., $[\alpha]_{D}^{18}$ yellow -21.4° in aqueous solution. It is converted by hydrolysis with dilute acids into a dextrorotatory sugar which has $[\alpha]_{D}^{18}$ yellow $+41.95^\circ$ (equilibrium value). Dimethylisopropylidene xylose, $C_{10}H_{18}O_5$, is a mobile, highly refractive liquid, b. p. 78–80°/0.5 mm., $[\alpha]_{D}^{18}$ yellow -43.3° when dissolved in water. The corresponding dimethyl-xylose has $[\alpha]_{D}^{18}$ yellow $+24^\circ$; it could not be caused to crystallise. When treated with phenylhydrazine in dilute acetic acid solution, it gives distinct evidence of the formation of an osazone, thus showing that the *iso*propylidene group of monoisopropylidene xylose is probably present in the $\alpha\beta$ -position; unfortunately, it could only be caused to

crystallise with great difficulty, and is so readily oxidised on exposure to air that an analysis could not be made. The methylated *isopropylidene xyloses* are oxidised about equally readily by dilute, alkaline permanganate with disappearance of the phloroglucinol reaction and production of large quantities of oxalic acid. It is therefore probable that the primary alcoholic group in position 5 is substituted, which is necessarily the case with the dimethyl derivative. The monomethyl compound is probably ϵ -methyl- $\alpha\beta$ -*isopropylidene xylose*. H. W.

Acetone Sugars. IV. Experiments with Galactose and Mannose. KARL FREUDENBERG and RALPH M. HIXON (*Ber.*, 1923, **56**, [B], 2119—2127; cf. Freudenberg and Doser, this vol., i, 652).—The series of reactions by which it has been shown that the hydroxyl group in position 3 is unsubstituted in the diacetone compounds [*diisopropylidene ethers*] of dextrose and *lævulose* has been applied to galactose and mannose; in these cases, however, the reactions occur in a different manner, which does not throw any light on the constitution of the sugar derivatives.

Galactose is converted by acetone in the presence of hydrogen chloride or sulphuric acid (cf. Svanberg and Sjöberg, this vol., i, 540) into *diacetone galactose* [*galactose diisopropylidene ether*], a colourless, very viscous liquid, b. p. 131—139°/0.2—0.5 mm., $[\alpha]_{\text{H}_2\text{O}}^{\text{yellow}} -60.9^\circ$ when dissolved in *s*-tetrachloroethane. It is transformed by toluene-*p*-sulphonyl chloride in the presence of pyridine into *toluene-p-sulphonyl* derivative, m. p. 91—92°, $[\alpha]_{\text{H}_2\text{O}}^{\text{yellow}} -64.7^\circ$ in *s*-tetrachloroethane. The compound reacts very readily with hydrazine, but the primary hydrazide could not be caused to crystallise, and gave only uninviting condensation products with benzaldehyde, *m*-nitrobenzaldehyde, piperonal, or acetone; it condenses, however, readily with phenylcarbimide to yield the *dianilide of diisopropylidenegalactosylhydrazinedicarboxylic acid*, $\text{C}_{12}\text{H}_{19}\text{O}_5\cdot\text{N}(\text{CO}\cdot\text{NHPh})\cdot\text{NH}(\text{CO}\cdot\text{NHPh})$, needles, m. p. 227° (decomp.). The primary hydrazine is accompanied by *as-di-diisopropylidenegalactosylhydrazine*, $(\text{C}_{12}\text{H}_{19}\text{O}_5)_2\text{N}\cdot\text{NH}_2$, needles, m. p. 129—130°, $[\alpha]_{\text{H}_2\text{O}}^{\text{yellow}} -77^\circ$ when dissolved in *s*-tetrachloroethane, which is oxidised by powdered potassium permanganate in the presence of anhydrous acetone to *tetradisopropylidenegalactosyltetrazen*,

$(\text{C}_{12}\text{H}_{19}\text{O}_5)_2\text{N}\cdot\text{N}\cdot\text{N}(\text{C}_{12}\text{H}_{19}\text{O}_5)_2$,
m. p. 103—104°, $[\alpha]_{\text{H}_2\text{O}}^{\text{yellow}} -76.3^\circ$ in *s*-tetrachloroethane.

Diacetonemannose [*mannose diisopropylidene ether*], needles, m. p. 118°, $[\alpha]_{\text{H}_2\text{O}}^{\text{yellow}} +14.3^\circ$ when dissolved in *s*-tetrachloroethane, is prepared in 84—90% yield from mannose and acetone containing 1% of hydrogen chloride. Its conversion into the toluene-*p*-sulphonyl derivative could not be satisfactorily effected. The substances react readily in the presence of pyridine, but the derivatives appear to react immediately with the solvent to form a quaternary ammonium salt. Interaction also takes place easily between sodium diacetone mannose and toluene-*p*-sulphonyl chloride in the presence of light petroleum, but the product is amorphous.

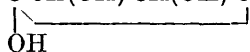
The *diisopropylidene ethers* of dextrose, galactose, mannose, and

lævulose are readily methylated by the action of methyl iodide on their sodium derivatives, which are readily formed when the parent compounds are treated with sodium in the presence of an indifferent solvent. They are more freely soluble than the parent sugars in light petroleum, ether, or benzene. They are decomposed by exposure to air or by sodium hydrogen carbonate. They remain as pale yellow, resinous masses when the solvent is removed. Previous to methylation, the solvent is removed under diminished pressure, and the residue is then treated with methyl iodide at 30–40°. *Diisopropylidene-methyl-galactose* is a very viscous liquid, b. p. 109–115°/0.2–0.5 mm., $[\alpha]_{D}^{19}$ yellow –63.2° in *s*-tetrachloroethane. *Diisopropylidene-methyl-mannose* has m. p. 37°, b. p. 118–124°/0.2–0.5 mm., $[\alpha]_{D}^{19}$ yellow –41.0° when dissolved in *s*-tetrachloroethane. 3-Methyl-dextrose and 3-methyl-fructose are obtained by the hydrolysis of the corresponding diacetone compounds with dilute sulphuric acid (cf. Irvine and Hogg, T., 1913, 103, 573); under similar conditions, *diisopropylidene-methyl-mannose* unexpectedly yields mannose. H. W.

The Behaviour of the More Important Carbohydrates (Dextrose, Galactose, Lævulose, Mannose, Maltose, Lactose, Sucrose) in Strong Acid, Alkali, Sulphite, and Hydrogen Sulphite Solutions. III. The Action of Alkalis on the Carbohydrates; the Action of Sodium Sulphite on the Carbohydrates, especially on Dextrose; the Action of Sodium Hydrogen Sulphite on the Carbohydrates. B. BLEYER and H. SCHMIDT (*Biochem. Z.*, 1923, 141, 278–296).—In the presence of alkali, dextrose, galactose, and lactose show primary and secondary rotational changes similar to those observed in acid solution (this vol., ii, 524), with the difference that increasing hydroxyl concentration shifts the equilibrium towards the β -form as shown by the lowering of specific rotation, whilst increasing hydrogen-ion concentration is shown to favour the α -modification (*loc. cit.*). The secondary changes in rotation produced by alkali are due to isomerisation and break down of the sugar into saccharins and trioses, whereas the corresponding changes produced by acid were ascribed to the synthesis of di- and poly-saccharides. It is postulated that sugar synthesis occurs by way of the α -form, and break-down through the β -form, with the intermediate formation of a reactive " γ -form,"

$$-C\cdot CH(OH)\cdot CH(OH)\cdot CH\cdot OH$$

to which the four carbon ring structure



is ascribed.

Dextrose solutions, when boiled with sodium sulphite for twenty minutes, become coloured and practically inactive, but on being neutralised the colour disappears and the solution becomes lævorotatory. From the decolorised and slightly acid solution, lævulose-phenylmethylsazone (m. p. 158°) was obtained. The increasing lævorotation in acid solution is due to the formation of relatively inactive bisulphite compounds by the aldehydic degradation products and by dextrose and mannose. Lævulose does not form such

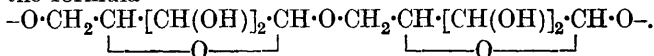
compounds, and its lævorotation therefore becomes more apparent. The author regards the aldehydic form of the reducing carbohydrates as participating in the state of equilibrium in aqueous solution, and from observations of the effect of sodium hydrogen sulphite in lowering the specific rotations of dextrose, galactose, and lactose, it is shown that this reagent displaces the equilibrium towards the aldehyde form. The behaviour of mannose in bisulphite solution is exceptional; it shows an initial lævorotation changing to a dextrorotation which is close to the normal specific equilibrium rotation in water.

J. P.

Sources of the Rare Sugars (Melibiose). T. SWANN HARDING (*Sugar*, 1923, 25, 514—516).—If in the method of preparing melibiose elaborated by Hudson and Harding (A., 1916, i, 120) glacial acetic acid be used for the final crystallisation in place of alcohol, the yield is improved and crystallisation occurs rapidly and certainly. After washing the sugar mass with alcohol, it is dried for twenty-four hours in a vacuum at room temperature, ground to a fine powder, and re-dried in a vacuum while the temperature is gradually raised to 120°. Previous work on the preparation of this disaccharide is reviewed.

J. P. O.

Constitution of Polysaccharides. II. Constitution of Xylan. S. KOMATSU, TETSUJI INOUE, and RISABURO NAKAI (*Mem. Coll. Sci. Kyoto Imp. Univ.*, 1923, 7, 25—30; cf. Heuser and Ruppel, A., 1922, i, 810).—Xylan from wheat straw was partly methylated, using methyl sulphate and sodium hydroxide, that from rice straw being methylated in the same manner, supplementing this methylation by treatment with silver oxide and methyl iodide. The dimethylxylan softened at 50—60°, and had $[\alpha]_D^{20} +30.45^\circ$ in chloroform. Hydrolysis with 5% hydrochloric acid converted it into a *dimethylxylose*, which, on oxidation with dilute nitric acid, gave $\alpha\beta$ -dimethoxyglutaric acid ($[\alpha]_D +132^\circ$ in alcohol). The dimethylxylose is therefore the $\beta\gamma$ -derivative and xylan must have the formula



E. E. T.

A Sulphuric Acid Ester of Starch. R. TAMBA (*Biochem. Z.*, 1923, 141, 274—277).—By the action on starch of a mixture of chlorosulphonic acid and chloroform in dry pyridine an *amylodisulphuric* acid was obtained, which by the action of alcoholic potassium hydroxide was converted into, and isolated as, the *potassium* salt, $C_6H_8O_5(SO_3)_2K_2\cdot 2\frac{1}{2}H_2O$. The product had no reducing action until hydrolysed by hot acids, and did not give a blue colour with iodine after complete removal of traces of unchanged starch. It had $[\alpha]_D^{19} +134.5^\circ$ ($c=0.766$).

J. P.

Fatty Acid Esters of Polymeric Carbohydrates. P. KARRER and ZORKA ZEGA (*Helv. Chim. Acta*, 1923, 6, 822—826).—In a previous paper (this vol., i, 276), cellulose hexapalmitate was described. A number of other cellulose and starch esters of fatty

acids have now been prepared by the action of the fatty acid chlorides on the carbohydrates in quinoline solution. *Cellulose hexastearate*, $C_{12}H_{14}O_{10}(CO \cdot C_{17}H_{35})_6$, forms a slightly yellow powder with no definite melting point ($83-118^\circ$); $[\alpha]_D^{18} -0.79^\circ$. *Starch hexapalmitate*, $C_{12}H_{14}O_{10}(CO \cdot C_{15}H_{31})_6$, sinters at 54° and melts completely at 75° ; $[\alpha]_D^{15} +53.54^\circ$. *Starch hexastearate*,

$C_{12}H_{14}O_{10}(CO \cdot C_{17}H_{35})_6$, sinters at 69° and is completely melted at 86° ; $[\alpha]_D^{18} +49.38^\circ$. Inulin condenses with palmityl chloride, giving an amorphous *inulin palmitate*, probably the compound, $C_6H_7O_5(CO \cdot C_{15}H_{31})_3$, sintering at 45° , m. p. 52.5° . *Inulin stearate* melts between 60° and 63° .

E. H. R.

Polysaccharides. XXI. Lichenin. II. P. KARRER, B. JOOS, and M. STAUB (*Helv. Chim. Acta*, 1923, 6, 800—816).—The close chemical similarity between lichenin and cotton cellulose has already been pointed out (this vol., i, 541). The further study of lichenin has now been facilitated by its preparation in a dry but completely soluble form. The damp lichenin obtained by extraction of Iceland moss with boiling water is soaked twice for twelve hours in 96% alcohol and then for two days in absolute ether. It is then collected on a filter and dried very slowly in a vacuum desiccator. It is thus obtained as a loose, white mass, which is easily powdered and dissolves to a clear colloidal solution in boiling water. The acetolysis of lichenin by the acetic anhydride-sulphuric acid mixture goes much more slowly than that of cotton-cellulose, either in the hot or cold, and the yield of octa-acetyl-cellobiose is much smaller from lichenin. The soluble lichenin is, however, much more readily attacked than the ordinary sparingly soluble form. It is not considered that the different behaviour of lichenin and cotton-cellulose denotes any essential constitutional difference; it is more probably due to different degrees of dispersity between substances having slightly different chemical constitutions. The points of resemblance between the two substances are tabulated.

The enzyme or mixture of enzymes present in the alimentary canal of the edible snail ferments soluble lichenin to dextrose completely in a few hours. Provisionally the enzyme is called snail *lichenase*. The optimum acidity for the fermentation is p_H 5.2, and the reaction proceeds for about 40% of its course unimolecularly; for the rest, the substrate attacked is proportional to the square root of the time. Sparingly soluble lichenin is attacked vigorously at first, but soon the rate falls off and becomes extremely slow. Cotton-cellulose is attacked to some extent, but sparingly and incompletely on account of its insolubility. The fermentation obviously depends on the dispersity of the substrate; the unimolecular portion of the soluble lichenin fermentation probably ends with the disappearance of the most highly disperse particles. In the case of a pure lichenase, the amount of hydrolysis is proportional to the square root of the concentration of the enzyme. This relation affords a means of comparing enzyme

preparations of different strengths and of standardising the preparations.

E. H. R.

Lignin. P. KARRER and B. BODDING-WIGER (*Helv. Chim. Acta*, 1923, **6**, 817—822; cf. A., 1921, i, 771).—Whilst air-dried beech, fir, or oak saw-dust dissolves readily in acetyl bromide, the vacuum-dried material is much less readily attacked. The lignin derivative, which can also be obtained from lignin itself, contains from 10—18% of bromine, 26—28% of acetyl, and about 7—8% of methoxyl. The reaction with acetyl bromide may be applied to the study of the composition and genesis of peats, of which the peatified portion is unattacked. Peats from different sources gave from 19—33% of residue when treated with acetyl bromide, and the residue contained from 1.34—3.51% of methoxyl. By distilling lignin with zinc dust, a viscous oil was obtained which, on redistillation at 2 mm. pressure, gave fractions boiling between 66° and 280°. The fractions all contained methoxyl (about 3%) and other oxygen, probably contained in furan rings, up to about 8%. The oxygen content of the oil was smaller when the original distillation was carried out at a higher temperature. From some of the fractions a small quantity of crystals separated from which were obtained a *hydrocarbon*, $(C_6H_5)_n$, m. p. 210—212°, yellow needles with a greenish-blue fluorescence. It is probably a polynuclear aromatic compound, partly hydrogenated.

E. H. R.

Pentosans in Lignin. EMIL HEUSER (*Cellulosechemie*, 1923, **4**, 77—78).—Referring to the observations by Hägglund (this vol., i, 1066) of the presence of small quantities of pentosan in preparations of lignin obtained by the hydrolysis of pinewood by highly concentrated hydrochloric acid, the author points out that the quantity of residual pentosan in such preparations is very variable and frequently amounts to mere traces or even nothing. Such residues are to be regarded simply as impurities remaining from the incomplete action of the cold concentrated mineral acid, and their presence is not to be accepted as evidence in favour of a constitutional union of the lignin and pentosan groups.

J. F. B.

Bacterial Degradation of Lignin Acids. HANS PRINGSHEIM and WALTER FUCHS (*Ber.*, 1923, **56**, [B], 2095—2097).—The lignin acids are prepared by treatment of pine sawdust with sodium hydroxide solution (5%) under pressure; the clear filtrate is acidified with hydrochloric acid. The precipitate is washed repeatedly with water until free from chlorides; after desiccation it constitutes a pale yellow, amorphous powder which is almost insoluble in water or alcohol, but very readily soluble in ammonia. The aqueous solution of the ammonium salt is treated at 37° in the presence of ammonium sulphate, potassium phosphate, magnesium sulphate, and chalk with a bacterial culture derived from forest earth. The product of the change differs from the original material in containing up to half its weight of substances soluble in alcohol. The recovered acid, in particular the part which is

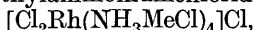
soluble in alcohol, has lost part of its methoxyl content under the influence of the bacteria, and the soluble portion is appreciably richer in carbon than the original material. The initial acids contain about 6% of pentosans, which are possibly not an integral component of lignin; they are almost completely removed by bacterial degradation, but this is certainly not the main change.

H. W.

The Chlorides of Rhodium. A. GUTBIER and H. BERTSCH (*Z. anorg. Chem.*, 1923, **129**, 67—82).—The following twenty-four new complex salts of rhodium chloride and organic ammonium chlorides were prepared. A. *Hexachlororhodiates* of the general formula $[\text{Rh}(\text{Cl}_6)](\text{NR}_4)_3$; dimethylammonium, red, monoclinic; trimethylammonium, transparent, reddish-brown; ethylammonium, garnet; diethylammonium, garnet; triethylammonium, dark red, monoclinic; *n*-propylammonium, carmine; isopropylammonium, garnet; dipropylammonium, dark red; tripropylammonium, carmine, monoclinic; *n*-butylammonium, light red; isobutylammonium, carmine; diisobutylammonium, light red, monoclinic; guanidinium, carmine, monoclinic; propylenediammonium, carmine; pyridinium, orange-red, monoclinic; β -picolinium, orange-red; lutidinium, orange-red; collidinium, red, monoclinic; quinolinium, red, monoclinic; isoquinolinium, dark red, monoclinic.

B. Tetramethylammoniumtrichlorohexachlorodirhodate, brown, hexagonal, and the tetraethyl derivative, reddish-brown, monoclinic; these two have the formulæ $[\text{Rh}_2\text{Cl}_9](\text{NR}_4)_3$.

C. Dichlorotetra-methylammoniumchloride-rhodichloride,



dark red, hexagonal. Dichlorodi-ethylenediammonium chloride-rhodichloride, $[\text{Cl}_2\text{Rh}(\text{C}_2\text{H}_4\text{N}_2\text{H}_6\text{Cl}_2)_2]\text{Cl}$, brick-red, tetragonal. Details of preparation of the above compounds and of rhodium chlorides are given, as well as methods for the recovery of rhodium from the residues.

W. T.

The Halogen Salts of Ruthenium. A. GUTBIER (*Z. anorg. Chem.*, 1923, **129**, 83—88).—The following compounds were prepared: propylenediammonium- μ -dichloro-octachloro-diruthenate, $[\text{Ru}_2\text{Cl}_{10}](\text{C}_3\text{H}_6\text{N}_2\text{H}_6)_2$, dark red; the α -picolinium salt, black needles; isoquinolinium salt, dark red needles and plates; the corresponding bromides of ethylenediammonium, black needles;

propylenediammonium black; α -picolinium, black; isoquinolinium, black. isoQuinoliniumhexachlororuthenate, $[\text{RuCl}_6](\text{C}_9\text{H}_7\text{NH})_2$, dark green; the corresponding triethylammonium bromide, dark blue plates; isoquinolinium bromide, dark blue. The annexed formula is given for the complex diruthenate anion.

W. T.

A New Type of Halogen Salts of Gold. A. GUTBIER (*Z. anorg. Chem.*, 1923, **129**, 89—92).—The following complex salts were prepared: dichlorodi-ethylenediammonium-dichloroauric chloride, $[\text{Cl}_2\text{Au}(\text{C}_2\text{H}_4\text{N}_2\text{H}_6\text{Cl}_2)_2]\text{Cl}$, yellow powder; the propylene-

diammonium salt, yellow powder; and the corresponding bromides, which were red. They were prepared from the tetra-chloro- and -bromo-auric acids, in the presence of the halogen hydride excess of the auric acid being avoided.

W. T.

Compound of Hexamethylenetetramine with Trichloroacetic Acid. L. DEBUCQUET (*J. Pharm. Chim.*, 1923, [vii], 28, 263—264).—When cold solutions of equimolecular quantities of hexamethylenetetramine and trichloroacetic acid in 95% ethyl alcohol are mixed, a voluminous, flocculent precipitate is formed which appears, after two days, as a lustrous, white, microcrystalline powder. The compound, which has no definite melting point, dissolves readily in water, and is soluble in ten times its weight of 95% ethyl alcohol, but is less soluble in chloroform, and almost insoluble in dry ether. The aqueous solution reacts acid towards litmus, and gives, with a 10% solution of silver nitrate, a voluminous precipitate soluble in nitric acid and in excess of ammonia.

W. T. K. B.

$\beta\gamma$ -Diaminopropanol and its Derivatives. ERNST PHILIPPI and REINHARD SEKA (*Annalen*, 1923, 433, 88—95).—Gabriel's method for the synthesis of $\beta\gamma$ -diaminopropyl alcohol (A., 1889, 486) has been revised and modified.

[With LEO ABLEIDINGER].— $\beta\gamma$ -Diphthalimidopropyl acetate, needles, m. p. 195°, is obtained by fusing a mixture of dibromopropyl acetate and potassium phthalimide at 170—175°; it is hydrolysed by means of hydrobromic acid (*d* 1.49) to $\beta\gamma$ -diaminopropyl alcohol dihydrobromide. $\beta\gamma$ -Diphthalimidopropyl alcohol, long, white needles, m. p. 207°, is prepared by heating a mixture of dibromopropyl alcohol and potassium phthalimide at 120—130°. The action of phosphorus pentachloride on diphthalimidopropyl alcohol in boiling benzene solution gives $\beta\gamma$ -diphthalimidopropyl chloride, white needles, m. p. 215—216°, which is hydrolysed by means of fuming hydrochloric acid at 170—180° to give $\beta\gamma$ -diaminopropyl chloride dihydrochloride, m. p. 218—219°, after softening with decomposition; the corresponding dichloroplatinate chars above 250°. $\beta\gamma$ -Dibromopropyl benzoate is a colourless, strongly refractive liquid, b. p. 176°/20 mm. The action of benzil on $\beta\gamma$ -diaminopropyl chloride in boiling aqueous-alcoholic solution gives 5 : 6-diphenyl-2-chloromethyl-2 : 5-dihydro-1 : 4-diazine, needles, m. p. 100° (decomp.). A rearrangement to an $\alpha\gamma$ -diamino-derivative (cf. Abderhalden and Eichwald, A., 1916, i, 795) does not, therefore, occur.

W. S. N.

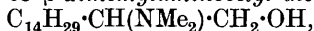
The Peptisation of Amino-acids under the Action of Acids and Alkalis. N. D. ZELINSKI and W. S. SADIKOV (*Biochem. Z.*, 1923, 141, 97—104).—The authors have made observations pointing to the possibility of amino-acids undergoing a condensation under the influence of the acidic or alkaline conditions of "cold hydrolysis" of proteins, with formation of secondary complexes not present as such in the native protein. Glycine in 25% sulphuric acid at room temperature showed a diminution in amino-nitrogen

titratable by formol, which became still less after boiling for six hours, but returned to the original value after eighteen hours' boiling. The maximum diminution was obtained by warming for one hour on the water-bath. Concentrated solutions of hydrochloric and formic acids and twice normal sodium hydroxide gave similar results. The free amino-nitrogen as determined by Van Slyke's method did not always agree with that obtained by formol titration, indicating the possible presence of proline-like complexes. In addition to the peptide and diketopiperazine linkings in these condensation products, a methylene linking is also postulated on the ground of the capacity of glycine to reduce methylene-blue after solution in alkali. Alanine and aspartic acid gave results similar to those obtained with glycine. J. P.

α -Oxides from Aldehydes and Carboxylic Acids. II.

JULIUS VON BRAUN (*Ber.*, 1923, 56, [B], 2178—2185).—In a recent communication (this vol., i, 1049), it has been shown that hept-aldehyde can be converted very smoothly into *n*-amylethylene oxide. A number of cases are now cited which show that the reaction is widely applicable. The observations appear of interest, since the oxides can be isomerised to aldehydes which are otherwise very difficult to prepare and also on account of the pronounced odour of the substances, which makes them very suitable for the study of the relationship between constitution and odour.

[With W. SCHIRMACHER.]—Ethyl α -bromopalmitate, m. p. 27°, b. p. 224—227°/11 mm., is conveniently prepared by treating palmitic acid with bromine and phosphorus, pouring the crude brominated product into an excess of cold ethyl alcohol, and completing the esterification by warming the alcoholic solution in the presence of hydrogen chloride. It is converted by a solution of dimethylamine in benzene into *ethyl α -dimethylaminopalmitate*, $C_{14}H_{29}\cdot CH(NMe_2)\cdot CO_2Et$, a viscous, almost odourless liquid, b. p. 215—217°/11 mm. (*methiodide*, m. p. 134°), which is reduced by sodium and alcohol to β -dimethylaminocetyl alcohol,

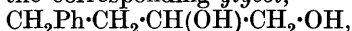


a colourless, viscous liquid, b. p. 210—213°/11 mm.; the *hydrochloride* is not crystalline, and the *methiodide* has m. p. 199—200°. The latter compound is transformed by silver oxide into the corresponding base, which decomposes when distilled in a vacuum into trimethylamine, palmitic acid (formed by oxidation of the corresponding aldehyde), and *hexadecylene $\alpha\beta$ -oxide*, $CH_3\cdot [CH_2]_{13}\cdot CH\begin{smallmatrix} \nearrow CH_2 \\ \searrow O \end{smallmatrix}$,

an almost odourless, colourless liquid, b. p. 175—180°/12 mm., m. p. 21—22°, d_4^{20} 0.8457, n_D^{20} 1.4445. The oxide is indifferent towards permanganate, phenylhydrazine, semicarbazide, or Schiff's solution. It appears to be isomerised readily to palmitaldehyde by treatment with acids or, to some extent, by distillation.

[With J. OSTERROTH.]— α -Bromo- γ -phenyl-*n*-butyric acid is converted by ethyl alcohol and sulphuric acid into *ethyl α -bromo- γ -phenyl-*n*-butyrate*, a very pale yellow liquid, b. p. 157°/14 mm., which is transformed into *ethyl α -dimethylamino- γ -phenyl-*n*-butyrate*,

a colourless liquid, b. p. $160^{\circ}/15$ mm. (the non-crystalline *hydrochloride* and *picrate* and the *methiodide*, m. p. 125° , are described). Reduction of the basic ester leads to the production of β -dimethylamino- δ -phenyl-*n*-butyl alcohol, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CH}(\text{NMe}_2)\cdot\text{CH}_2\cdot\text{OH}$, a colourless liquid, b. p. $172\text{--}173^{\circ}/22$ mm. (the *hydrochloride* and *picrate* are non-crystalline; the *methiodide* has m. p. 155°). Distillation of the quaternary base derived from β -dimethylamino- δ -phenyl-*n*-butyl alcohol results in the production of trimethylamine and δ -phenylbutylene $\alpha\beta$ -oxide, $\text{C}_{10}\text{H}_{12}\text{O}$, a liquid with a very pleasant odour of roses, b. p. $106\text{--}109^{\circ}/31$ mm., d_4^{20} 1.0029, n_D^{20} 1.5129. The oxide is slowly isomerised by sulphuric acid (20%) to the corresponding aldehyde. It is converted by water at $160\text{--}170^{\circ}$ into the corresponding *glycol*,



a viscous liquid, b. p. $180^{\circ}/13$ mm., and by a solution of dimethylamine in benzene into β -hydroxy- δ -phenylbutyldimethylamine, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{NMe}_2$, b. p. $145\text{--}147^{\circ}/15$ mm. (the non-crystalline *hydrochloride* and *picrate* and the *methiodide*, m. p. 170° , are described).

[With W. MÜNCH.]—In a similar manner, *ethyl α -bromo- γ -phenoxybutyrate*, $\text{OPh}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHBr}\cdot\text{CO}_2\text{Et}$, b. p. $179\text{--}180^{\circ}/12$ mm., is transformed successively into *ethyl α -dimethylamino- γ -phenoxybutyrate*, a colourless liquid, b. p. $174^{\circ}/13$ mm., and β -dimethylamino- δ -phenoxybutyl alcohol, a colourless, almost odourless liquid, b. p. $186\text{--}187^{\circ}/14$ mm. The latter substance is transformed successively into the *methiodide*, m. p. 117° , and the quaternary base which, when distilled, does not yield quite homogeneous δ -phenoxybutylene $\alpha\beta$ -oxide.

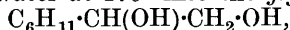
[With W. KAISER.]—*Ethyl α -bromocyclohexylacetate*,



b. p. $133\text{--}135^{\circ}/15$ mm., is transformed somewhat slowly into *ethyl α -dimethylaminocyclohexylacetate*, b. p. $123\text{--}124^{\circ}/13$ mm. (the non-crystalline *picrate* and the *hydrochloride*, m. p. $173\text{--}174^{\circ}$ [decomp.] are described), which is remarkably smoothly reduced to β -dimethylamino- β -cyclohexylethyl alcohol,



b. p. $124\text{--}126^{\circ}/13$ mm. (the corresponding *hydrochloride* is not crystalline; the *methiodide* has m. p. $155\text{--}156^{\circ}$). The quaternary base derived from the alcohol decomposes very smoothly when distilled into trimethylamine and cyclohexylethylene oxide, a colourless liquid with a very pleasant, fruity odour, b. p. $63\text{--}65^{\circ}/14$ mm., d_4^{20} 0.9359, n_D^{20} 1.4518. The oxide is remarkable for the unusual stability of the oxide ring. After agitation with sulphuric acid (20%) during twelve hours, the isomerisation to cyclohexylacetaldehyde is barely appreciable. It is transformed with difficulty by a solution of dimethylamine in benzene into β -dimethylamino- α -cyclohexylethyl alcohol, $\text{C}_6\text{H}_{11}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{NMe}_2$ (*methiodide*, m. p. 191°) and by water at 170° into the *glycol*,



colourless crystals, m. p. 43° , after slight previous softening, b. p. about $150^{\circ}/13$ mm.

H. W.

Preparation and Chlorination of $\alpha\beta$ -Alkylacetylcarbamides. ELWYN ROBERTS (T., 1923, 123, 2779—2782).

Preparation and Stability of Cuprous Nitrate and Other Cuprous Salts in presence of Nitriles. HOWARD HOULSTON MORGAN (T., 1923, 123, 2901—2907).

The Action of Organo-magnesium Compounds on Nitriles. Vinylacetonitrile. P. BRUYLANTS and J. GEVAERT (*Bull. Soc. Chim. Belg.*, 1923, 32, 317—324).—Magnesium ethyl bromide acts with vigour on vinylacetonitrile, giving a red, granular mass, and evolving ethane copiously. After hydrolysis, five products were isolated: dipropenyl, the two geometrical isomerides of crotononitrile, and two other products. Of these β -methyl- α -ethenylglutarodinitrile has b. p. 267—270°/760 mm., 145—146°/20 mm., or 131—132°/11 mm., m. p. 13—14°, d_4^{20} 0.9465 and n_D^{20} 1.4594. By acid hydrolysis, this compound yields the corresponding imide, m. p. 144°, and, on acid hydrolysis, the corresponding β -methyl- α -ethenylglutaric acid, m. p. 127—128°, b. p. 203—205°/15 mm. In addition to the dinitrile (which is a dimeride of vinylacetonitrile), a liquid boiling at 215—225°/15 mm., which deposited crystals, m. p. about 150°, was isolated from the reaction mixture. Analysis showed this to be a trimeride of vinylacetonitrile. H. H.

cycloPropene. N. J. DENJANOV and MARIE DOJARENKO (*Ber.*, 1923, 56, [B], 2200—2207).—The preparation of cyclopropene, $\text{CH}_2 < \begin{smallmatrix} \text{CH} \\ | \\ \text{CH} \end{smallmatrix}$, and its behaviour towards bromine have been investigated.

The decomposition of cyclopropyltrimethylammonium hydroxide occurs in accordance with the schemes: $\text{CH}_2 > \begin{smallmatrix} \text{CH}_2 \\ | \\ \text{CH}_2 \end{smallmatrix} \text{CH} \cdot \text{NMe}_3 \cdot \text{OH} \rightarrow \text{CH}_2 < \begin{smallmatrix} \text{CH} \\ | \\ \text{CH} \end{smallmatrix} (\text{CMe}:\text{CH}) + \text{NMe}_3 + \text{H}_2\text{O}$ and $\rightarrow \begin{smallmatrix} \text{CH}_2 \\ | \\ \text{CH}_2 \end{smallmatrix} \text{NMe}_2 + \text{MeOH}$, the change in the first direction being the more pronounced. The base is decomposed rapidly in a small quartz flask at about 300°; the apparatus is shielded from light and air. The gaseous product consists of cyclopropene mixed with a small proportion of allylene, from which it can be freed by treatment with ammoniacal cuprous chloride solution. cycloPropene is condensed to a colourless liquid by means of ether and solid carbon dioxide. It polymerises easily and rapidly, particularly under the direct influence of light. It readily absorbs oxygen with the formation of a pale yellow, viscous liquid. It is converted by an alcoholic solution of iodine into an unstable iodide. It unites so energetically with bromine that it must be diluted with carbon dioxide during the preparation of the bromides. Under these conditions, the crude hydrocarbon yields a mixture of dibromocyclopropane, $\text{CH}_2 < \begin{smallmatrix} \text{CHBr} \\ | \\ \text{CHBr} \end{smallmatrix}$, a colourless liquid with a sweet odour, b. p. 45°/27 mm., 135—136°/743 mm., m. p. about 0°, d_4^{20} 2.1436, d_4^{20} 2.1241, d_4^{20} 2.1040, n_D^{20} 1.5369, $\alpha\alpha\beta\beta$ -tetra-

bromopropane (allylene tetrabromide), b. p. 121—123°/17.5—20 mm., d_4^{20} 2.7225, d_4^{25} 2.7011, d_4^{30} 2.6800, n_D^{25} 1.617, and $\alpha\alpha\gamma\gamma$ -tetrabromopropane, b. p. 154—156°/19 mm., d_4^{20} 2.7405, d_4^{25} 2.7213, d_4^{30} 2.702, n_D^{25} 1.6225. Dibromocyclopropane reacts very slowly with bromine in diffused light, slowly in direct sunlight. It is converted by zinc dust and alcohol into cyclopropene free from allylene.

cycloPropyldimethylamine, $\begin{array}{c} \text{CH}_2 \\ | \\ \text{CH}_2 \end{array} > \text{CH} \cdot \text{NMe}_2$, is a colourless, mobile liquid, b. p. 59.8—60.3°/731—732 mm., d_4^{20} 0.7644, d_4^{25} 0.7497, n_D^{25} 1.4015. The chloroplatinate, $\text{C}_{10}\text{H}_{24}\text{N}_2\text{PtCl}_6$, long, orange-red needles, the picrate, long, thin leaflets, m. p. 191—192° (decomp.), the chloroaurate and the methiodide, colourless crystals, are described.
H. W.

Molecular Models: Benzene. JARED KIRTLAND MORSE (*Physical Rev.*, 1922, 19, 243).—In a three-dimensional model of the benzene molecule, the carbon nuclei are placed at the corners of a regular octahedron and the hydrogen nuclei along its axes; three of the hydrogen nuclei are placed at a distance y and the remaining three at a distance z from their respective corners of the octahedron of edge x . Equations are given from which it is deduced that if $x = 2.514 \times 10^{-8}$ cm. (Bragg), then $y = 2.214 \times 10^{-8}$ cm., and $z = 3.212 \times 10^{-8}$ cm. If the expressions given are substituted for the distinctive axes in models of naphthalene and anthracene, axial ratios in agreement with those determined crystallographically can be predicted.
A. A. E.

The Formation of a Non-volatile Residue in Xylene. P. DEKKER (*Chem. Weekblad*, 1923, 20, 575—577).—Samples of xylene subjected to several hours' boiling were found to leave a considerable residue on distillation, amounting to 5 g. per 100 c.c. after twenty-four hours' boiling. When the heating was carried out in absence of air, the non-volatile residue was still formed, although not in such large quantities; hence it is not due to oxidation. The samples were found to give strong reactions for aldehydes, to the presence of which the formation of the residue is ascribed; after shaking with strong sulphuric acid, prolonged heating produced no effect.
S. I. L.

Action of Hydroxylamine on γ -Trinitrotoluene. MICHELE GIUA (*Gazzetta*, 1923, 53, 657—660).—Borsche (this vol., i, 778) has shown that the action of hydroxylamine on ethers of nitrophenols may lead to replacement of the alkyloxy-group by the hydroxylamine residue with formation of β -nitroarylhydroxylamines. The possibility of this replacement was first pointed out by Michael and Browne (A., 1887, 663), and the action of hydroxylamine on nitro-compounds containing a labile nitro-group has been investigated by Nietzki and Dietschy (A., 1901, i, 196), Wieland and Gambarjan (A., 1906, i, 830), Angeli and Angelico (*Gazzetta*, 1901, 31, i, 27), and Meisenheimer (A., 1904, i, 150; 1906, i, 642; 1919, i, 389).

In continuation of his work on the action of bases on nitro-

derivatives containing a labile nitro-group (this vol., i, 485), the author now finds that the action of hydroxylamine on γ -trinitrotoluene is somewhat complex owing to the readiness with which the β -nitroarylhydroxylamines undergo change, and is influenced greatly by the duration of heating. In absolute alcoholic solution, the anhydrous compounds react under definite conditions in accordance with the equation: $C_6H_2Me(NO_2)_3 + 2NH_2 \cdot OH = C_6H_2Me(NO_2)_2 \cdot NH \cdot OH + (NOH)_2[\xrightarrow{Me} N_2O + H_2O] + H_2O$.

β -4 : 6-Dinitro-*m*-tolylhydroxylamine, $OH \cdot NH - \text{C}_6\text{H}_2(NO_2)_2$, thus

obtained, forms minute, reddish-yellow crystals, m. p. 106–107° (decomp.), dyes the skin intensely yellow, gives a pale yellow solution in concentrated sulphuric acid, and yields a red coloration with either sodium hydroxide in alcoholic solution or ammonia in acetone solution. It forms an *acetyl* derivative, $C_6H_2Me(NO_2)_2 \cdot NH \cdot OAc$, separating in yellow crystals, m. p. 206–207° (decomp.), and when treated with acetic anhydride yields 6-nitro-3 : 4-dinitrosotoluene, $NO_2 \cdot C_6H_2Me(NO)_2$, which crystallises in lustrous, reddish-yellow prisms or lamellæ, m. p. 209–210°. T. H. P.

The Sulphonation and Nitration of Naphthalene. H. E. FIERZ-DAVID (*J. Soc. Chem. Ind.*, 1923, 42, 421–426T).—A series of investigations on the sulphonation of naphthalene has confirmed the rule established by Armstrong and Wynne that derivatives are never obtained containing sulphonie groups in the ortho-, para-, or peri-position. The disulphonic acids never contain two sulphonie groups in the same benzene nucleus. Sulphonation at temperatures below 40° with the minimum quantity of sulphuric acid to form monosulphonic acid gives a mixture containing 96% of the 1-acid and 4% of the 2-acid. The 2-acid is formed directly, not by transformation from the 1-acid. At 165°, there is formed an equilibrium mixture containing 85% of 2-acid and 15% of 1-acid. The proportion of each acid varies with the temperature, but neither can be obtained exclusively. When naphthalene is treated with just sufficient sulphuric anhydride to form disulphonic acid, below 40° there is obtained a mixture containing 70% of 1 : 5-, about 25% of 1 : 6-, and probably a little 2 : 7-naphthalenedisulphonic acid. The 1 : 5-disulphonic acid is readily isolated through its insoluble barium salt, which crystallises with $1H_2O$, not $4H_2O$ as stated by Armstrong. Between 120° and 135°, the 1 : 5-disulphonic acid gradually disappears, in favour of the 2 : 7-acid. Above 140°, the 2 : 6-disulphonic acid appears; this also forms a sparingly soluble barium salt, but since the 1 : 5- and the 2 : 6-acids are never present together, the question of their separation does not arise. The statement that above 180° the 2 : 6-acid is the sole product is incorrect; the proportion of 2 : 6-acid probably never exceeds 30%. At 165°, taking 2 parts of 100% sulphuric acid to 1 part of naphthalene, sulphonation is complete in three hours, and the product contains 24% of 2 : 6-, 10% of 1 : 6-, and 65% of 2 : 7-

disulphonic acid. The anhydride of the 2 : 6-acid can be obtained in the pure form by heating the acid with water at 135° in a closed vessel; the other isomerides remain in solution. The free sulphonic acids generally crystallise readily and are not deliquescent.

The nitro-group never enters in the ortho-position to a sulphonic group, often in the peri- and sometimes in the meta-position. Nitration never proceeds quantitatively; as a rule 4—14% escapes nitration. Reduction of the different nitrosulphonic acids to aminosulphonic acids does not always proceed smoothly. The yield of 1 : 3 : 8-naphthylaminedisulphonic acid (ϵ -acid) from naphthalene-1 : 6-disulphonic acid, never exceeds 43%; in addition, there are formed 15% of 2 : 4 : 7-naphthylaminedisulphonic acid (Andresen acid) and 42% of unknown acids. Similarly, the yield of Cleve's acid (1 : 6- and 1 : 7-naphthylaminesulphonic acids) from naphthalene-2-sulphonic acid is never more than 65% of theory. The reduction of the nitro-2-sulphonic acids is very sensitive to acids; aminonaphtholsulphonic acids are liable to be formed.

When naphthalene-2-sulphonic acid is acted on by nitrous acid in sulphuric acid containing a trace of mercuric oxide or selenium, a new diazonium compound, probably having the constitution

$\text{OH} \cdot \text{C}_{10}\text{H}_5 \begin{smallmatrix} \text{N}_2^{(1)} \\ \text{SO}_3^{(2)} \end{smallmatrix}$, is formed. This reaction has previously been observed in the anthracene series, but is new to the naphthalene series.

The author gives a list of the known salts of naphthalene- and nitronaphthalene-sulphonic acids and their solubilities as far as they are known.

E. H. R.

The Action of Sulphur on Organic Compounds. VI. LUDWIK SZPERL (*Roczniki Chemji*, 1923, ii, 291—313).—A short summary is given of the first five parts of the present series (*Chemik Polski*, 1917, 15, 10; 1918, 16, 111), dealing with the action of sulphur on various aromatic compounds. In the present paper, the action of sulphur on α - and β -naphthylcarbinols is described and the results are shown to be similar to those previously obtained with benzyl alcohol. Heating with small quantities of sulphur leads in each case to the production of dinaphthylcarbinyll ether, whilst the action of one molecular proportion of sulphur leads to the formation of small quantities of dinaphthastilbenes ($\alpha\alpha$ and $\beta\beta$, respectively), naphthaldehydes, and the corresponding acids, in addition of products containing sulphur. In the case of the β -compound, dinaphthylethane is also produced, doubtless owing to the reduction of the stilbene primarily formed.

1-Bromomethylnaphthalene was prepared by the method of Wislicenus and Elvert (A., 1917, i, 202), and had m. p. 52—53° when pure; by means of potassium acetate, it was converted into α -naphthylcarbinyll acetate, a nearly colourless liquid, b. p. 172—173°/13 mm., and this was hydrolysed by means of baryta to the alcohol, m. p. 59—60° (Bamberger and Lodter, A., 1888, 375). When heated with 1/100 mol. of sulphur at 160—180° for six hours, it yields water,

a very small quantity of hydrogen sulphide, and a 55% yield of *di-α-naphthylcarbinyl ether*, plates m. p. 119—120°. When heated with one molecular proportion of sulphur for ten hours at 185° and then at 200—210° for fifty hours, it gives water, hydrogen sulphide, small quantities of *α-naphthaldehyde*, *α-naphthoic acid*, and a compound of unknown constitution containing sulphur, m. p. 142·5—143·5° (*picrate*, m. p. 200—201°), in addition to traces of fluorescent material, probably *dinaphthylethylene*. When *di-α-naphthylcarbinyl ether* was heated with one molecular proportion of sulphur under similar conditions, the product contained, in addition to *α-naphthoic acid*, *s-di-α-naphthylethylene*, m. p. 161—162° (*picrate*, m. p. 210—211°), possessing a blue fluorescence in solution. The corresponding saturated compound, *s-di-α-naphthylethane*, does not possess this property; it was prepared by the action of sodium on 1-bromomethylnaphthalene in the presence of dry benzene and has m. p. 159—160° (*picrate*, m. p. 204—205°) (compare Bamberger and Lodter, *loc. cit.*).

β-Methylnaphthalene was converted into the *ω*-bromo-compound, m. p. 51°, and this yielded *β-naphthylcarbinyl acetate*, m. p. 51—53°, the crystalline form of which is described in detail; this was finally converted into the alcohol.

When heated with 1/100 molecular proportion of sulphur, the alcohol yields *s-di-β-naphthylethylene*, m. p. 253—254°, and *di-β-naphthylcarbinyl ether*, colourless plates, m. p. 123·5—124·5°. With one molecular proportion of sulphur, *β-naphthoic acid*, traces of *di-β-naphthylethylene*, a *hydrocarbon*, $C_{22}H_{18}$, m. p. 181—182° (forming a *dipicrate*, m. p. 197—198°), and a compound, $C_{22}H_{14}S_2$, m. p. 350—351°, previously obtained from *β-methylnaphthalene* and sulphur by Friedmann (A., 1916, i, 736) were obtained. The hydrocarbon, $C_{22}H_{18}$, is shown to be *s-di-β-naphthylethane* by its synthesis from 2-bromomethylnaphthalene and sodium; it is not fluorescent, and it is suggested that the compound to which Bamberger and Lodter assigned the above constitution (*loc. cit.*) was probably unsaturated.

No thiophen derivatives appear to be formed in the reactions studied. G. A. R. K.

Attempted Preparation of Methylenecyclopropane. Dimethylcyclopropylmethylamine. N. J. DEMJANOV and MARIE DOJARENKO (*Ber.*, 1923, 56, [B], 2208—2212).—The authors have attempted to prepare methylenecyclopropane by the thermal decomposition of *cyclopropylmethyltrimethylammonium hydroxide*, $\begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix} > CH \cdot CH_2 \cdot NMe_3 \cdot OH$. The amount of hydrocarbon (which consists mainly of erythrene, $CH_2:CH:CH:CH_2$) is, however, relatively very small; the main product of the change is *cyclopropylmethyl-dimethylamine*.

The best yields of hydrocarbons, not exceeding 6·5%, are obtained when the base is rapidly decomposed; the gases are treated with bromine, whereby in different experiments which do not appear to proceed quite uniformly *αβγδ-tetrabromo-n-butane*, m. p. 117—

118°, *methylenecyclopropane dibromide*, $\begin{smallmatrix} \text{CH}_2 \\ | \\ \text{CH}_2 \end{smallmatrix} > \text{CBr} \cdot \text{CH}_2 \text{Br}$, a liquid which crystallises when cooled with solid carbon dioxide, and (?) $\alpha\beta\delta$ -*tetrabromo-n-butane* are obtained.

cycloPropylmethyldimethylamine, $\begin{smallmatrix} \text{CH}_2 \\ | \\ \text{CH}_2 \end{smallmatrix} > \text{CH} \cdot \text{CH}_2 \cdot \text{NMe}_2$, is a colourless, mobile, very volatile liquid, b. p. 99—99.5°/734.5 mm., 99.5—100.1°/742 mm., d_4^{20} 0.7963, d_4^{25} 0.7880, d_4^{30} 0.7835, d_4^{35} 0.7705, n_D^{20} 1.4245. The *hydrochloride*, long, very hygroscopic prisms, m. p. (indefinite) 158—160°, the *chloroplatinate*, small, orange-coloured prisms, the *chloroaurate*, leaflets, the *picrate*, long yellow prisms, m. p. 103.5—104°, and the *methiodide* are described.

The cases of decomposition of quaternary ammonium hydroxides by the authors and by Willstätter and his co-workers are sufficiently numerous to allow the following generalisations to be made. (1) When the group $\text{NMe}_3 \cdot \text{OH}$ is attached to a ring, the main product of the decomposition is the hydrocarbon, and the production of the amine is of secondary importance; (2) cyclic bases with the side chain $\cdot \text{CH}_2 \cdot \text{NMe}_3 \cdot \text{OH}$ yield very little semicyclic hydrocarbon and much amine; (3) cyclic bases which contain the group $\text{NMe}_3 \cdot \text{OH}$ in the side chain in such a manner that a hydrogen atom is attached to the vicinal carbon atom yield chiefly hydrocarbons containing a double bond in the side chain, the hydrogen being taken from the vicinal carbon atom. H. W.

Melting-point Curves of Binary Mixtures: Aniline-Crotononitrile and Aniline-Vinylacetonitrile. FR. LAFORTUNE (*Bull. Soc. chim. Belg.*, 1923, **32**, 314—317).—Aniline has m. p. —6.2°, and crotononitrile, m. p. —72.1°. These compounds do not form a compound, but a eutectic at about 63% of the nitrile, with m. p. about —85°. Similarly, vinylacetonitrile, m. p. —86.8°, does not form a compound with aniline, but a eutectic at about 74% of the nitrile, m. p. about —95°. H. H.

Substituted Phenyldichloroamines. KENNEDY JOSEPH PREVITÉ ORTON and (the late) JOHN EDWIN BAYLISS (*T.*, 1923, **123**, 2790—2792).

The Freezing-point-Solubility Diagram of the System Tetryl [Trinitrophenylmethylnitroamine]-Picric Acid. C. A. TAYLOR and WILLIAM H. RINKENBACH (*Ind. Eng. Chem.*, 1923, **15**, 1070—1071).—The freezing-point curves of mixtures of tetryl (m. p. 128.72°) and picric acid (121.9°) were determined. They show a discontinuity between concentrations of 44% and 63% of tetryl apparently due to the formation of a compound of 1 mol. of tetryl with 1 mol. of picric acid. All these mixtures have an extreme tendency to supercool. C. I.

The Tenaciousness of Organic Residues. I. JULIUS VON BRAUN and KARL MOLDAENKE (*Ber.*, 1923, **56**, [B], 2165—2172).—The firmness with which organic radicles are attached to carbon, nitrogen, sulphur, and arsenic has been the subject of numerous investigations. A critical review of the literature shows that the

residues cannot be arranged in any order which holds good for their relative fixity to all elements, and as different methods lead on the whole to the same arrangement of groups with regard to any one element, it follows that the experimental technique is not at fault, but that the discordance is a natural phenomenon. The main difficulty in the uniform further development of affinity series towards carbon on the one hand and the remaining elements on the other lies in the impossibility of applying the usual reagents, such as phosphorus chloride or cyanogen bromide, to the removal of aromatic residues. The difficulty can be overcome indirectly, since if two aryl residues, R'_{ar} and R''_{ai} , make a different affinity demand on an atom of carbon or nitrogen, this must be exhibited in the inverse order in the cases of the groups $R'_{ai}CH_2-$ and $R''_{ai}CH_2-$. A series of experiments has therefore been undertaken on the relative firmness of the attachment of groups of the benzyl type to nitrogen, sulphur, and arsenic, and the procedure has the further advantage that it can be extended to the halogens. It is shown with regard to nitrogen that the radicles can be arranged in the series $-C_6H_5 \cdot CH_2-$, $\alpha-C_{10}H_7 \cdot CH_2-$, $\beta-C_{10}H_7 \cdot CH_2 \cdot CH_2-$ and that this order is maintained with regard to bromine and chlorine. As far as the naphthalene residues are concerned, the results are in harmony with the observations of Skraup, who employed the carbinol and oxazole method, but a discrepancy exists with regard to phenyl and benzyl, which is also apparent in the hexa-aryl-ethane series.

α -Naphthylmethyl chloride, long, four-sided rods, m. p. 34° , b. p. $162-163^\circ/14$ mm., is prepared in relatively poor yield by the action of hydrochloric acid on α -naphthylmethyl alcohol. It is more conveniently obtained by the action of phosphorus pentachloride on *benzo- α -naphthylmethylamide*, $C_{10}H_7 \cdot CH_2 \cdot NHBz$ (lustrous leaflets, m. p. 154°), or *benzodi- α -naphthylmethylamide*, $(C_{10}H_7 \cdot CH_2)_2NBz$ (short prisms, m. p. 134°). In a similar manner, α -naphthylmethyl bromide, m. p. 50° , b. p. $170-175^\circ/15$ mm., is readily prepared by the use of phosphorus pentabromide. *Benzo- β -naphthylmethylamide*, short rodlets, m. p. 144° , and *benzodi- β -naphthylmethylamide*, m. p. $120-121^\circ$, are similarly transformed into β -naphthylmethyl chloride, m. p. 48° , b. p. $162^\circ/15$ mm., and β -naphthylmethyl bromide, m. p. 56° , b. p. $165-169^\circ/14$ mm. The rate of hydrolysis of the halogenated compounds by hot water has been comparatively estimated.

α -Naphthylmethyldimethylamine, $C_{10}H_7 \cdot CH_2 \cdot NMe_2$, is a colourless liquid, b. p. $148-152^\circ/16$ mm. (*hydrochloride*, m. p. 245° ; *picrate*, m. p. 145°), which is converted by cyanogen bromide into the quaternary salt, $(C_{10}H_7 \cdot CH_2)_2NMe_2Br$, m. p. 226° , dimethylcyanamide, and α -naphthylmethyl bromide. In a similar manner, β -naphthylmethyldimethylamine, b. p. $130-132^\circ/14$ mm. (*hydrochloride*, m. p. 234° ; *picrate*, m. p. 152°), is transformed by cyanogen bromide into dimethylcyanamide, β -naphthylmethyl bromide, and the quaternary salt, $(C_{10}H_7 \cdot CH_2)_2NMe_2Br$, m. p. 217° . The *chloroplatinate* of the corresponding quaternary chloride forms small, pale yellow crystals, m. p. $164-166^\circ$.

α -Naphthylmethyl chloride is converted by a solution of methylamine in benzene at 100° into a mixture of α -naphthylmethylmethylamine, $C_{10}H_7 \cdot CH_2 \cdot NHMe$, b. p. 156 — $158^\circ/15$ mm. (*hydrochloride*, m. p. 170° ; *picrate*, m. p. 206°), and *di- α -naphthylmethylmethylamine*, $(C_{10}H_7 \cdot CH_2)_2NMe$, colourless rodlets, m. p. 87 — 88° , b. p. 278 — $280^\circ/15$ mm. (*hydrochloride*, m. p. 220° ; *picrate*, m. p. 166°). β -Naphthylmethylmethylamine is a liquid, b. p. 148 — $150^\circ/15$ mm. (*hydrochloride*, m. p. 188° ; *picrate*, m. p. 105°), whereas *di- β -naphthylmethylmethylamine* has m. p. 87 — 88° , b. p. 276 — $278^\circ/15$ mm. (*hydrochloride*, m. p. 235° ; *picrate*, m. p. 158°). The action of β -naphthylmethyl chloride on α -naphthylmethylmethylamine in the presence of benzene leads to the formation of α -naphthylmethyl- β -naphthylmethylmethylamine, cubic crystals, m. p. 145° , b. p. 272 — $274^\circ/14$ mm. (*hydrochloride*, m. p. 225° ; *picrate*, m. p. 159°). The tertiary base is decomposed by cyanogen bromide with the production of α -naphthylmethyl bromide; α -naphthylmethyltrimethylammonium bromide, $C_{10}H_7 \cdot CH_2 \cdot NMe_3Br$, has m. p. 213 — 214° , whereas the corresponding β -compound has m. p. 205 — 206° .

Benzyl- α -naphthylmethylmethylamine, $C_{10}H_7 \cdot CH_2 \cdot NMe \cdot CH_2Ph$, a pale yellow, viscous liquid, b. p. 220 — $222^\circ/15$ mm., is smoothly prepared from α -naphthylmethyl chloride and an excess of benzylmethylamine in the presence of benzene at 100° ; the *hydrochloride*, m. p. 218° , and the *picrate*, m. p. 219° , are described. The base is decomposed by cyanogen bromide with production of the quaternary bromide, $C_{26}H_{26}NBr$, m. p. 179 — 180° , benzyl bromide, and the cyanide, α - $C_{10}H_7 \cdot CH_2 \cdot NMe \cdot CN$.

H. W.

***o*-cyclohexyleyclohexanol.** [2-Hydroxydicyclohexyl.]
PIERRE BEDOS (*Compt. rend.*, 1923, **177**, 958—960; cf. this vol., i, 779).—2-Hydroxydicyclohexyl (colourless liquid, b. p. 134 — $136^\circ/13$ mm., d^{18}_D 0.971, n^{18}_D 1.4914; *phenylurethane*, prisms, m. p. 122°), is formed by the interaction of magnesium cyclohexyl chloride and cyclohexene oxide, and, on oxidation with chromic acid, in acetic acid solution, affords 2-cyclohexyleyclohexanone, colourless liquid, b. p. 128 — $130^\circ/12$ mm., d^{22}_D 0.969, n^{22}_D 1.4840 (*semicarbazone*, m. p. 180 — 182° , with preliminary softening and decomposition at 175°). The above alcohol is probably the *cis*-compound. The reduction of 2-cyclohexylidenecyclohexanone with sodium and alcohol (or a combination of this process with Paal-Skita reduction) affords a mixture of two stereoisomeric 2-hydroxydicyclohexyls, b. p. 136 — $138^\circ/13$ mm.; this mixture with phenylcarbimide gives two *phenylurethanes*, neither of which can be obtained in a pure state (the respective m. p. found being 108 — 112° and 122 — 128°). Oxidation of the mixture of alcohols affords 2-cyclohexyleyclohexanone, identical with the ketone described above.

E. E. T.

Phenol Solutions. KARL GLENZ (*Helv. Chim. Acta*, 1923, **6**, 826—833).—A number of properties of aqueous solutions of phenol indicate that the dissolved substance exists in two modifications. From a saturated solution, part of the phenol can be precipitated

with salt, but not from a more dilute solution. Dilution of a phenol solution diminishes its acidity more rapidly than would be expected; thus a 6.7% solution has p_H 4.58 and a 1% solution p_H 6.23. The acidity of a phenol solution is also reduced by warming. The percentage adsorption of phenol by charcoal is greater from a concentrated than from a dilute solution, whereas the reverse is to be expected. Addition of salt to a phenol solution increases the acidity before any salting out effect is apparent. Addition of salt to a dilute solution increases the surface tension to that of a more concentrated solution. It is concluded that concentrated solutions contain a polymerised form of phenol which is more acid than unimolecular phenol, can be salted out, is readily adsorbed, and has a higher surface tension in solution. The possibility of the existence of phenol in the keto-form, $H_2 \cdot C_6H_4 \cdot O$, is also discussed.

E. H. R.

Derivatives of the Four Isomeric Sulphonic Acids of *m*-Tolyl Methyl Ether. ROBERT DOWNS HAWORTH and ARTHUR LAPWORTH (T., 1923, 123, 2982—2996).

Reduction of *m*-Methoxybenzyl Bromide by Hydrogen Iodide. JOHN BALDWIN SHOESMITH (T., 1923, 123, 2828—2830).

Chloro-*o*-xlenols. I. 5-Chloro-*o*-3-xlenol, 6-Chloro-*o*-3-xlenol, and 5-Chloro-*o*-4-xlenol. LEONARD ERIC HINKEL, WILLIAM THOMAS COLLINS, and ERNEST EDWARD AYLING (T., 1923, 123, 2968—2973).

Compounds of Antimonic Acid and Pyrocatechol. R. WEINLAND and RUDOLF SCHOLDER (Z. anorg. Chem., 1923, 127, 343—368).—Antimony pentoxide combines with pyrocatechol to form *tripyrocatechylantimonic acid*, which is easily soluble in water, from which it crystallises in thick, yellowish-green tablets, $SbO(O \cdot C_6H_4 \cdot OH)_3 \cdot 6H_2O$. The salts of *potassium* ($\frac{1}{2}H_2O$), *ammonium* ($\frac{1}{2}H_2O$), *sodium* ($4\frac{1}{2}H_2O$), *silver*, *zinc* ($8H_2O$), *iron* (ferrous) ($8H_2O$), *nickel* ($8H_2O$), *cobalt* ($8H_2O$), *manganese* ($8H_2O$), *copper* ($8H_2O$), and *aluminium* ($15H_2O$) are described. Some salts contain excess of pyrocatechol, and are regarded as co-ordination compounds of the type $\left[SbO \begin{smallmatrix} \leftarrow (O \cdot C_6H_4 \cdot OH)_2 \\ O \cdot C_6H_4 \cdot O \end{smallmatrix} \right] \left[M \begin{smallmatrix} C_6H_4(OH)_2 \\ 2H_2O \end{smallmatrix} \right]$. Such are the *magnesium*, *calcium*, *barium* salts, and the similarly constituted *potassium* and *chloropenta-aquochromic* salts. In addition, a *mercuric* salt, $[SbO(O \cdot C_6H_4 \cdot O)_3]_2Hg_3$, three *pyridine* salts, $[Sb(O \cdot C_6H_4 \cdot O)_3]H(C_5H_5N)$, $[Sb(O_2 \cdot C_6H_4)_3]H_2C_5H_5N$, and $[SbO(O_2 \cdot C_6H_4)_3]H_2C_5H_5N \cdot H_2O$, two *quinoline* salts, $[Sb(O_2 \cdot C_6H_4)_3]H_2C_9H_7N$ and $[SbO(O_2 \cdot C_6H_4)_3]H_2C_9H_7N$, an anomalous *ammonium* salt, $[Sb(O_2 \cdot C_6H_4)_3]H_3 \cdot 3NH_3$, and a *potassium* salt, $[Sb_2O_2(O \cdot C_6H_4 \cdot OH)_2(O_2 \cdot C_6H_4)_3]K_2 \cdot 6\frac{1}{2}H_2O$, are described.

H. H.

Spirans. IX. Preparation and Properties of Amino- and Nitro-derivatives of Benzylidenepentaerythritol. DAN RADULESCU and I. TANASESCU (*Bul. Soc. Ştiinţe Cluj*, 1922, i, 192—200; from *Chem. Zentr.*, 1923, iii, 138—139; cf. this vol., i, 1211).—

Benzylidenepentaerythritol, $\text{CHPh} \begin{smallmatrix} \text{O-CH}_2 \\ \text{O-CH}_2 \end{smallmatrix} > \text{C} \begin{smallmatrix} \text{CH}_2\text{:O} \\ \text{CH}_2\text{:O} \end{smallmatrix} > \text{CHPh}$, shows molecular asymmetry, although it has no asymmetric carbon atom. It cannot be resolved by physical methods. Certain derivatives were accordingly prepared. *Di-o-nitrobenzylidenepentaerythritolspiran*, $\text{C}_{19}\text{H}_{18}\text{O}_8\text{N}_2$, is obtained from benzylidenepentaerythritol and *o*-nitrobenzaldehyde. It forms needles with m. p. 166°. *Di-m-nitrobenzylidenepentaerythritolspiran* is a yellow, crystalline substance, m. p. 188—189°. *Di-p-nitrobenzylidenepentaerythritolspiran* forms needles, m. p. 236—237°. *Di-p-dimethylaminobenzylidenepentaerythritolspiran*, from pentaerythritol and *p*-dimethylaminobenzaldehyde, forms leaflets, m. p. 223°. The *picrate* and the *chloroplatinate* are microcrystalline. The *o*-nitro-compound above-mentioned gives with phenylhydrazine, *o*-amino-benzaldehydephenylhydrazone, $\text{C}_{13}\text{H}_{13}\text{N}_3$, greenish-yellow crystals. *Di-m-aminobenzylidenepentaerythritolspiran*, $\text{C}_{19}\text{H}_{22}\text{O}_4\text{N}_2$, is obtained by reduction of the corresponding nitro-spiran. It is a yellow, crystalline substance, m. p. 225°. *Di-o-aminobenzylidenepentaerythritolspiran* is an amorphous, yellow substance, m. p. 164°; the *hydrochloride* has m. p. 172°. G. W. R.

Kakishibu. I. Constitution of Shibuol. I. SHIGERU KOMATSU and NAOHIKO MATSUNAMI (*Mem. Coll. Sci. Kyoto Imp. Univ.*, 1923, 7, 15—23).—Kakishibu, the pale yellow, cloudy extract of unripe kaki fruit, contains a phenolic substance, $\text{C}_{14}\text{H}_{20}\text{O}_9$, probably a phlobatannin, for which the name *shibuol* is proposed. Shibuol (1—2%) may be obtained from kakishibu by precipitation either with a mixture of alcohol and ether, or with acetic acid, or with concentrated hydrochloric acid or with basic lead acetate. It is converted, when fused with potassium hydroxide, into gallic acid, phloroglucinol (49.7%) and a substance, $\text{C}_{12}\text{H}_8\text{O}_5$.

Kakigoma, $\text{C}_{11}\text{H}_9\text{O}_5$, a brown, amorphous substance obtained from the pulp of the dried fruit *dojo-hatiya*, after purification by extraction with sulphuric acid, is soluble in alkalis, insoluble in organic solvents, and, on fusing with potassium hydroxide, gives phloroglucinol (17.88%), gallic acid, and a substance, $\text{C}_{13}\text{H}_9\text{O}_5$. E. E. T.

Catalytic Hydrogenation under Pressure in the Presence of Nickel Salts. VII. Aldehydes. JULIUS VON BRAUN and GERD KOCHENDORFER (*Ber.*, 1923, 56, [B], 2172—2178).—The catalytic reduction of aldehydes under pressure has been examined in the hope of elucidating the constitution and mode of formation of some of the compounds of unexpectedly high boiling point which have been encountered previously by other workers in experiments on catalytic hydrogenation by various methods. Under the experimental conditions adopted, it is found that ketones are converted smoothly into the corresponding secondary

alcohols, and aromatic aldehydes into the primary alcohols. When, however, the aldehydic group is present in an aliphatic chain, there are obtained, in addition to the primary alcohols, secondary alcohols which arise from the doubling of the aldehyde carbon chain. Their formation is ascribed to the condensation of enolised with unchanged aldehyde, $\text{CHR}:\text{CH}\cdot\text{OH} + \text{H}\cdot\text{CO}\cdot\text{CH}_2\text{R} \rightarrow \text{CHR}:\text{CH}\cdot\text{CO}\cdot\text{CH}_2\text{R}$, and subsequent reduction of the unsaturated ketone thus produced. The hypothesis is in harmony with the observation that similar effects are not produced with aromatic aldehydes or ketones.

Styryl methyl ketone is almost quantitatively reduced to γ -hydroxy- α -phenylbutane, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{OH}$, b. p. 117—121°/12 mm. With acetophenone, on the other hand, complete hydrogenation cannot be effected, and the product consists of a mixture of unchanged ketone and phenylmethylcarbinol. Benzaldehyde is hydrogenated rapidly and completely to benzyl alcohol. Similarly, *o*-aminobenzaldehyde dissolved in decahydronaphthalene gives *o*-aminobenzyl alcohol, m. p. 82°, in 80% yield. Cinnamaldehyde is converted into a mixture of phenylpropyl alcohol and γ -hydroxy- α -*di*-phenylhexane, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{Ph}$, a colourless liquid, b. p. 224—227°/9 mm. The latter compound is converted by sodium acetate and acetic anhydride into the corresponding *acetate*, $\text{C}_{20}\text{H}_{24}\text{O}_2$, a colourless liquid, b. p. 225—230°/18 mm.; by phosphorus chloride into the *chloride*, $\text{C}_{18}\text{H}_{21}\text{Cl}$, a liquid, b. p. 215—217°/10 mm.; by chromic acid in the presence of glacial acetic acid into the *compound*, $\text{C}_{18}\text{H}_{20}\text{O}$, a pale yellow liquid, b. p. 214—218°/12 mm., which does not give crystalline condensation products with hydroxylamine or semicarbazide, and by zinc chloride into the saturated *hydrocarbon*, $\text{C}_{18}\text{H}_{20}$, a colourless liquid, b. p. 204—208°/14 mm., d_4^{25} 1.028, n_D^{25} 1.5770; the latter compound is identified as 1- β -phenylethyl-1 : 2 : 3 : 4-tetrahydronaphthalene, $\text{C}_6\text{H}_4 \begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}(\text{CH}_2\cdot\text{CH}_2\text{Ph})\cdot\text{CH}_2 \end{array}$, since it is converted by lead oxide at 620—650° into naphthalene and styrene contaminated with a little ethylbenzene. The behaviour of hydrocinnamaldehyde is similar to that of cinnamaldehyde.

Phenylacetaldehyde is hydrogenated to a mixture of phenylethyl alcohol and β -hydroxy- α -*di*-phenyl-*n*-butane,

$\text{CH}_2\text{Ph}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CH}_2\text{Ph}$,
colourless crystals, m. p. 41°, b. p. 204—208°/10 mm. The latter compound is converted into the corresponding *acetate*, a liquid, b. p. about 200°/17 mm., the *chloride*, b. p. 192—193°/15 mm., and the *ketone*, which could not be isolated in the completely homogeneous condition. It is converted by zinc chloride or by 2*N*-sulphuric acid at 260—280° into the unsaturated *hydrocarbon*, $\text{C}_{16}\text{H}_{16}$, b. p. 172—173°/9 mm., d_4^{25} 1.044, n_D^{25} 1.5944, which possibly contains small amounts of 1-benzylhydrindene in addition to α -*di*-phenyl- Δ^{α} - or - Δ^{β} -butene.

Heptaldehyde is hydrogenated at 140—150° to a mixture of heptyl alcohol and *hexylheptylcarbinol*, $\text{C}_6\text{H}_{13}\cdot\text{CH}(\text{OH})\cdot\text{C}_7\text{H}_{15}$, an almost odourless, fairly mobile liquid, b. p. 153—155°/9 mm. (the

corresponding *acetate*, b. p. 152—155°/14 mm., and the *chloride*, b. p. 150—155°/15 mm. are described).

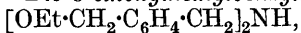
Dipropenyl glycol does not combine with more than four atomic proportions of hydrogen even at 200° and is thereby converted into a mixture of the stereoisomeric octane- $\delta\epsilon$ -diols. The possibility that the glycols are intermediate products in the formation of the secondary alcohols described above appears therefore to be invalidated. H. W.

The Catalytic Reduction of some Nitriles. H. RUPE and E. HODEL (*Helv. Chim. Acta*, 1923, 6, 865—880; cf. Rupe and Glenz, this vol., i, 100).—Experiments on the reduction of benzonitrile and phenylacetonitrile (benzyl cyanide) with hydrogen in presence of nickel have elucidated the mechanism of the reaction. The reductions were carried out in cold aqueous alcoholic solution in presence of acetic acid and a large proportion of nickel catalyst, about twice the weight of the nitrile. The first product of the reaction is the aldimine, CHR:NH , part of which is reduced further to the primary amine, $\text{CH}_2\text{R}\cdot\text{NH}_2$. Part of the aldimine, however, is hydrolysed to aldehyde and ammonia, and the former condenses with the primary amine to form the Schiff's base, $\text{CHR:N}\cdot\text{CH}_2\text{R}$, which is then reduced to secondary amine. The relative proportions of primary and secondary base formed depend on the ease with which the aldimine is hydrolysed into aldehyde and ammonia. When the reaction is carried out in presence of phenylhydrazine, more primary base is formed, since the aldehyde condenses preferentially with the phenylhydrazine to form a phenylhydrazone, which is itself reduced to some extent to primary base and aniline. When 25 g. of benzonitrile were reduced there were formed 3.2 g. of benzaldehyde, 4.6 g. of benzylamine, and 11.8 g. of dibenzylamine. In presence of phenylhydrazine, the products were 6.8 g. of benzaldehyde (from the phenylhydrazone), 8.8 g. of benzylamine, 1.5 g. of dibenzylamine, and 9.1 g. of aniline. Phenylhydrazine itself was found to be reduced rapidly to aniline and ammonia. Benzylideneaniline is reduced rapidly to benzylaniline. By the reduction of 40 g. of benzyl cyanide, 4.8 g. of β -phenylethylamine, and 27.2 g. of di- β -phenylethylamine were obtained, whereas in presence of phenylhydrazine there were formed 5.8 g. of primary and 2.4 g. of secondary amine from 20 g. of the nitrile. Benzylidenehexylamine was readily reduced to benzylhexylamine, whereas phenylethylphenylethylideneamine, from phenylacetaldehyde and phenylethylamine, gave but a poor yield of secondary amine on account of the instability of the Schiff's base. E. H. R.

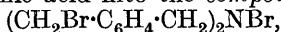
Syntheses in the Fatty-aromatic Series. XIV. Homo-*o*-xylylene Bromide. JULIUS VON BRAUN and FRIEDRICH ZOBEL (*Ber.*, 1923, 56, [B], 2142—2152; cf. A., 1916, i, 470).—The projected course of the preparation of homo-*o*-xylylene bromide is indicated by the scheme: $\text{OR}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{NH}_2 \rightarrow$
 $\text{OR}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{OH} \rightarrow \text{OR}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{Br} \rightarrow$
 $\text{OR}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CN} \rightarrow \text{OR}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CO}_2\text{H} \rightarrow$
 $\text{OR}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CO}_2\text{R}' \rightarrow \text{OR}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH} \rightarrow$
 $\text{CH}_2\text{Br}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{Br}$. Complete success is achieved when R

is the ethyl, but not the methyl or phenyl, group. The tendency towards ring formation is greater with homo-*o*-xylylene bromide than with xylylene bromide; numerous examples of its conversion into cyclic compounds are cited.

ω -Ethoxy-*o*-toluonitrile, b. p. $122^{\circ}/12$ mm., is readily obtained in almost theoretical yield by the action of alcoholic sodium ethoxide on *o*-cyanobenzyl bromide. It is easily reduced in decahydronaphthalene solution at 130° to a mixture of the corresponding primary and secondary bases, which are smoothly separable by fractional distillation. *o*-Ethoxymethylbenzylamine, $\text{OEt}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{NH}_2$ (yield 40–52%), is a colourless liquid, b. p. $130^{\circ}/12$ mm. (*hydrochloride*, leaflets, m. p. 152° ; *picrate*, needles, m. p. 148°). *Bis-o-ethoxymethylbenzylamine*,

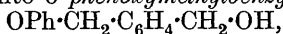


is a reddish-yellow, viscous liquid, b. p. $237^{\circ}/12$ mm.; the *picrate* has m. p. 93° . The non-crystalline *benzoyl* derivative is converted by fuming hydrobromic acid into the compound,



a colourless, crystalline powder, m. p. 124° , in which the bromine atom is very mobile.

o-Phenoxymethylbenzylamine is converted by nitrous acid in acetic acid solution into *o*-phenoxymethylbenzyl alcohol,



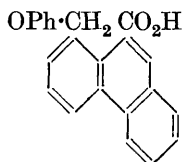
a colourless, crystalline mass, m. p. 50° , b. p. $216^{\circ}/15$ mm. The replacement of the hydroxy-group of the compound by bromine without loss of the phenyl radicle is a matter of difficulty, but can be effected by cautious treatment of it with phosphorus tribromide in the presence of chloroform, whereby *o*-phenoxymethylbenzyl bromide, colourless crystals, m. p. 54° , is produced. This compound is converted by aqueous-alcoholic potassium cyanide solution into ω -phenoxy-*o*-tolylacetonitrile, m. p. 78° , b. p. $220^{\circ}/17$ mm., which is hydrolysed in alkaline solution to ω -phenoxy-*o*-tolylacetic acid, m. p. 105° . Ethyl ω -phenoxy-*o*-tolylacetate, b. p. $225^{\circ}/15$ mm., is prepared from the acid by means of ethyl alcohol and sulphuric acid; it is reduced by sodium and alcohol to β -*o*-tolylethyl alcohol, b. p. $120^{\circ}/15$ mm., the phenoxy-group being replaced by hydrogen during the reaction.

[With O. KÜHN.]—Sodium ω -phenoxy-*o*-tolylacetate, lustrous leaflets, condenses with *o*-nitrobenzaldehyde in the presence of

acetic anhydride to give the substance, $\text{OPh}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2)\cdot\text{CO}_2\text{H}$, small, pale yellow crystals, m. p. 152 – 153° , which is smoothly reduced by ferrous hydroxide and ammonia to the corresponding *amino-acid*, colourless or yellow crystals, m. p. (for either form) 142° after softening at 138° . The latter acid is

transformed by successive treatment with nitrous acid and copper powder into *phenoxymethylphenanthrenecarboxylic acid* (annexed formula), pale yellow prisms, m. p. 201° .

o-Ethoxymethylbenzylamine is converted successively into *o*-ethoxymethylbenzyl alcohol, a colourless liquid, b. p. $146^{\circ}/16$ mm.;



o-ethoxymethylbenzyl bromide, a colourless liquid which could not be caused to crystallise, b. p. 135—137°/16 mm.; *ω*-ethoxy-*o*-tolyl-acetonitrile, b. p. 150°/16 mm.; *ω*-ethoxy-*o*-tolylacetic acid, a colourless, very viscous liquid, b. p. 190°/16 mm., and ethyl *ω*-ethoxy-*o*-tolylacetate, b. p. 156°/17 mm. Partial replacement of the ethoxyl group by hydrogen occurs during the reduction of the ester by sodium and alcohol, but the main product of the change is *β*-*o*-ethoxymethylphenylethyl alcohol, $\text{OEt}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$, an almost odourless liquid, b. p. 149—152°/12 mm. The alcohol is converted by protracted treatment with fuming hydrobromic acid at 100° into *o*-homoxilylene bromide, long needles, m. p. 53°, b. p. 168°/10 mm., the yield being 60% of that theoretically possible.

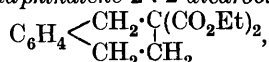
isoChroman, $\text{C}_6\text{H}_4\begin{smallmatrix} \text{CH}_2\cdot\text{O} \\ | \\ \text{CH}_2\cdot\text{CH}_2 \end{smallmatrix}$, b. p. 90°/12 mm., is normally

formed as by-product during the reaction, but can be made the main product if the duration is sufficiently shortened; its constitution is deduced from its analysis and the absence of a hydroxyl group, from its conversion into *o*-homoxilylene bromide by fuming hydrobromic acid, and its formation from the bromide by the action of water, or, preferably, of dilute potassium carbonate solution. *o*-Homoxilylene bromide is converted by potassium sulphide in aqueous-alcoholic solution into thioisochroman,

$\text{C}_6\text{H}_4\begin{smallmatrix} \text{CH}_2\cdot\text{S} \\ | \\ \text{CH}_2\cdot\text{CH}_2 \end{smallmatrix}$, b. p. 128—130°/13 mm., which could not be

obtained quite free from the corresponding oxygen compound; the additive compound with mercuric chloride, $\text{C}_6\text{H}_{10}\text{S}\cdot\text{HgCl}_2$, a colourless powder, m. p. 201°, and the methiodide, $\text{C}_{10}\text{H}_{13}\text{IS}$, colourless leaflets, m. p. 123°, are described.

Ethyl sodiomalonate and *o*-homoxilylene bromide give ethyl 1 : 2 : 3 : 4-tetrahydronaphthalene-2 : 2-dicarboxylate,



a colourless, odourless liquid, b. p. 180°/13 mm., which is hydrolysed to 1 : 2 : 3 : 4-tetrahydronaphthalene-2 : 2-dicarboxylic acid, a colourless, crystalline powder, m. p. 176° (decomp.); the acid is transformed by loss of carbon dioxide into 1 : 2 : 3 : 4-tetrahydronaphthalene-2-carboxylic acid, m. p. 97—98°.

o-Homoxilylene bromide is converted by a solution of dimethylamine in benzene into the very hygroscopic *N*-dimethyltetrahydroisouquinolinium bromide, $\text{C}_6\text{H}_4\begin{smallmatrix} \text{CH}_2\cdot\text{NMe}_2\text{Br} \\ | \\ \text{CH}_2\cdot\text{CH}_2 \end{smallmatrix}$, which is identified by

conversion through the chloride into the previously described chloroplatinate, m. p. 230°.

β-*o*-Tolylethyl bromide, a colourless liquid, b. p. 112—115°/16 mm., is prepared by the action of fuming hydrobromic acid on *β*-*o*-tolylethyl alcohol at 120°; it is readily converted by bromine at 125—130° into a mixture of dibrominated substances including *o*-homoxilylene bromide, but the preparation of the latter in this manner does not appear to be practicable.

N-Phenyltetrahydroisouquinoline, a colourless, odourless liquid,

b. p. 198°/16 mm., is prepared in almost quantitative yield by the action of an excess of aniline on *o*-homoxylene bromide; the non-crystalline *hydrochloride*, the *chloroplatinate*, and the *picrate*, yellow leaflets, m. p. 120°, are described. H. W.

The Catalytic Reduction of α - and β -Naphthonitrile. H. RUPE and F. BECHERER (*Helv. Chim. Acta*, 1923, 6, 880—892).—The catalytic reduction of the naphthonitriles follows the same general course as that of other nitriles (this vol., i, 1199). At the normal dilution (30 g. in 370 c.c. of mixed solvent), the products obtained from 30 g. of α -naphthonitrile were 4.5 g. of α -naphthaldehyde, 1.2 g. of α -naphthylmethylamine, and 15 g. of di- α -naphthylmethylamine. *α -Naphthylmethylamine* is a pale yellow oil which fumes in air, b. p. 162—164°, at 12 mm.; its *hydrochloride* forms colourless leaflets. *Di- α -naphthylmethylamine* forms yellow, spherical crystal aggregates, m. p. 62°, decomposing when distilled. Its salts are very sparingly soluble, and the nitrate can be used for the gravimetric estimation of nitric acid (cf. this vol., ii, 577). When the reduction is carried out at about twice the above dilution, naphthaldehyde is not formed, but a considerable quantity of α -naphthylcarbinol is obtained. The reduction of β -naphthonitrile does not go to completion, only about 70% of the theoretical quantity of hydrogen being absorbed. The cause of this was found to be the sparing solubility of the Schiff's base formed by condensation of β -naphthaldehyde with the primary amine; the Schiff's base was precipitated from solution and escaped further reduction. The products of reduction of 50 g. of β -naphthonitrile were 5.4 g. of di- β -naphthylmethylamine, 25.0 g. of Schiff's base, and 7.5 g. of β -naphthylcarbinol. *β -Naphthylmethyl- β -naphthylideneamine*, $C_{10}H_7 \cdot CH:N \cdot CH_2 \cdot C_{10}H_7$, crystallises in lustrous scales, m. p. 175°. *Di- β -naphthylmethylamine* crystallises in spherical aggregates of needles, m. p. 80°. Its salts are very sparingly soluble. E. H. R.

Action of Heat on the Acids obtained from French and American Resins by Crystallisation. E. KNECHT (*J. Soc. Dyers and Col.*, 1923, 39, 338—340).—The author's previous conclusion that resin consists mainly of anhydrides (Knecht and Hibbert, A., 1919, i, 338) of the formula $(C_{20}H_{29}O_2)_2O$ is defended and additional evidence adduced in favour of this contention. *l*- and *d*-Acids of m. p. 161° obtained from the resins by repeated recrystallisation and further purification were heated in a current of carbon dioxide. The presence of water in the cool parts of the tube was evident when the temperature had reached 145°, and about half of both *d*- and *l*-acids was found to have melted. The indefinite melting points of resin acids is therefore ascribed to the formation of anhydrides. H. C. R.

Higher Terpene Compounds. XIII. The Effect of Higher Temperatures on the Pine Resin Acids. L. RUZICKA and H. SCHINZ (*Helv. Chim. Acta*, 1923, 6, 833—846).—The statement of Knecht and Hibbert that when resin acids from American and French resins are heated for some hours at 180° in a current of

carbon dioxide they are converted into anhydrides (A., 1919, i, 338) does not accord with the observation of Ruzicka and Meyer that by distillation of colophony, involving heating at 250–260° for four hours, the resin acids themselves are obtained with no trace of anhydride (A., 1922, i, 547). Repetition of Knecht and Hibbert's experiment with pure abietic acid showed that no anhydride formation occurred. When abietic acid was heated at 300° for eight hours, decomposition took place, resulting in the formation of 0.28 mol. of water, 0.21 mol. of carbon dioxide, 0.06 mol. of carbon monoxide, 0.05 mol. of methane, and 0.02 mol. of hydrogen per mol. of abietic acid. The residue consisted of hydrocarbons and a mixture of acidic substances evidently formed by loss of hydrogen or of methane from abietic acid. The hydrocarbons were a mixture of abietene, $C_{19}H_{30}$, and abietin, $C_{19}H_{28}$. In all probability, anhydride formation takes place to some extent when abietic acid is heated above 250°. The anhydride cannot be distilled, but decomposes according to the equation $(C_{19}H_{29}CO)_2O \rightarrow C_{19}H_{28} + C_{19}H_{30} + CO + CO_2$. This is by no means the only reaction occurring, for the quantity of abietene formed exceeds the abietin, as it does in the distillation of American colophony. The decomposition of *d*-pimaric acid, from French colophony, when heated at 300°, appears to take a similar course, but the products have not been identified.

E. H. R.

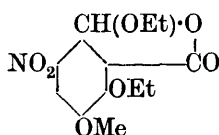
Iodo-derivatives of *p*-Hydroxybenzoic Acid. P. BRENANS and C. PROST (*Compt. rend.*, 1923, **177**, 768–770).—3-Iodo-4-hydroxybenzoic acid (m. p. 173°, decomposing at about 200°), was prepared from 3-amino-4-hydroxybenzoic acid. The new acid forms an *acetyl* derivative, m. p. 172°, and is converted by a mixture of ethyl alcohol and sulphuric acid into the *ethyl* ester (m. p. 117°) soluble in sodium carbonate and decomposing barium carbonate. 3:5-Di-iodo-4-hydroxybenzoic acid (subliming and decomposing at 230° without melting) was obtained by the action of iodine, in presence of alcohol and mercuric oxide on the above iodo-acid or on *p*-hydroxybenzoic acid, a little 2:4:6-tri-iodophenol also being produced. The di-iodo-acid forms an *acetyl* derivative, m. p. 225°, and is converted by alcohol and sulphuric acid into the *ethyl* ester, m. p. 123°, which decomposes barium carbonate and dissolves in aqueous sodium carbonate.

E. E. T.

Derivatives of Nitro-opianic Acid. RUDOLF WEGSCHEIDER and NOE L. MÜLLER (*Annalen*, 1923, **433**, 33–48).—The action of acetyl nitrate on opianic acid in cold acetic anhydride solution gives nitro-opianic anhydride, *nitro-opianic acid nitrate*, small, colourless, glistening, prismatic needles, m. p. 108–109°, and nitro-opianic acid acetate. The action of boiling methyl alcohol on the nitrate, or of boiling methyl-alcoholic hydrogen chloride on the acetate, gives methyl *ψ*-nitro-opianate. The acetate is also formed by heating opianic acid (4 parts), sodium acetate (4 parts), and acetic anhydride (10 parts) (Leibermann and Kleemann, A., 1887, 47), but if the following proportions are taken, 2 parts, 3 parts, and 10 parts, respectively, and the mixture is heated at 175° for six hours, the product is an intensely yellow *sodium* salt,

u u 2

which explodes on heating. This has probably a quinonoid structure; it is converted by means of glacial acetic acid or hydrochloric acid into *nitromethylnoropianic acid acetate*, small, iridescent leaflets, m. p. 204—205°, the yellow *silver* salt of which is converted by contact with cold methyl iodide into nitro-opianic acid acetate. Nitromethylnoropianic acid reacts with boiling acetyl chloride to give *acetylnitromethylnoropianic acid acetate*, glistening leaflets (monoclinic, von Lang), m. p. 145—146°, the reverse change being effected by the action of boiling 0.1*N*-potassium hydroxide solution. This acetate is converted by boiling with water into nitromethylnoropianic acid acetate. Methyl *n*-nitro-opianate diacetate (monoclinic, von Lang) (Wegscheider and Müller, A., 1908, i, 896) is converted by the action of warm ethyl-alcoholic hydrogen chloride, or of warm benzene-alcoholic sodium ethoxide, into ethyl ψ -nitro-



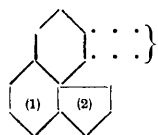
opianate. The latter, which need not be isolated, is converted by means of an excess of sodium ethoxide into the ψ -ethyl ester (annexed formula) (short, white needles, m. p. 87—89°) of 6-nitro-4-methoxy-3-ethoxyphthalaldehydic acid, m. p. 174—175° (ψ -methyl ester, felted white needles, m. p. 123°). The ψ -ethyl ester is obtained from the acid by boiling it with ethyl-alcoholic hydrogen chloride. The aldehydic acid is converted by the action of boiling, fuming hydrochloric acid into nitromethylnoropianic acid; the reverse change is brought about by keeping the pale sulphur-yellow *silver* salt of nitromethylnoropianic acid in contact with ethyl-alcoholic ethyl iodide, but if a benzene solution of methyl iodide is used, the product is *methyl n-nitromethylnoropianate*, glistening, yellow needles, m. p. 136—139°. The corresponding ψ -methyl ester, large, colourless tablets, m. p. 177—178°, is obtained by keeping a methyl-alcoholic solution of the acid, saturated with hydrogen chloride. The egg-yellow *potassium*, scarlet *dipotassium*, and greenish-yellow, explosive *disilver* salts of nitromethylnoropianic acid are described.

W. S. N.

Ring-chain Tautomerism. VIII. The Effect of the cyclo-Hexane Nucleus on the Carbon Tetrahedral Angle. ERIC WILLIAM LANFEAR and JOCELYN FIELD THORPE (T., 1923, 123, 2865—2870).

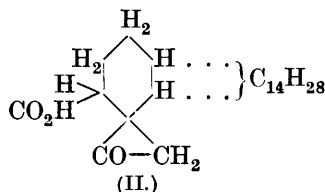
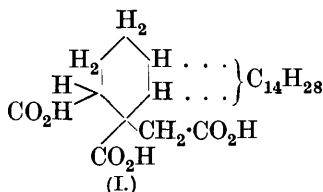
Succinylfluorescein and its Derivatives. SIDNEY BIGGS and FRANK GEO. POPE (T., 1923, 123, 2934—2943).

The Number of Atoms in Ring II of the Molecules of Cholesterol and Bile Acids. A. WINDAUS, A. ROSENBAACH, and TH. RIEMANN (Z. physiol. Chem., 1923, 130, 113—125).—Ring



(2) of the cholesterol molecule (annexed skeleton formulæ) may contain five or six carbon atoms. By successive oxidation of cholesterol a tribasic acid, $C_{25}H_{42}O_6$, is obtained, and this acid loses a molecule of carbon dioxide and one of water to form the monobasic acid, $C_{24}H_{40}O_3$, of which (III) represents the methyl ester. This acid on oxidation yields a tribasic acid, $C_{24}H_{40}O_6$ (Windaus, A., 1912, i, 449), which,

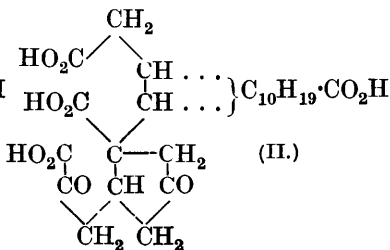
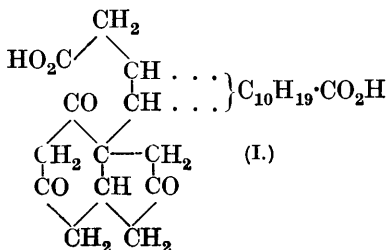
assuming a five-membered ring, would have the formula (I). When this tribasic acid is heated at 215° for thirty minutes, a ketonic acid, $C_{23}H_{38}O_3$, is formed, and when this ketonic acid is oxidised a tribasic acid, $C_{23}H_{38}O_6$, m. p. $180-185^{\circ}$, is obtained (*trimethyl* ester, needles, m. p. 74°). This acid loses carbon dioxide when boiled in acetic acid containing hydrochloric acid; it is therefore a derivative of malonic acid. If ring II in cholesterol were six-membered it would not be possible for this substance to be a malonic acid derivative. The acid formed on heating the acid $C_{23}H_{38}O_6$ has the formula $C_{22}H_{38}O_4$, needles, m. p. 210° (*anhydride*, leaflets, m. p. 124°). The monobasic acid, $C_{24}H_{40}O_3$, forms a *methyl* ester, needles, m. p. 65° , difficult to hydrolyse, and the monobasic acid, $C_{23}H_{38}O_3$, also forms a *methyl* ester, prisms, m. p. 70° , but this is easily hydrolysed. From this fact it is considered that formula



(II) represents the most probable constitution of the acid $C_{23}H_{38}O_3$. This is confirmed by the fact that oxidation of the *methyl* ester of the acid $C_{24}H_{40}O_3$, which has the formula (III), needles, m. p. 65° , results in formation of the *monomethyl* ester of the tri-carboxylic acid $C_{24}H_{40}O_6$, m. p. 189° , which on distillation in a high vacuum yields the acid, $C_{23}H_{38}O_3$, itself (*semi-carbazone*, m. p. 226°). The acid $C_{24}H_{40}O_3$, m. p. 147° , when dissolved in acetic acid and treated with zinc amalgam and hydrochloric acid, is reduced to form an acid, $C_{24}H_{42}O_2$, leaflets, m. p. 156° , which is also formed when the lactone obtained by oxidation of the acid $C_{24}H_{40}O_3$ is reduced by Clemmensen's method. The *methyl* ester of this acid, $C_{25}H_{44}O_2$, melts at 56° , and forms leaflets with a nacreous lustre.

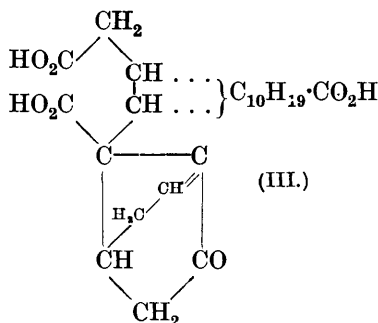
W. O. K.

Bile Acids. XVI. Biliobanic Acid. HEINRICH WIELAND and LEW FUKELMAN (*Z. physiol. Chem.*, 1923, 130, 144—151).—



Biliobanic acid, $C_{24}H_{34}O_7$, obtained from cholic acid on oxidation

with bromine in alkaline solution, appears to have the formula (I).

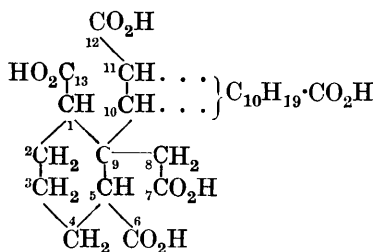


fuming nitric acid. *iso*Cilicianic acid, when treated with concentrated sulphuric acid, yields an *unsaturated acid*, $\text{C}_{23}\text{H}_{32}\text{O}_7$, m. p. 320—321°, to which the annexed formula (III) is assigned. W. O. K.

Bile Acids. XVII. *iso*Deoxycholic Acid. HEINRICH WIELAND, ERNST HONOLD, and JOSÉ PASCUAL-VILA (*Z. physiol. Chem.*, 1923, **130**, 326—337).—Ethyl cholate dissolved in ether and treated with carbonyl chloride yields a *chloro-carbonyl ester*,

$\text{COCl} \cdot \text{O} \cdot \text{C}_{23}\text{H}_{38}\text{O}_2 \cdot \text{CO}_2\text{Et}$,
m. p. 140—141° (decomp.). When fused, this compound loses carbon dioxide and 3-chloro-7:13-dihydroxycholanolic acid,

$\text{C}_{24}\text{H}_{39}\text{O}_4\text{Cl}$,
colourless needles, m. p. 196—197°, is formed; this may be converted by sodium in amyl-alcoholic solution into the unsaturated 7:13-dihydroxycholenic acid, $\text{C}_{24}\text{H}_{38}\text{O}_4$, compact, glistening prisms, m. p. 216—217°. This compound is dimorphous, also forming slender needles, m. p. 181°, and it is reduced in acetic acid solution by hydrogen in presence of palladium to form β -isodeoxycholic acid (7:13-dihydroxycholenic acid), slender



needles, m. p. 226—227°. Oxidation of this acid with chromic acid results in the formation of diketocholanolic acid, m. p. 171—172° (ethyl ester, m. p. 149—151°). When this acid is oxidised by fuming nitric acid, β -isocholoidanic acid (annexed formula), $\text{C}_{24}\text{H}_{36}\text{O}_{10}$, is obtained, fine needles, m. p. 273° (decomp.), whilst on oxidation with potassium permanganate, the first product is ψ -deoxybilianic acid, $\text{C}_{24}\text{H}_{36}\text{O}_7$, which on further oxidation yields β -isocholoidanic acid. *Methyl chlorocarbonyl deoxycholate*, from methyl deoxycholate and carbonyl chloride, forms needles, m. p. 137—138° (decomp.), whilst the corresponding derivative of ethyl deoxycholate melts at 114° (decomp.). *Methyl 3-chloro-7-hydroxycholate*, colourless needles, m. p. 121—122°,

It crystallises in long, slender needles, sometimes rhombohedral prisms, m. p. 303°, $[\alpha]_{\text{D}}^{16} - 27.2^\circ$. It forms a *sodium salt*, $\text{C}_{24}\text{H}_{32}\text{O}_7 \cdot \text{Na}_2$, a *dimethyl ester*, $\text{C}_{26}\text{H}_{38}\text{O}_7$, long needles, m. p. 186—187°, and an *oxime*, $\text{C}_{24}\text{H}_{35}\text{O}_7\text{N}$, needles, m. p. 196°. Further oxidation yields *isocilicianic acid*, (II), $\text{C}_{24}\text{H}_{34}\text{O}_{10}$, long needles, m. p. 316—317°, which is very stable towards oxidising agents. This tribasic acid is also obtained by direct oxidation of cholic acid with

results from heating methyl chlorocarbonyldeoxycholate. The chlorocarbonyl ester of cholesterol melts at 117—118°, and decomposes to form cholesteryl chloride, m. p. 86—90°. The chlorocarbonyl esters dissolved in ether, benzene, or ethyl acetate on treatment with ammonia yield the corresponding *urethanes*—that of methyl cholate, fine felted needles, m. p. 142° (*methyl phenetidine-urethane cholate*, needles, m. p. 172—173°); of methyl deoxycholate, m. p. 150—151°, and that of cholesterol, long needles, m. p. 217°. W. O. K.

The Synthesis of Hæmotricarboxylic Acid and a Hæmotetracarboxylic Acid. WILLIAM KÜSTER [with A. HUGEL] (*Z. physiol. Chem.*, 1923, **130**, 1—23).—Ethyl cyanomethylsuccinate, b. p. 167—168°/25 mm., prepared by the condensation of ethyl bromoacetate with ethyl cyanoacetate in alcoholic solution in presence of sodium ethoxide, reacts with ethyl β -iodopropionate or ethyl β -chloropropionate in presence of sodium ethoxide to yield *ethyl γ -cyanopentane- $\alpha\gamma\delta$ -tricarboxylate*, a colourless, viscid oil, b. p. 208°/28 mm. When heated at 130—135° with alcohol containing sulphuric acid, *ethyl pentane- $\alpha\gamma\delta$ -tetracarboxylate* is obtained, a colourless, viscid liquid, b. p. 222°/12 mm., and from this ester on hydrolysis there are obtained two *pentane- $\alpha\gamma\delta$ -tricarboxylic acids* (*hæmotricarboxylic acids*). One has m. p. 177°, the other m. p. 140—141°; they are presumably the *cis*- and *trans*-forms, and are also obtained directly from the cyano-derivative by boiling it with dilute sulphuric acid. Attempts to resolve these acids through their brucine salts were unsuccessful. The following *brucine* salts of the acid, m. p. 177°, were obtained: $(C_{23}H_{26}O_4N_2)_2 \cdot C_8H_{12}O_6 \cdot 4H_2O$, long, prismatic needles, m. p. 154—156°, $[\alpha]_D^{30} -29.5^\circ$ ($c=2.5\%$ in water);

$(C_{23}H_{26}O_4N_2)_3 \cdot C_8H_{12}O_6 \cdot 4H_2O$, thin, prismatic needles, m. p. 148—151°, $[\alpha]_D^{30} -30.97^\circ$ ($c=10\%$ in water), and of the acid, m. p. 140—141°, the *brucine* salt $(C_{25}H_{26}O_4N_2)_2 \cdot C_8H_{12}O_6$, $[\alpha]_D^{30} -20.31^\circ$ to -26.04° ($c=2.5-3\%$ in water). The product of the bromination with phosphorus and bromine of the acid, m. p. 177°, is a mixture. If this mixture is hydrolysed with sodium hydroxide in presence of copper, an unsaturated tricarboxylic acid, Δ^5 -*pentene- $\alpha\gamma\delta$ -tricarboxylic acid*, may be isolated. This substance forms fine, prismatic needles, m. p. 112°, soluble in water, alcohol, ether, or acetic acid (*silver* salt, $C_8H_7O_6Ag_3$). A *diethyl* ester, $C_{12}H_{18}O_6$, b. p. 206°/20 mm., is formed on boiling with absolute alcohol containing sulphuric acid, and on reduction of the acid with 2% sodium amalgam, the hæmotricarboxylic acid, m. p. 176—177°, was again obtained. In addition to this acid, a syrup was obtained, yielding an *acid*, isolated as the *calcium* salt, $(C_8H_7O_7)_2Ca_3$, and *silver* salt, $(C_8H_7O_7Ag_3)$, and on reduction a new salt, $C_8H_9O_7Ag_3$, was also obtained.

Similarly, when the acid, m. p. 140—141°, is brominated an isomeric *unsaturated acid*, $C_8H_{10}O_6$, rosettes of needles, m. p. 114° (*silver* salt, $C_8H_7O_6Ag_3$), may be obtained from the product. This forms a *diethyl* ester, $C_{12}H_{18}O_6$, b. p. 199—201°/15 mm. From another fraction of the bromination product, when it is boiled with

40% potassium hydroxide solution, an acid is obtained, forming the *calcium* salt, $(C_8H_7O_7)_2Ca_3$, and the *silver* salt, $C_8H_7O_7Ag_3$, and on reduction a *calcium* salt, $(C_8H_9O_7)_2Ca_3$.

Condensation of ethyl cyanotricarballylate with ethyl iodo-propionate results in the formation of ethyl γ -cyanopentane- $\alpha\beta\gamma$ -tetracarboxylate, colourless oil, b. p. 227—228°/8—10 mm., and this when hydrolysed with concentrated hydrochloric acid yields pentane- $\alpha\beta\gamma$ -tetracarboxylic acid (*hæmotetracarboxylic acid*), small, prismatic needles, m. p. 148° (*silver* salt, $C_9H_8O_8Ag_4$; *copper* salt, $C_9H_8O_8Cu_4$, emerald-green precipitate; *barium* salt, $[C_9H_8O_8]_2Ba_4$). The *anhydride*, $C_9H_{10}O_7$, was obtained on treatment of the acid with acetyl chloride. It forms a white powder, m. p. 220—221°. No pure product other than this hæmotetracarboxylic acid was obtained from the hydrolysis mixture. W. O. K.

Production of Benzaldehyde and Benzoic Acid. CARBIDE AND CARBON CHEMICALS CORPORATION (Brit. Pat. 197319).—A high yield of benzaldehyde or benzoic acid, or a mixture of the two, is obtained by the interaction of molecular oxygen (*e.g.*, air, oxygen) and dibenzyl, at a temperature of from 150° to 204°, in the absence of a catalyst. W. T. K. B.

Substitution in Vicinal Trisubstituted Benzene Derivatives. II. WILLIAM DAVIES and LEON RUBENSTEIN (T., 1923, 123, 2839—2852).

The Solubility of the Hydroxybenzaldehydes and the Hydroxytolualdehydes NEVIL VINCENT SIDGWICK and ERIC NEWMARCH ALLOTT (T., 1923, 123, 2819—2826).

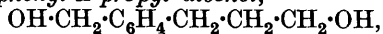
Benzopolymethylene Compounds. X. Oxidation of Δ^1 -Dihydronaphthalene by Ozone. JULIUS VON BRAUN and FRIEDRICH ZOBEL (*Ber.*, 1923, 56, [B], 2139—2142).— Δ^1 -Dihydronaphthalene (*cf.* von Braun and Kirschbaum, A., 1920, i, 407) is readily oxidised to β -*o*-aldehydophenylpropaldehyde,



which is converted by dilute sulphuric acid into indene-2-aldehyde, $C_6H_4 \langle \begin{smallmatrix} CH \\ CH_2 \end{smallmatrix} \rangle C \cdot CHO$. This is the first member of the indene series to be isolated which has a reactive group situated on the five-membered ring.

Δ^1 -Dihydronaphthalene dissolved in glacial acetic acid is treated with ozone and the di-ozonide decomposed by means of zinc dust. The product on distillation yields a resinous residue and β -*o*-aldehydophenylpropaldehyde, a colourless liquid, b. p. 153°/13 mm., d_4^{18} 1.142, n_D^{15} 1.563, which becomes somewhat discoloured, but not otherwise appreciably altered when preserved. It does not readily yield crystalline derivatives with the customary reagents for aldehydes, but with aniline it gives the *dianil*, $C_{22}H_{20}N_2$, pale yellow crystals, m. p. 154°. It is oxidised by permanganate in alkaline suspension to *o*-carboxyphenylpropionic acid, m. p. 166°. It is

reduced by aluminium amalgam in the presence of moist ether to γ -o-hydroxymethylphenyl-n-propyl alcohol,



a very viscous, pale yellow liquid, b. p. about $185^\circ/13$ mm., which, during distillation, suffers partial, intramolecular loss of water with production of Δ^1 -dihydronaphthalene. The aldehyde is converted by warm, dilute sulphuric acid (10%) into resinous products, (?) indene and *indene-2-aldehyde*. The yield of the latter is nearly 50% of that theoretically possible. It crystallises in colourless needles, m. p. 50 — 51° , which decompose rapidly when preserved. It is relatively stable towards acids, but very sensitive towards alkalis. The following derivatives are described: the *anil*, yellow leaflets, m. p. 99° ; the *p-tolil*, m. p. 122° ; the *oxime*, colourless needles, m. p. 125 — 127° ; the *semicarbazone*, m. p. 237° . It does not yield a well-crystallised derivative with phenylhydrazine or diphenylmethanedimethyldihydrazine. H. W.

3 : 4-Dimethylcyclopentan-1-one. FRANZ FALTIS and HERMANN WAGNER (*Annalen*, 1923, **433**, 103—112).—3 : 4-Dimethylcyclopentan-1-one may be encountered as a product of the oxidation of hydrobixin; the ketone, which has never been described, has therefore been synthesised.

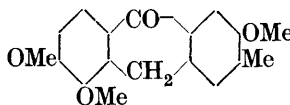
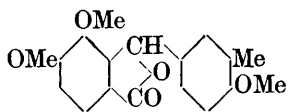
The action of a 15% solution of sodium iodide in acetone, at 100° , on β -bromobutyric acid, gives β -iodobutyric acid, which has m. p. 32° (corr.) (cf. Marx, *Diss.*, Freiburg i. B., 1881). A mixture of β -iodobutyric acid and two-thirds its weight of crotonic acid is heated at 110° , finally at 135 — 140° , with copper powder and ground pumice; the products of this reaction are two forms of $\beta\beta'$ -dimethyladipic acid, (a) monoclinic leaflets, m. p. 133° (corr.), (b) snow-white, microcrystalline crusts, m. p. 104 — 105° (corr.), sinters 102° . From each acid a ketone is obtained by heating with acetic anhydride. The acid, m. p. 133° , gives a ketone, of which the *semicarbazone* forms colourless, slender, glistening needles, m. p. 175.5 — 176° (corr.), sinters and partly decomp. 171° ; the *semicarbazone* of the ketone from the acid, m. p. 104 — 105° , forms long, flat, lustrous needles, m. p. 201 — 202° (corr.) (decomp.), sinters 195° .

W. S. N.

Condensation Products of Hemipinic Anhydride with Phenol Ethers and their Conversion into Anthracene Derivatives. A. BISTRZYCKI and K. KRAUER (*Helv. Chim. Acta*, 1923, **6**, 750—770).—It was shown by Bistrzycki and Zen-Ruffinen (A., 1920, i, 436) that a number of phenylphthalide derivatives, including 3-*p*-hydroxyphenylmeconine, 3-*p*-methoxyphenylmeconine, and similar substances, cannot be reduced to the corresponding diphenylmethane derivative. It was suspected that reduction was hindered or prevented by the para-methoxy-group present in all these compounds, and this idea has now been confirmed by the preparation of a number of ψ -meconine derivatives having the para-position free. These compounds, which were obtained by condensing hemipinic anhydride with *o*- and *m*-tolyl methyl

ethers and with veratrol and reducing the ketonic acids to the phthalides, can be readily reduced to the diphenylmethane derivatives.

4' : 5 : 6-Trimethoxy-3'-methylbenzophenone-2-carboxylic acid, obtained by condensing hemipinic anhydride with *o*-tolyl methyl ether by means of aluminium chloride, forms colourless, six-sided prisms, m. p. 218—219.5°. Its constitution follows from the work of Bistrzycki and de Schepper on the condensation of hemipinic anhydride with anisole (A., 1899, i, 151). Reduction of the compound with zinc and hydrochloric acid in acetic acid solution gives 6'-methoxy-*m*-tolyl- ψ -meconine (annexed formula), forming star-shaped aggregates of prisms, m. p. 128.5—129.5°. Reduction of this compound, or of the ketone, with finer zinc produces 4' : 5 : 6-trimethoxy-3'-methyldiphenylmethane-2-carboxylic acid, crystallising in fine needles, m. p. 129—130°. When this is dissolved in cold concentrated sulphuric acid it is rapidly converted into 3 : 7 : 8-trimethoxy-2-methyl-10-anthrone (annexed formula), which crystallises in bunches of colourless needles, m. p. 204—205°. This compound has no tendency to pass into the anthranol form, but by acetylation it gives 10-acetoxy-3 : 7 : 8-trimethoxy-2-methylanthracene, forming microscopic, yellow needles, m. p. 140°. Oxidation of the anthrone with chromic acid gives 3 : 7 : 8-trimethoxy-2-methylanthraquinone, yellow needles, m. p. 218°, which, when demethylated with aluminium chloride, gives 3 : 7 : 8-trihydroxy-2-methylanthraquinone, reddish-brown needles, m. p. 318—320°. When distilled with zinc dust, this gives 2-methylanthraquinone, which confirms the constitution of the anthrone given above; the alternative form of ring closure would give a 1-methylanthraquinone derivative. The constitution of the trihydroxymethylanthraquinone is also confirmed by its absorption spectrum, which, being very similar to that of flavopurpurin, confirms the methylflavopurpurin formula. 3 : 7 : 8-Triacetoxy-2-methylanthraquinone forms yellow needles, m. p. 204—205°.

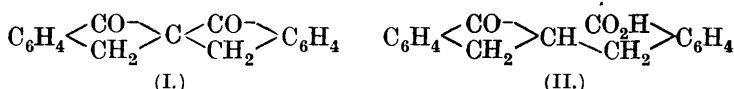


4' : 5 : 6-Trimethoxy-2'-methylbenzophenone-2-carboxylic acid, from hemipinic anhydride and *m*-tolyl methyl ether, has m. p. 167—169°, and forms a white, amorphous silver salt, sensitive to light. 6'-Methoxy-*o*-tolyl- ψ -meconine crystallises in fine, white needles, m. p. 124—125°, and 4' : 5 : 6-trimethoxy-2'-methyldiphenylmethane-2-carboxylic acid forms colourless, prismatic needles, m. p. 136—138°, softening from 130°. From this was obtained 3 : 7 : 8-trimethoxy-1-methyl-10-anthrone, colourless needles, m. p. 163—164°, which on acetylation gives 10-acetoxy-3 : 7 : 8-trimethoxy-1-methylanthracene, yellow needles, m. p. 120°. Oxidation of the anthrone gives 3 : 7 : 8-trimethoxy-1-methylanthraquinone, yellow needles, m. p. 197°, giving by demethylation 3 : 7 : 8-trihydroxy-1-methylanthraquinone, very small, brown needles, m. p. above 330°.

Hemipinic acid was condensed with veratrole by Bentley and

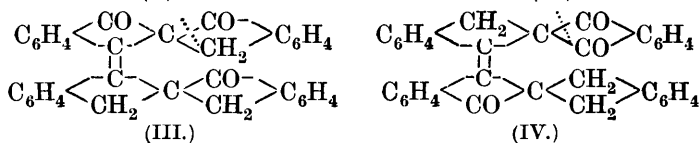
Weizmann (T., 1908, 93, 435), whose results are confirmed. Reduction of the condensation product gives 5':6'-dimethoxyphenyl-ψ-meconine (annexed formula), colourless, microscopic needles, m. p. 132.5—133.5°, and 3':4':5:6-tetramethoxydiphenylmethane-2-carboxylic acid, colourless, microscopic needles, m. p. 145—147°. 1:2:6:7-Tetramethoxy-10-anthrone forms yellow, prismatic needles, m. p. 174—175°, and 10-acetoxy-1:2:6:7-tetramethoxyanthracene forms yellow, stellate aggregates of leaflets, m. p. 183—184°. The tetramethoxyanthraquinone obtained by Bentley and Weizmann (*loc. cit.*) when demethylated gives 1:2:6:7-tetrahydroxyanthraquinone, brownish-orange needles, m. p. above 330°. E. H. R.

Spirans. VIII. Dibenzylindandione and the Constitution of Coloured Anhydroindandiones. DAN RADULESCU and I. TANASESCU (*Bul. Soc. Ştiinţe Cluj*, 1922, 1, 185—191; from *Chem. Zentr.*, 1923, iii, 137—138; cf. A., 1913, i, 37).—It has been shown (*loc. cit.*) that the spiran I is hydrolysed by an alkali to the acid II, from which the spiran, I, can again be obtained by elimination of water. The coloured anhydro-derivatives III and IV behave differently. They give an intense blue coloration with



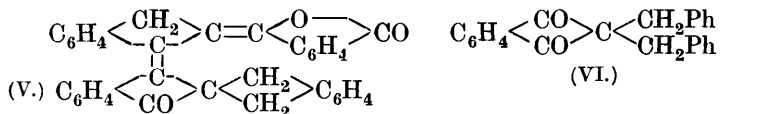
(I.)

(II.)



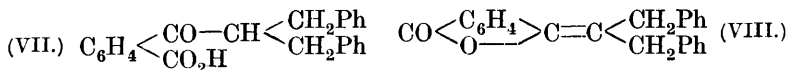
(III.)

(IV.)



(V.)

(VI.)



alkali hydroxides. The structural analogy of the two compounds is shown by the similarity of their absorption spectra. Both compounds give acids of the same formula, $\text{C}_{34}\text{H}_{24}\text{O}_4$, probably by fission at the dotted line. The acid obtained from the compound IV does not apparently yield the spiran again on dehydration, but a compound of different properties having the composition indicated by formula V. The authors synthesised the compound VI, which by hydrolysis yields the compound VII. The latter is very similar to II, but on dehydration yields VIII. The formation of a lactone ring is to be expected in this case on stereochemical grounds. In the case of the acid II, lactone formation results in a ring with seven carbon atoms which by rearrangement gives the

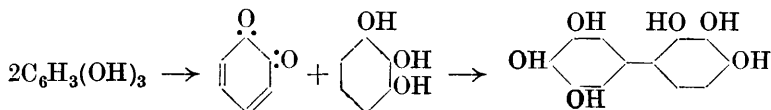
more stable system I. The compound VI, like the dialkylindandiones, does not give ketone reactions and yields with strong sulphuric acid anhydro-compounds analogous to III and IV.

2:2-Dibenzylindandione (VI) is obtained from the reaction of sodium ethoxide (2 mols.) with diketohydrindene (1 mol.) and benzyl chloride (2 mols.). It forms needles, m. p. 158—158.5°. By treatment with potassium hydroxide and subsequent acidification, β -diphenylpropanephthaloylic acid (VII) is obtained as an amorphous, transparent mass. Dehydration of the last compound gives the *keto-lactone* (VIII) which forms snow-white, silky crystals, with m. p. 131°. G. W. R.

Products of the Destructive Distillation of Sodium Anthraquinone-1- and -2-sulphonates. ARTHUR GEORGE PERKIN and WILLIAM GAWAN SEWELL (T., 1923, 123, 3032—3040).

The Constitution of Purpurogallin. RICHARD WILLSTÄTTER and HUGO HEISS (*Annalen*, 1923, 433, 17—33).—Perkin's formula for purpurogallin (P., 1913, 29, 354) does not account for the indifference of the carbonyl group in its ethers, and does not help to elucidate the mechanism of its formation by the oxidation of pyrogallol. An alternative formula, free from these defects, is now suggested.

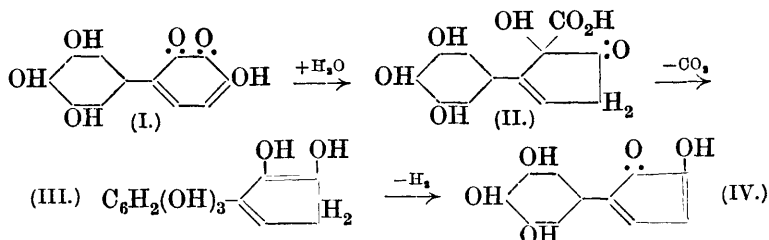
The first step in the formation of purpurogallin is the production of 3-hydroxy-*o*-benzoquinone. A dimeric form of this substance has been isolated by Perkin and Steven (T., 1906, 89, 802; cf. Perkin, *loc. cit.*, also T., 1913, 103, 650, and Willstätter and Müller, A., 1911, i, 728) by the oxidation of pyrogallol by means of quinone, or of amyl nitrite and acetic acid; it is converted into purpurogallin with difficulty, by boiling with water. In the presence of an excess of pyrogallol, however, the hydroxyquinone can become stabilised in a different manner, isomerisation to 3:4:5-triketo- Δ^1 -cyclohexene being followed by condensation of the latter with a further molecule of pyrogallol. The product of this reaction,



a hexahydroxydiphenyl for which the above formula is preferred, is then oxidised to give an *o*-quinone (I), which undergoes a kind of benzilic acid rearrangement, similar to the formation of croconic acid from rhodizonic acid, with formation of the *cyclopentenone* derivative (II). Carbon dioxide is eliminated spontaneously from (II), and the resulting dihydroxypentadiene derivative (III) is then oxidised to purpurogallin (IV).

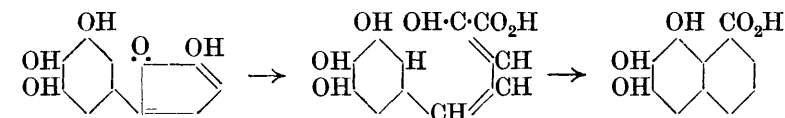
This explanation of the mechanism of the formation of purpurogallin receives support from the following facts. Purpurogallin monomethyl ether is formed by oxidising a mixture of pyrogallol and its 1-methyl ether, or of pyrogallol and 3-methoxy-*o*-quinone; the latter may be taken as such, or produced *in situ* by oxidising pyrogallol methyl ether. But 3-methoxy-*o*-quinone, which cannot

isomerise to a triketocyclohexane derivative, and therefore cannot undergo condensation to a diphenyl derivative, cannot be further



oxidised, alone, to purpurogallin dimethyl ether. Moreover, in the oxidation of gallic acid, from two molecules one molecule of carbon dioxide is eliminated. This is readily comprehensible,

because if the dicarboxylic acid (annexed formula), formed by the condensation of gallic acid with its *o*-quinone, passes next into the enol form, one carboxyl group will be spontaneously eliminated. Further transformation of the resulting monocarboxylic acid will give purpurogallincarboxylic acid. Purpurogallin is converted into the isomeride, purpurogallone (Perkin, *loc. cit.*) by heating with alkali. This is explained as being a second benzilic



acid transformation; the conversion of purpurogallincarboxylic acid into purpurogallonecarboxylic acid doubtless follows a similar course.

Incidentally, the *methyl* ester of purpurogallincarboxylic acid is prepared by direct esterification of the acid, or by the oxidation of methyl gallate in aqueous-alcoholic solution by means of peroxidase and hydrogen peroxide. It forms dark brownish-red, rhombic (or monoclinic or triclinic) prisms, decomp. $260-270^\circ$, after darkening at 240° . In the presence of alkali and air, it gives an intense blue coloration, which changes to cyanine-red on addition of mineral acid.

W. S. N.

Production of Dinitroperylenequinone. HANS PEREIRA (Brit. Pat. 199720).—Perylenequinone or mononitroperylenequinone is nitrated, *e.g.*, with a boiling mixture of glacial acetic acid and nitric acid (*d* 1.4). [Cf. *J.S.C.I.*, 1923, Dec.] W. T. K. B.

Steric Hindrance; Study of the Double Bond of some Ethylenic Camphor Derivatives by Means of Catalytic Hydrogenation. JEAN DÉTRIE (*Bull. Soc. chim.*, 1923, [iv], 33, 1263—1284).—Hydrogenation of *d*-ethylidenecamphor, *d*-hexahydrobenzylidenecamphor, *d*-benzylidenecamphor, *d*-methylsalicylidene-

camphor, *d*- and *l*-anisylidenecamphor in presence of finely divided platinum leads to the conclusion that the reduction of the ethylenic bond takes place more readily when it is situated between a ring and a side-chain than when between two rings. In the latter case, the velocity of hydrogenation depends on the position of substituents in the ring, being less when the substituent is in the ortho-position with respect to the carbon atom linked to the double bond than when the substituent occupies the para-position. The following are described: *o*-methoxyhexahydrobenzylcamphor, $C_{18}H_{30}O_2$, a syrupy liquid, b. p. 185—190°/12 mm., d^{20}_D 0.99, $[\alpha]_D^{20} +54^\circ$; hexahydroanisylcamphor, $C_{18}H_{30}O_2$, b. p. 185—190°/12 mm., d^{20}_D 0.98. H. J. E.

Demonstration of Tautomeric Forms by Means of Catalytic Reduction. GUIDO CUSMANO and ROSALBA BOCCUCCI (*Gazzetta*, 1923, 53, 649—657).—Reduction of buchu-camphor by means of hydrogen in presence of platinum black at the ordinary temperature yields two geometric isomerides of 3-hydroxytetrahydrocarvone, $CHMe < \begin{smallmatrix} CO-CH(OH) \\ CH_2-CH_2 \end{smallmatrix} > CHPr^3$, together with other products, including probably the glycol obtained by Kondakov and Bachtshéev (*A.*, 1901, i, 334) by reducing buchu-camphor by means of sodium amalgam. It is therefore evident that buchu-camphor does not react exclusively in accordance with the formula proposed by Semmler and McKenzie (*A.*, 1906, i, 373). Each of the two 3-hydroxytetrahydrocarvones yields the same two isomeric 3-bromotetrahydrocarvones, both of these giving tetrahydrocarvone on reduction.

Isomeride (1) of 3-hydroxytetrahydrocarvone is a mobile liquid, b. p. 234°, with a burning taste and the odour of mint; its *semicarbazone* forms colourless, rectangular plates, sometimes twinned, m. p. 180—181° (decomp.), and its *oxime*, long, colourless needles, m. p. 120—121°. *Isomeride* (2), obtained in only small amount, gives a *semicarbazone* which forms rosettes of prismatic crystals, m. p. 225° (decomp.), tends to undergo pulverisation, and rapidly becomes yellow in the light.

The liquid 3-bromotetrahydrocarvone, $CHMe < \begin{smallmatrix} CO-CHBr \\ CH_2-CH_2 \end{smallmatrix} > CHPr^3$, has b. p. 136—140°/5 mm.; the solid isomeride forms a lustrous, white powder, m. p. about 125°, and undergoes gradual alteration. T. H. P.

Piperitone. VI. The Reduction of Piperitone. REGINALD SLATER HUGHESDON, HENRY GEORGE SMITH, and JOHN READ (*T.*, 1923, 123, 2916—2925).

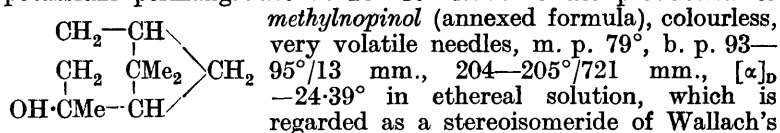
Pinane. A. LIPP (*Ber.*, 1923, 56, [B], 2098—2107).—The hydrogenation of pinene in the presence of nickel according to Sabatier and Senderens and of platinum according to Foken and Willstätter has been examined. Although the steric uniformity of the pinane thus produced is not established, the results point to the conclusion that the former method yields mainly *trans*-

derivatives with lower density and index of refraction, whereas the latter process gives *cis*-compounds with higher density and index of refraction (cf. Auwers, A., 1919, i, 578; Skita, A., 1920, i, 832). It is placed beyond doubt that the carbon skeleton of pinene remains intact in pinane.

A sample of pinene having $[\alpha]_D -38.08^\circ$ obtained from French oil of turpentine is converted by hydrogen in the presence of nickel at $220-230^\circ$ into pinane, $C_{10}H_{18}$, which, after being treated with alkaline potassium permanganate solution, has b. p. $162-164^\circ/720$ mm., $d_4^{17.5} 0.8519$, $n_D^{17.5} 1.45942$, $[\alpha]_D -16.1^\circ$; it is stable towards air or permanganate solution. In the presence of platinum black, *d*-pinene, $[\alpha]_D +47.5^\circ$, gives a pinane, b. p. $163-164^\circ/720$ mm., $d_4^{20} 0.8566$, $n_D^{20} 1.4624$, $[\alpha]_D +23.080$, whereas *l*-pinene gives a product, b. p. $164.8-165.8^\circ/716$ mm., $d_4^{20} 0.8562$, $n_D^{20} 1.4620$, $[\alpha]_D -18.9^\circ$. This product undergoes alteration in boiling point and particularly in density, although its composition remains unchanged when it is passed over nickel pumice at $200-205^\circ$.

The action of bromine on pinane dissolved in glacial acetic acid leads to the production of a tetrabromide, $C_{10}H_{16}Br_4$, a viscous, reddish-brown liquid which is possibly not homogeneous; it appears to be a monocyclic substance and therefore only indirectly related to pinane. In spite of the presence of the tetramethylene ring, pinane is very stable toward solutions of hydrogen chloride or bromide in glacial acetic acid, by which it is converted above 230° into non-homogeneous products. Hydriodic acid reduces it with difficulty to hydroaromatic substances containing small proportions of aromatic hydrocarbons. The behaviour of pinane thus resembles closely that of pinene.

The oxidation of pinane dissolved in glacial acetic acid by solid potassium permanganate at $28-30^\circ$ leads to the production of



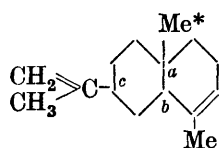
methylpinol (annexed formula), colourless, very volatile needles, m. p. 79° , b. p. $93-95^\circ/13$ mm., $204-205^\circ/721$ mm., $[\alpha]_D -24.39^\circ$ in ethereal solution, which is regarded as a stereoisomeride of Wallach's methylpinol, m. p. $58-59^\circ$ (cf. A., 1907, i, 936), since, like this substance, it is readily converted into terpen hydrate by cold dilute sulphuric acid. The acidic products of the oxidation of pinane include pinonic acid and small quantities of terebic acid. When treated with concentrated nitric acid (*d* 1.4) at the temperature of boiling water, pinane is converted into terebic, (?) norpinic, terephthalic, and oxalic acids. Pinonic acid is isolated from the products of the oxidation of pinane by chromium trioxide in glacial acetic acid solution. H. W.

The Nature of the Products of Fractionation of some Turpentine and the Constants of their Pure Constituents. G. DUPONT and L. DESALBRES (*Bull. Soc. chim.*, 1923, [iv], 33, 1252-1262).—A series of fractionations of pinenes obtained from both Bordeaux and Aleppo turpentine with an examination of the optical properties of the fractions obtained led to the conclusion

that a partial separation of the optically active isomerides had been effected. Similar results were obtained by a series of fractional crystallisations. Synthetic mixtures of active and inactive pinene yielded corroborative evidence. An investigation of inactive pinene showed it to be a single substance and not racemic. Physical constants of the turpentines from both sources are given from which calculations of those for the pure pinenes are made, the data used being based on the yields of nitrosochloride obtainable from the mixture.

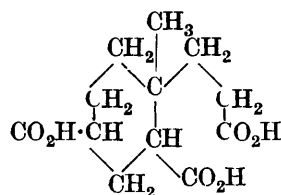
H. J. E.

Higher Terpene Compounds. XIV. Seline and the Sesquiterpene Alcohols of Celery-seed Oil. L. RUZICKA and M. STOLL (*Helv. Chim. Acta*, 1923, 6, 846—855).—In a previous



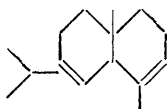
paper (this vol., i, 119), the constitution given in the annexed formula was provisionally assigned to α -selinene. The methyl group* attached to the quaternary carbon atom (a) might conceivably be attached to one of the other quaternary carbon atoms (b) or (c). It is now shown that the tricarboxylic acid obtained

by oxidation of α -selinene can be readily esterified and the triethyl ester can be readily hydrolysed. The ready esterification of the acid precludes the possibility that either carboxyl group is attached to a tertiary carbon atom, and since the only formula for α -selinene which will give such a tricarboxylic acid is that given above, the

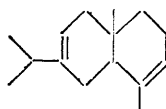


formula receives considerable support. The formula of the tricarboxylic acid is therefore fixed (annexed formula); its *ethyl* ester is a colourless, viscous oil, b. p. $170^{\circ}/0.2$ mm. When α -selinene is boiled with alcoholic sulphuric acid it undergoes isomerisation, the double bond of the *isopropylene* group migrating into the ring.

The product of the reaction is probably a mixture of δ - and ϵ -seline of the formulæ

 δ -Seline.

and

 ϵ -Seline.

The product forms a colourless oil, b. p. $130^{\circ}/12$ mm., d_4^{25} 0.9234; n_D^{25} 1.5167. By dehydrogenation with sulphur, it gives a much higher yield of eudalene than α -selinene. It is improbable that the two double bonds form a conjugated system in one ring. Attempts to hydrogenate the inverted selinene with sodium and amyl alcohol were unsuccessful, whereas this treatment will reduce a cyclic conjugated system.

From the fraction of celery-seed oil, b. p. 140 — $170^{\circ}/12$ mm., was isolated a small quantity, about 1% of the original oil, of a sesquiterpene alcohol, b. p. 157 — $164^{\circ}/12$ mm., having the com-

position $C_{15}H_{26}O$, $[\alpha]_D +4.7^\circ$, d_4^{13} 0.9618, n_D^{13} 1.5049. Evidence was obtained of the presence of a primary or secondary and of a tertiary alcohol. No naphthalenic hydrocarbon could be obtained by dehydrogenation with sulphur.

[With FR. LIEBL and S. PONTALTI.] *Attempts to dehydrogenate some sesquiterpenes.*—Hydrocarbons derived from hydrogenated naphthalene can be dehydrogenated with sulphur at 180 – 250° , and the naphthalene hydrocarbon can be detected by means of its picric acid compound. This procedure has been applied to caryophyllene, santalene, and cedrene, none of which is found to be a naphthalene derivative. E. H. R.

Higher Terpene Compounds. XV. The Sesquiterpene Fractions of Hyssop Oil, *Eucalyptus globulus* Oil, and Gurjun Balsam; and Guaiacol. L. RUZICKA, S. PONTALTI, and FR. BALAS (*Helv. Chim. Acta*, 1923, 6, 855–865).—The fraction of hyssop oil boiling between 110° and $180^\circ/12$ mm. contains both a hydrocarbon and alcohols of the sesquiterpene series. The hydrocarbon, $C_{15}H_{24}$, when finally freed from oxygen-containing compounds by treatment with permanganate, formed a colourless oil, b. p. $125^\circ/12$ mm., d_4^{17} 0.9116, n_D^{17} 1.5012. By dehydrogenation with sulphur, it was converted into cadaline, which was identified by its picrate and styphnate. The sesquiterpene of hyssop oil, forming 2–3% of the oil, is therefore of the cadinene type. The sesquiterpene alcohol fraction obtained by redistillation of the 110 – $180^\circ/12$ mm. fraction contained a primary or secondary alcohol, b. p. $150^\circ/12$ mm., and a tertiary alcohol (not reacting with phthalic anhydride), forming a green, viscous oil, b. p. 150 – $152^\circ/12$ mm., d_4^{17} 0.9784, n_D^{17} 1.5096. Its formula is probably $C_{15}H_{26}O$. By loss of water, it forms a sesquiterpene which appears to be the same as that described above. The sesquiterpene compounds of *Eucalyptus globulus* oil also belong to the cadinene type, unlike other eucalyptus oils, which are of the eudesmol type.

The sesquiterpene alcohol, guaiacol, obtained from gum guaiacum and other sources, does not react with phthalic anhydride and is therefore probably a tertiary alcohol. It can be dehydrated by heating with 85% formic acid, forming a sesquiterpene, b. p. 128 – $130^\circ/12$ mm., $[\alpha]_D -16.8^\circ$, d_4^{19} 0.9115, n_D^{19} 1.5022. By dehydrogenation of this oil with sulphur, a blue oil, b. p. 130 – $160^\circ/12$ mm. was obtained, giving a picrate crystallising in black needles, m. p. 115° . This does not correspond with a naphthalene hydrocarbon.

The sesquiterpenes from gurjun balsam, α - and β -gurjunene, are probably tricyclic compounds; but when the hydrochloride of gurjunene is treated with sodium acetate, the regenerated hydrocarbon has constants corresponding with a hydronaphthalene derivative, b. p. 123 – 129° , d_4^{15} 0.9233, n_D^{15} 1.5105, $[\alpha]_D -39.0^\circ$. By catalytic hydrogenation, it forms a hydrocarbon, $C_{15}H_{28}$, b. p. 125 – 130° , d_4^{15} 0.9021, n_D^{15} 1.4910. By dehydrogenation with sulphur, however, it did not give a naphthalene hydrocarbon. If it is, after all, a naphthalene derivative; its behaviour with sulphur is exceptional. E. H. R.

Properties of Loroglossin and its Products of Hydrolysis ; Glucose and Loroglossigenin. MARC BRIDEL and PIERRE DELAUNEY (*Compt. rend.*, 1923, **177**, 776—778).—Air-dried loroglossin, $C_{30}H_{42}O_{18}$, contains 6.26% of water, which it loses at 50° in a vacuum. When heated, it shrinks at 133.5°, and becomes transparent at 143.4°. It has $[\alpha]_D -45.65^\circ$, its solution has saponin-like properties, and gives no precipitate with Goulard's extract. On hydrolysis by emulsin, loroglossin affords 2 mols. of dextrose and 1 mol. of *loroglossigenin*, m. p. 77°, soluble in cold 5% sodium hydroxide solution, and giving a feeble violet coloration with ferric chloride. Loroglossigenin is non-reducing; its solution in concentrated sulphuric acid has the same colour as that of a similar solution of loroglossin. E. E. T.

The Constitution of Cantharidin. II. SAMUEL COFFEY (*Rec. trav. chim.*, 1923, **42**, 1026—1032; cf. this vol., i, 695).—The author's previous difficulty with the sulphonation of *p*-xylic acid has been overcome by modifications in the experimental method. The chief impurity in the product is sulphur, which was removed by conversion into thiosulphate, and finally by sublimation over molecular silver. Small quantities of dimethylhexahydrophthalic acid were obtained, however, and shown not to be identical with deoxycantharidic acid, thus showing that Gadamer's formula for cantharidin is correct. H. H.

The Preparation of Melanins containing Nitrogen. OSKAR ADLER (*Biochem. Z.*, 1923, **141**, 304—309).—By treatment of *p*-aminobenzoic acid with hydrogen peroxide and ferric chloride (this vol., i, 591), a 56% yield of *p*-aminobenzoic-melanic acid was obtained in the form of a black powder, soluble in alkalis or alcohol, and insoluble in dilute acid, ether, or light petroleum. On heating the melanic acid at 270° for one hour, it was converted into *p*-amino-benzoic-melanin, a black, amorphous powder. From tyrosine, by similar methods, *tyrosine-melanic acid* and *tyrosine-melanin* were prepared. Both melanins were insoluble in dilute alkalis, acids, or organic solvents. J. P.

Tannins. III. Turkish Tannin. P. KARRER, ROSA WIDMER, and MAX STAUB (*Annalen*, 1923, **433**, 288—305).—It is shown that Turkish tannin is even less homogeneous than Chinese tannin (cf. Karrer, Salomon, and Peyer, this vol., i, 352; also Fischer and Freudenberg, A., 1915, i, 437). By fractional precipitation by means of aluminium hydroxide, it can be separated into fractions, for which $[\alpha]_D$, in alcohol, varies between +15.7° and +43.7°. The yield of dextrose, obtained by hydrolysing for seventy hours by means of 5% sulphuric acid does not vary much from fraction to fraction, but the higher the rotation of the fraction taken the more gallic acid and the less ellagic acid are obtained. Since the dextrose and ellagic acid contents are not parallel, it is evident that the acid is not present as a simple glucoside. Moreover, if it were present in that form, the tannin fraction containing more of it should, on being methylated by means of diazomethane, and

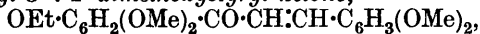
then acetylated by heating with sodium acetate and acetic anhydride, give a higher value when the acetyl was estimated; but this is not so. Thus it seems likely that the ellagic acid is present actually as part of the tannin molecule, perhaps partly replacing gallic acid.

In contrast with Chinese tannin, Turkish tannin is not fully galloylated. This is shown as follows. 1-Acetyltetra(triacetyl-galloyl)glucose can be obtained by the successive action of cold glacial acetic acid-hydrobromic acid, acetyl bromide, and acetic anhydride-sodium acetate at 100°, on samples of pentagalloylglucose obtained from penta(triacetylgalloyl)glucose by (a) acid hydrolysis, (b) alkaline hydrolysis. Samples prepared in the latter way contain free gallic acid, which actually separates during the first operation. Hence the deduction is drawn that pure 1-acetyltetra(triacetyl-galloyl)glucose can be obtained by the method outlined, provided the starting material contains some completely galloylated dextrose. But when these reactions are applied to various fractions of Turkish tannin, pure 1-acetyltetra(triacetylgalloyl)glucose, $[\alpha]_D + 43^\circ$ to $+45^\circ$, is not obtained; instead, more soluble products are obtained, for which $[\alpha]_D$ varies between $+56.7^\circ$ and $+77.88^\circ$, whilst the acetyl content varies between 43% and 44%. Clearly, the sugar (not necessarily dextrose, although this is assumed) present in Turkish tannin is combined with a varying number of gallic acid molecules. Probably 25–30% of the gallic acid is depsidic, the remainder being in direct combination with the dextrose molecule. W. S. N.

Tannins and Similar Substances. XIV. The Carbon Skeleton of Catechin. KARL FREUDENBERG and ERNST COHN (*Ber.*, 1923, **56**, [B], 2127–2131).—The identity of synthetic 2 : 4 : 6 : 3' : 4'-pentamethoxy- $\alpha\gamma$ -diphenylpropane with the ether obtained by Kostanecki and Lampe (*A.*, 1907, i, 73, 334; 1908, i, 86) from Gambier catechu has caused Freudenberg (*A.*, 1920, i, 752) to consider that the catechins are derived from $\alpha\gamma$ -diphenylpropane, but this hypothesis has been doubted by Nierenstein (*T.*, 1920, **117**, 972, 1156; 1921, **119**, 164; 1922, **121**, 601; this vol., i, 124). Additional evidence in favour of the conception is now adduced.

Tetramethyl-*d*-catechin is reduced by sodium and alcohol, and the crude phenol which is thereby produced is transformed by *p*-nitrobenzoyl chloride and sodium hydroxide into 6-*p*-nitrobenzoxy-2 : 4 : 3' : 4'-tetramethoxy- $\alpha\gamma$ -diphenylpropane, lemon-yellow prisms, m. p. 141–142°; this is hydrolysed by aqueous sodium hydroxide solution to 2-hydroxy-4 : 6 : 3' : 4'-tetramethoxy- $\alpha\gamma$ -diphenylpropane, coarse, colourless prisms, m. p. 89–90°, which is thus obtained in the crystalline condition. It is converted by ethyl sulphate and potassium hydroxide into 2 : 4 : 3' : 4'-tetramethoxy-6-ethoxy- $\alpha\gamma$ -diphenylpropane, m. p. 49–50°. The synthesis of the latter compound is effected in the following manner. 2 : 4-Dimethylphloracetophenone is transformed by ethyl sulphate and potassium hydroxide into 2 : 4-dimethyl-6-ethylphloracetophenone, colourless needles, m. p. 73–74°, which condenses with veratraldehyde in the

presence of alcohol and sodium hydroxide solution to 2 : 4-dimethoxy-6-ethoxyphenyl-3' : 4'-dimethoxystyryl ketone,



sulphur-yellow, rectangular platelets, m. p. 136—137°. The compound is reduced by hydrogen in the presence of spongy platinum to 2 : 4 : 3' : 4'-tetramethoxy-6-ethoxy- α -diphenylpropane, m. p. 49—50°, which is identical in all respects with the product derived from the catechin.

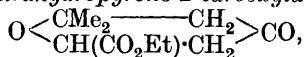
2-Hydroxy-4 : 6-dimethoxyphenyl β -3' : 4'-dimethoxyphenylethyl ketone, $\text{OH} \cdot \text{C}_6\text{H}_4(\text{OMe})_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_3(\text{OMe})_2$, colourless platelets, m. p. 125—126°, is prepared by the catalytic reduction of 2-hydroxy-4 : 6-dimethoxyphenyl 3' : 4'-dimethoxystyryl ketone in the presence of platinum; it is converted by ethyl sulphate into 2 : 4-dimethoxy-6-ethoxyphenyl β -3' : 4'-dimethoxyphenylethyl ketone, long needles, m. p. 89—90°. The oxygen atom of the carbonyl groups of these compounds could not be replaced by hydrogen.

H. W.

Tetrahydro- γ -pyrones. III. Catalytic Hydrogenation of Mesityloxidoxalic Esters. W. BORSCHKE and K. THIELE (*Ber.*, 1923, **56**, [B], 2132—2135).—The catalytic hydrogenation of ethyl α -mesityloxidoxalate occurs much more rapidly than that of the corresponding β -compound. This is in harmony with Dieckmann's conception (*A.*, 1920, i, 813), that the α -variety is an open-chain compound, whereas the β -form is a derivative of γ -pyrone.

Ethyl α -mesityloxidoxalate is converted by the hydrochloride of phenylcarbamhydrazide and sodium acetate into ethyl 1-carbanilido-3-isobutylenepyrazole-5-carboxylate, colourless needles, m. p. 238—239°, and by 2-nitro-4-cyanophenylhydrazine into ethyl 2'-nitro-4'-cyanophenyl-3-isobutylenepyrazole-5-carboxylate, slender, pale yellow needles, m. p. 190°. It is converted by hydrogen in the presence of colloidal palladium into ethyl α -hydroxy- γ -keto- ϵ -methyl- Δ^a -heptenoate, $\text{CHMe}_2 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH} : \text{C}(\text{OH}) \cdot \text{CO}_2\text{Et}$, an almost colourless liquid, b. p. 130—133°/20 mm. (the copper derivative, $[\text{C}_{10}\text{H}_{15}\text{O}_4]_2\text{Cu}$, crystallises in green needles, m. p. 151—152°). The ester is also prepared by the action of sodium on an ethereal solution of methyl isobutyl ketone and ethyl oxalate, and is further characterised by its 2-nitro-4-cyanophenylhydrazone, $\text{C}_{17}\text{H}_{20}\text{O}_5\text{N}_4$, slender, pale yellow needles, m. p. 184—185°.

Ethyl β -mesityloxidoxalate is very slowly hydrogenated in alcoholic solution in the presence of colloidal palladium to ethyl 6 : 6-dimethyl-4-ketotetrahydropyrone-2-carboxylate,



a pale yellow liquid, b. p. 150—152°/18 mm., which does not show any tendency to crystallise and possibly contains small quantities of unreduced original material.

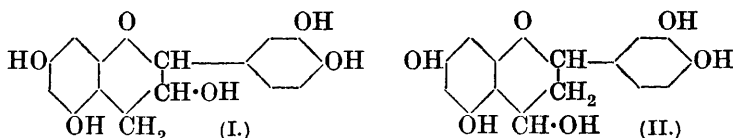
The phenylcarbamhydrazone of ethyl β -mesityloxidoxalate, $\text{C}_{17}\text{H}_{21}\text{O}_4\text{N}_3$, crystallises in colourless, lustrous needles, m. p. 219°, whereas the 2-nitro-4-cyanophenylhydrazone, $\text{C}_{17}\text{H}_{18}\text{O}_5\text{N}_4$, forms red prisms, m. p. 175°.

H. W.

The Constitution of Catechin. I. JAMES J. DRUMM (*Proc. Roy. Irish Acad.*, 1923, **36**, 41—49).—Phosphorus pentachloride acts vigorously on catechin tetramethyl ether to give the *chloride of catechin tetramethyl ether*, m. p. 112°, which, when heated rapidly, loses hydrogen chloride to give *dehydrocatechin tetramethyl ether*, $C_6H_2(OMe_2) \begin{smallmatrix} \diagup O-CH \cdot C_6H_3(OMe)_2 \\ \diagdown CH:CH \end{smallmatrix}$, m. p. 133.5—134.5°. When this

compound is treated with bromine in chloroform solution, hydrogen bromide is evolved and a bright red, crystalline *monobromide*, to which the formula $C_6H_2(OMe_2) \begin{smallmatrix} \diagup OBr \cdot C_6H_3(OMe)_2 \\ \diagdown CH-CH \end{smallmatrix}$ is assigned, is precipitated.

This monobromide, on treatment with alcoholic ammonia, yields a colourless base, m. p. 133—134°, which, on treatment with a chloroform solution of hydrogen chloride, yields its *anhydrohydro-*



chloride, m. p. 126—128°. It is considered that either formula I or II represents the structure of catechin. *Ethylcatechin tetramethyl ether*, m. p. 123°, and *n-butylcatechin tetramethyl ether*, m. p. 79—80°, were also prepared.

H. H.

Synthesis of Derivatives of Phenothioxin. SRI KRISHNA (*T.*, 1923, **123**, 2782—2786).

Derivatives of Thionaphthacoumarin. SAMUEL SMILES and LESLIE RALPH HART (*T.*, 1923, **123**, 2907—2913).

Synthesis of Substituted Thianthrens. II. SRI KRISHNA (*T.*, 1923, **123**, 2786—2790).

The Distribution Equilibrium of Quinine between Water and Ether at 0°. W. D. TREADWELL [with R. GONSETT and A. TRIPET] (*Helv. Chim. Acta*, 1923, **6**, 744—749).—Measurements of the distribution of quinine between water and ether at 0° show that the usual distribution law is followed, the molecular weight of quinine in ethereal solution being twice the molecular weight in aqueous solution. The solubility of quinine is 1 part in 188 parts of absolute ethyl ether and 1 part in 15 parts of ether saturated with water. The very divergent solubilities given in the literature are probably due to the use of ether containing varying proportions of water.

E. H. R.

The Alkaloids of the Java Coca Leaf. A. W. K. DE JONG (*Rec. trav. chim.*, 1923, **42**, 980—999).—A method is described by which the alkaloids (mainly cocaine and tropacocaine) may be extracted from coca leaves by means of ammoniacal benzene at 55°. The alkaloids are decomposed by boiling with mineral acid, and the ecgonine produced may be estimated polarimetrically. The following rotatory powers are quoted: ecgonine monohydrate

$[\alpha]_D -45.6^\circ$, hydrochloride $[\alpha]_D -47.1^\circ$, anhydrous benzoylecgonine $[\alpha]_D -63.3^\circ$, anhydroecgonine $[\alpha]_D -84.6^\circ$. Anhydroecgonine hydrochloride exhibits mutarotation. *Ecgonine benzoate* has m. p. 145° , *tropacocaine benzoate*, m. p. $60-61^\circ$. The hydrochlorides of ecgonine and of anhydroecgonine both form *pentamercurichlorides*, whilst ψ -tropine hydrochloride forms a *dimercurichloride*. H. H.

Preparation of Creatinine from Creatine. GRAHAM EDGAR and W. S. HINEGARDNER (*J. Biol. Chem.*, 1923, **56**, 881—886).—Creatine is converted into creatinine hydrochloride (a) by evaporating its solution in hydrochloric acid to dryness, (b) by treating the anhydrous substance with gaseous hydrogen chloride, or (c) by heating it in a closed vessel on a steam-bath for twenty-four hours with a slight excess of hydrochloric acid. Free creatinine is then obtained either by saturating a concentrated solution of the hydrochloride with ammonia or by adding the solid salt to its own weight of concentrated ammonia, cooling in ice, and filtering. Creatinine is best crystallised by dissolving in 5 parts of water previously heated at 65° , adding twice the volumes of acetone, and cooling to 0° . E. S.

Constitution of Morphine. HEINRICH WIELAND and ERNST KORALEK (*Annalen*, 1923, **433**, 267—271).—The experimental results are given of an uncompleted attempt to carry out the degradation of methyltetrahydromorphimethine by progressive methylation. The reduction of codeine in alcoholic solution by means of palladium black and hydrogen gives, as sole product, a *dihydrocodeine*, m. p. $112-114^\circ$, *hydrochloride*, m. p. 256° (cf. Mannich and Löwenheim, A., 1921, i, 121; Freund, Melber, and Schlesinger, A., 1920, i, 757). Its methiodide is converted by boiling for a short time with 10% sodium hydroxide solution into *methyl dihydromorphimethine* (*de-N-methyl dihydrocodeine*), an oil, *hydrochloride*, m. p. 133° , *methiodide*, m. p. 160° (cf. Vongerichten, A., 1899, i, 551; Freund, Melber, and Schlesinger, *loc. cit.*). The reduction of methylmorphimethine, or of either of its dihydro-derivatives, by means of palladium-hydrogen in alcoholic solution gives methyltetrahydromorphimethine, *hydrochloride*, m. p. 226° .

[With E. WASER.]—Morphothebaine hydrobromide is converted by heating at 170° with hydrobromic acid in an atmosphere of carbon dioxide, into 6-hydroxyapomorphine, *hydrobromide*, small, colourless needles, m. p. $261-262^\circ$ (decomp.). The aqueous solution of the salt is coloured reddish-brown by the addition of ferric chloride or of concentrated nitric acid; it immediately reduces silver nitrate. Solutions of the free base in alkali rapidly darken on exposure to the air. W. S. N.

On the Alkaloids of *Sinomenium acutum*, Rehd. et Wils., Sinomenine and Diversine. I. HEIZABURO KONDO, EIJI OCHIAI, and TOMOICHI NAKAJIMA (*J. Pharm. Soc. Japan*, 1923, No. **497**, 511—524).—With alcohol and other suitable reagents, two alkaloids, sinomenine and diversine, have been isolated from *Sinomenium acutum*. *Sinomenine*, $C_{19}H_{23}O_4N$ or $C_{19}H_{21}O_4N$, forms

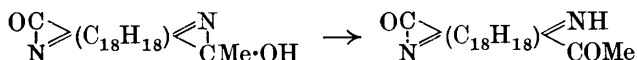
radiating groups of white crystals; it has m. p. 161° , on further heating, it becomes crystalline and again melts at 182° , $[\alpha]_D^{25} -70.76^{\circ}$; the *hydrochloride*, $(2H_2O)$, forms prisms, m. p. 231° , and has $[\alpha]_D^{17} -82.4^{\circ}$ (anhydrous). Sinomenine has strong reducing power and precipitates silver and gold from their salts. It is soluble in sodium hydroxide solution, and gives a greenish-blue coloration with ferric chloride. It contains two methoxyl and one *N*-methyl groups; and yields a *methiodide*, colourless prisms, m. p. 251° . The *monobenzoyl* compound forms colourless prisms, m. p. 225° (*chloroaurate* decomposes at 178°); the *monomethyl* compound forms needles, m. p. 175° (*hydrochloride*, short prisms, decomposes at 252°).

Diversine, $C_{20}H_{27}O_5N$, is yellow and amorphous, m. p. $80-93^{\circ}$, $[\alpha]_D^{17} +6.98^{\circ}$. It is more strongly reducing than sinomenine and precipitates metallic gold and platinum from their salts; it gives a dark brown coloration with ferric chloride. The *hydrochloride*, $C_{20}H_{27}O_5N.HCl$, a yellow, amorphous substance, decomposes at $135-140^{\circ}$. Diversine contains two methoxyl and one *N*-methyl groups, and gives a *methiodide*, $C_{20}H_{27}O_5N.MeI$, a slightly coloured, amorphous compound. When heated with benzoic anhydride, it gives a mixture of mono- and di-benzoyl compounds.

K. K.

Strychnine and isoStrychnine. II. E. OLIVERI-MANDALÀ and G. COMELLA (*Gazzetta*, 1923, **53**, 619—628).—Oxidation of strychnine by means of permanganate yields the acid obtained by Leuchs (A., 1908, i, 563), together with a second acid which is a product of more advanced degradation of the strychnine molecule, and forms a calcium salt yielding indole on dry distillation (cf. this vol., i, 702). The second acid is amorphous and unstable, and gives analytical results which do not accord with any formula. Oxidation of bromostrychnine oxide under similar conditions yields, first, a crystallisable acid, whereas more profound decomposition of the molecule results in the formation only of amorphous products which readily resinify and respond to the reactions for pyrrole.

Further evidence is adduced in support of the view that the passage of strychnine into the isomeric *isostrychnine* may be represented by the scheme



Strychnine is not affected by the Grignard reagent, whereas *isostrychnine*, if dried at 105° , reacts with excess of magnesium ethyl bromide, giving 1 mol. of ethane per mol. of the base; this behaviour is in accord with the presence of a secondary nitrogen atom in the *isostrychnine* molecule. That the latter contains a nitrogen atom with a function different from that of the nitrogen in strychnine is shown by the fact that the normal base, by virtue of its tertiary nitrogen atom, reacts with hydrogen peroxide, giving

the corresponding amino-oxide, $\text{OC} \begin{smallmatrix} \diagup \\ \text{N} \end{smallmatrix} \text{C}_{20}\text{H}_{21}\text{O} \text{:N}\cdot\text{O}$, whereas the *iso*-base remains unaltered. That *iso*strychnine contains a ketonic group is shown by its ready reaction with semicarbazide.

According to Perkin and Robinson's formula for strychnine (T., 1910, 97, 305), the optical activity of this base is due to the carbon atom which determines the secondary alcoholic function, but the authors regard the activity as caused by the grouping $\text{>CMe}\cdot\text{OH}$. Since the latter changes into $\cdot\text{CMe}$ in *iso*strychnine, this should be optically inactive. Of a number of preparations of *iso*strychnine examined, some were inactive, but others exhibited traces of activity, possibly owing to the presence of impurity.

The amorphous acid obtained by oxidation of strychnine oxide decomposes carbonates and blackens, without melting, at about 200°. Two preparations, dried at 105°, gave C, 52.39, 52.62; H, 4.12, 3.90; N, 5.58, 6.13.

Bromostrychnine oxide, $\text{NO}\cdot\text{C}_{20}\text{H}_{21}\text{OBr} \begin{smallmatrix} \text{C} \\ \diagup \\ \text{N} \end{smallmatrix} \text{O}$, $3\text{H}_2\text{O}$, forms groups of large, hard prisms, m. p. 175° (decomp.). Its *hydrobromide*, $\text{C}_{21}\text{H}_{21}\text{O}_3\text{N}_2\text{Br}\cdot\text{HBr}$, decomposes above 300°, and its *picrate* forms yellow needles. It gives all the reactions of amino-oxides, and by bromine water is reduced to bromostrychnine with liberation of oxygen.

The *acid*, $\text{C}_{21}\text{H}_{21}\text{O}_6\text{N}_2\text{Br}$, obtained on oxidation of bromostrychnine oxide by means of permanganate, does not melt at 300°, and appears to contain intact the fundamental nucleus of strychnine, as it answers to certain of the colour reactions characteristic of the base.

The dissociation constant of *iso*strychnine is 0.53×10^{-11} at 25°, and for two preparations the specific rotation is found to be $[\alpha]_D^{17} + 7.27^\circ$ and $[\alpha]_D^{18} + 6.28^\circ$.

Bromoisostychnine, $\text{C}_{21}\text{H}_{21}\text{O}_2\text{N}_2\text{Br}\cdot\text{H}_2\text{O}$, is obtained as an amorphous, white powder which blackens, without melting, at about 300°. It is not soluble in alkali carbonate or hydroxide solution, so that the molecule of water, which is lost at 105°, has not converted the group $\cdot\text{CO}\cdot\text{N}\cdot$ into $\text{NH}+\text{CO}_2\text{H}$; with *iso*strychnine itself, conversion into *iso*strychnic acid is effected only by heating with sodium ethoxide.

*iso*Strychnine semicarbazone, $\text{C}_{21}\text{H}_{22}\text{ON}_2\cdot\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, crystallises in needles, m. p. 215° (decomp.). T. H. P.

Yohimbine (Quebrachine). III. Esterification of Yohimbic Acid. ELLEN FIELD (T., 1923, 123, 3003—3006).

2-Pyrrolidylcarbinol. N. J. PUTOCHIN (*Ber.*, 1923, 56, [B], 2216—2217).—2-Pyrrolidylcarbinol, $\text{NH} \begin{smallmatrix} \text{CH}_2 \\ \diagup \\ \text{CH}(\text{CH}_2\cdot\text{OH}) \end{smallmatrix} \text{CH}_2$, a colourless, viscous, unpleasant smelling liquid, b. p. 148—153°/12 mm., is prepared in 40% yield by the reduction of proline ethyl ester by sodium in the presence of ethyl alcohol; the *chloroplatinate*, $(\text{C}_5\text{H}_{11}\text{ON})_2\cdot\text{H}_2\text{PtCl}_6$, orange-yellow crystals, m. p. 204° (decomp.)

after darkening at 192°, and the *chloroaurate*, m. p. 152°, are described.
H. W.

Synthesis of Proline. N. J. PUTOCHIN (*Ber.*, 1923, 56, [B], 2213—2216).—The synthesis of proline has been accomplished in accordance with the scheme: $\text{NH}_2 \cdot \text{CNa}(\text{CO}_2\text{Et})_2 + \text{CH}_2\text{Br} \cdot \text{CH}_2 \cdot \text{CH}_2\text{Br} \rightarrow \text{CH}_2\text{Br} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{C}(\text{NH}_2)(\text{CO}_2\text{Et})_2 \rightarrow \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ | \\ \text{CH}_2 \cdot \text{NH} \end{array} > \text{C}(\text{CO}_2\text{Et})_2 \rightarrow \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ | \\ \text{CH}_2 \cdot \text{NH} \end{array} > \text{CH} \cdot \text{CO}_2\text{Et}$. The yield is about 25% of that theoretically possible.

Ethyl oximinomalonate, b. p. 172°/12 mm., is reduced to ethyl aminomalonate (hydrochloride, m. p. 162°) by the action of aluminium amalgam in the presence of moist ether or catalytically in the presence of spongy platinum. The ester hydrochloride is converted by sodium ethoxide and trimethylene bromide in alcoholic solution and subsequent treatment of the product with concentrated hydrochloric acid into proline, m. p. 205°, which is isolated through its copper salt.
H. W.

Complex Thiocyanates of Tervalent Elements. II. G. SCAGLIARINI and G. TARTARINI (*Gazzetta*, 1923, 53, 617—619; cf. this vol., i, 547).—By means of the method previously employed, degradation products of chromithiocyanates intermediate between $(\text{NH}_4)_3[\text{Cr}(\text{SCN})_6]$ and $\text{Cr}(\text{SCN})_3$ have been obtained, use being made of piperidine and piperazine to fix the decomposition products of the ion $\text{Cr}(\text{SCN})_6'''$.

Piperidine chromihexathiocyanate, $(\text{C}_5\text{H}_{11}\text{N}, \text{H})_3[\text{Cr}(\text{SCN})_6]$, forms pale violet, cubical crystals; *piperidine aquochromipentathiocyanate*, $(\text{C}_5\text{H}_{11}\text{N}, \text{H})_2[\text{Cr}(\text{SCN})_5\text{OH}_2] \cdot \text{H}_2\text{O}$, violet, prismatic plates; *piperazine aquochromipentathiocyanate*, $(\text{C}_4\text{H}_{10}\text{N}_2, \text{H})_2[\text{Cr}(\text{SCN})_5\text{OH}_2] \cdot \text{H}_2\text{O}$, violet, cubical crystals, and *piperazine aquochromitetrathiocyanate*, $(\text{C}_4\text{H}_{10}\text{N}_2, \text{H})_2[\text{Cr}(\text{SCN})_4(\text{OH})\text{OH}_2]$, violet needles.
T. H. P.

The Structure of Apophyllenic Acid. ALFRED KIRPAL and EWALD REITER (*Annalen*, 1923, 433, 112—116).—Mumm and Gottschaldt (A., 1922, i, 862) found that, by the action of silver oxide on the methiodide of 3-methyl 4-ethyl 2:6-dimethylcinchomerionate, it is the 4-carbethoxyl, and not the 3-carbomethoxyl, group which is attacked. 2:6-Dimethylapophyllenic acid was accordingly described as a 4-betaine, and its formation was ascribed to the greater ease of formation of a 4-betaine ring. An alternative explanation is that the 3-carbomethoxyl group is prevented by the 2-methyl group (steric hindrance) from undergoing the reaction, and that otherwise a 3-betaine would be formed. This is certainly borne out by the production, by the action of silver oxide on 3-methyl 4-ethyl cinchomerionate methiodide (prisms, decomp. 170°), of a greater quantity of the 4-ethyl ester of cinchomeronic acid methylbetaine than of the 3-methyl ester. Any difference in ease of hydrolysis of the ester groups is due to position, and not to a difference in their alkyl groups, because a similar result attends

the use of *dimethyl cinchomeronate methiodide* (pale yellow needles, decomp. 157°), the 4-methyl ester preponderating in the product. The alkaline half-hydrolysis of neutral cinchomeric ester gives almost exclusively the 3-ester. Similar behaviour might have been expected in hydrolysing the above methiodides; but the actual results, being different, must be attributed to the tendency to formation of a 3-betaine. A 3-betaine formula for apophyllenic acid is held to be reconcilable with Pfeiffer's views on the structure of betaines (A., 1922, i, 720) (cf. Mumm and Gottschaldt, *loc. cit.*).

The same ester is formed by the action of diazomethane on apophyllenic acid as by the action of methyl iodide on its silver salt.

W. S. N.

Supposed Cases of Isomerism in the Isatin Series. A. HANTZSCH (*Ber.*, 1923, 56, [B], 2110—2119).—A further communication in the controversy between Hantzsch and Heller concerning the existence of isomerides in the isatin series (cf. Heller, A., 1920, i, 766; 1921, i, 891; Heller and Benade, A., 1922, i, 582; Hantzsch, A., 1921, i, 597; 1922, i, 1177).

The supposed isomerides in the isatin series do not exist. The isomerides described by Heller are either not homogeneous (dimethylisatin III or the isomeric dimethylisatin silver), do not correspond with the empirical formula of isatin (dimethylisatin IV), or are true polymeric, generally dimeric, compounds, as in the case of most of the other supposed isomerides. In connexion with the differences in colour of the silver salts obtained in the isatin series by different workers, it is pointed out that it is well established that such discordances can exist in the colour of solid compounds and particularly in deeply coloured silver salts, but that such differences are quite unimportant. Dimethylisatin silver has been considered by Heller to be a *N*-silver salt because of its grey colour (in contrast with the customary silver salts) and of the impossibility of converting it into the corresponding methyl ether. All these silver salts, which are characterised by their smooth conversion into *O*-alkyl ethers and, as now shown, by their primary transformation into *O*-acyl derivatives, have been considered by Heller to be *N*-salts chiefly because isatindianil which is free from oxygen gives a silver salt and a similar compound cannot be obtained from the supposed dimethylisatin lactim; the author considers that the salt formation from the dianil has no bearing on the conception of the isatin salts, and brings forward evidence to prove that dimethylisatin lactim does not exist.

Dimethylisatin silver, which in the pure state is bordeaux-red like the other silver salts, and not grey as described by Heller, is converted by pure benzoyl chloride in the presence of anhydrous ether and absence of moisture at the atmospheric temperature into *dimethylisatin O*-benzoate, $C_6H_2Me_2 < \begin{smallmatrix} CO \\ -N \end{smallmatrix} \geq C \cdot OBz$, large, blood-red crystals, m. p. 118—119°; it is hydrolysed by sodium hydroxide solution into dimethylisatin and benzoic acid. If the reagents are not completely pure and dry, the reaction between the silver salt

and benzoyl chloride leads to the production of much regenerated dimethylisatin and *tetramethylisatoid* (annexed formula) which has been described by Heller as dimethylisatinlactim. It has m. p. 204—205° (decomp.). Its isatoid structure is deduced from determinations of its molecular weight in benzene and camphor and from the similarity of its absorption spectrum when dissolved in chloroform with that of tetramethylisatoid monomethyl ether and its dissimilarity from dimethylisatin *O*-methyl ether. It dissolves in aqueous alkali, giving a bluish-red solution of the salt, from which it is precipitated unchanged by immediate, exact neutralisation with acid. If, however, an excess of acid is used, the precipitate is not homogeneous; such mixtures have been described by Heller as "dimethylisatol." They consist in part of tetramethylisatoid anhydride, $C_{20}H_{16}O_3N_2$ (Heller's dimethylisatin IV), m. p. 297—300°, which is conveniently prepared by treating tetramethylisatoid with boiling glacial acetic acid. The action of glacial acetic acid and acetic anhydride on tetramethylisatoid gives a very stable, pale yellow product, m. p. 243°, which appears to be an acetyl derivative.

H. W.

The Preparation of Homologues of Isatin : Preparation of 7-Bromo-5-methylisatin. (Mlle) MARCELLE RESSY and ANDRÉI P. ORTODOCSU (*Bull. Soc. chim.*, 1923, [iv], **33**, 1297—1299). —The preparation was effected by a method similar to that used in the case of the isomeride (this vol., i, 833). Acetylation and subsequent bromination of *p*-toluidine yielded aceto-*o*-bromo-*p*-toluidide. The corresponding benzoyl derivative was also prepared. Hydrolysis of either of these substances by means of alcoholic potassium hydroxide resulted in the formation of *o*-bromo-*p*-toluidine. Condensation of the hydrochloride of this base with hydroxylamine hydrochloride and chloral hydrate gave the dibromodi-*p*-tolylamidine of the oxime of glyoxalic acid from which oximinobromoaceto-*p*-toluidide is obtained on hydrolysis. The last-named substance in solution in boiling sulphuric acid yields, on being added to water, orange-red prismatic needles of 7-bromo-5-methylisatin, m. p. 180°. The oxime has m. p. 230° and the phenylhydrazone 242°. The substance is stated to possess greater tinctorial power than its isomeride. Benzoyl-*o*-bromo-*p*-toluidide, m. p. 125°, forms lustrous needles which have in appearance some resemblance to boric acid.

H. J. E.

The Action of Sulphur on Organic Compounds. VII. Quinoline and Sulphur. LUDWIK SZPERL and TADEUSZ W. JEZIEŃSKI (*Roczniki Chemji*, 1923, **3**, 177—183; cf. this vol., i, 1191). —Quinoline was heated at 220—235° with sulphur in molecular proportions for 185 hours in an atmosphere of carbon dioxide. After removing the unchanged quinoline, the solid residue was found to consist of two compounds which were separated, after being purified by sublimation, by means of boiling benzene. The soluble compound, C_9H_5NS , obtained in very small amount, formed fine, pale yellow

needles, m. p. 249—251°; it forms an orange *picrate*, m. p. 258—261°, and a *sulphate* carbonising at 270°. The compound insoluble in benzene crystallises from acetic acid, melts at 305—305.5°, and forms a red *picrate*, m. p. 278—279°; the sulphate forms golden-yellow crystals which become red on keeping. The compound is thus identical with Edinger and Lubberger's thioquinanthrene (A., 1897, i, 204). It is suggested that the original formula, $(C_9H_5NS)_n$, is correct, and not that proposed later by Edinger and Ekeley (A., 1902, i, 230). Oxidation of the compound with nitric acid gives nicotinic acid.

G. A. R. K.

Internal Metallic Complexes of the Hydroxyquinolines.

G. BARGELLINI and I. BELLUCCI (*Gazzetta*, 1923, **53**, 605—616).—According to Noelting and Trautmann (A., 1891, 325), Kostanecki (A., 1891, 579), and Möhlau and Steimmig (*Z. Farb. Text. Chem.*, 1904, **3**, 358), only those hydroxyquinolines with the hydroxyl group in the 8-position are able to function as mordant colouring matters. The mordant dyeing properties of chemical compounds are considered by Werner and Thomann (A., 1908, i, 440) to depend on the capacity to form co-ordinated complex salts, and this view is supported by much direct experimental evidence.

Metallic derivatives of 8-hydroxyquinoline have been prepared by Skraup (A., 1883, 92) and by Fox (T., 1910, **97**, 1119), and the authors now describe the nickel and palladium compounds. With concentrated potassium chloroplatinate solution, 8-hydroxyquinoline in acetic acid solution yields a red, crystalline precipitate which sublimes under reduced pressure; with cobalt acetate, it gives a brownish-yellow coloration, and with ferrous sulphate a reddish-brown precipitate which undergoes rapid alteration in the air. The ability to form internal metallic complexes and hence lakes is not influenced by replacing the hydrogen atoms of 8-hydroxyquinoline by other atoms or groups, since copper, nickel, palladium, and ferrous salts are formed by 5:7-dibromo-8-hydroxyquinoline (cf. Bedall and Fischer, A., 1881, 613) and by hydroxymethyl-8-hydroxyquinoline (cf. Manasse, A., 1903, i, 28; Cohn, A., 1911, i, 567). Hydroxyquinolines with the hydroxyl in positions other than the 8-position are incapable of yielding internal metallic complexes.

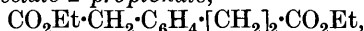
The *nickel* compound of 8-hydroxyquinoline, $(C_9H_6ON)_2Ni$, forms a greenish-yellow, pulverulent precipitate, and is highly stable towards heat or reagents. It decomposes on prolonged heating at 350—400°, and sublimes unchanged as a greenish-yellow, microcrystalline deposit when heated at 300° either under reduced pressure or in a current of carbon dioxide. The *palladium* compound, $(C_9H_6ON)_2Pd$, forms a canary-yellow, microcrystalline precipitate, sublimes at about 300°, and decomposes at about 400°.

T. H. P.

Decahydroisoquinoline. LOUIS HELFER (*Helv. Chim. Acta*, 1923, **6**, 785—799).—Decahydroisoquinoline cannot be prepared by hydrogenation of *isoquinoline*, and attempts to prepare it from β -cyclohexylethylamine or its derivatives by the action of methylal were unsuccessful. Success was eventually attained by a method

similar to Ladenburg's piperidine synthesis. The method was first applied to the preparation of tetrahydroisoquinoline. From homo-*o*-phenylenediacetic [phenylene-1-acetic-2-propionic] acid (Einhorn and Lumsden, A., 1896, i, 45) homo-*o*-xylylenediamine [1-aminomethyl-2- β -aminoethylbenzene] was prepared, through the ethyl ester, hydrazide, azide, and urethane. Distillation of the hydrochloride of the diamine gave tetrahydroisoquinoline. In a similar manner, distillation of the corresponding hexahydro-diamine hydrochloride, obtained from hexahydrophenylene-1-acetic-2-propionic acid, gave decahydroisoquinoline.

Ethyl phenylene-1-acetate-2-propionate,



is a nearly colourless oil of agreeable odour, b. p. 198—199°/16 mm. By hydrazine hydroxide at 125—130° this is converted into *o*-phenylene-acetopropionohydrazide, white, silky needles, m. p. 170—171°. Nitrous acid converts this into the corresponding *azide*, a yellow oil which was not isolated, but was converted directly into the *urethane*, $\text{CO}_2\text{Et}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot[\text{CH}_2]_2\cdot\text{NH}\cdot\text{CO}_2\text{Et}$, white needles, m. p. 81°. When this is heated under pressure at 120—130° with hydrochloric acid, it gives the hydrochloride of the diamine. 1-Aminomethyl-2- β -aminoethylbenzene is a colourless oil with a strong basic odour, b. p. 268—270°/735 mm.; when exposed to air it forms a white, crystalline *carbonate*; its *hydrochloride* forms fine needles, m. p. 258°, and the *picrate*, small, yellow needles, m. p. 224°.

Hydrogenation of phenylene-1-acetic-2-propionic acid proceeds smoothly when the substance is pure and a highly active platinum black is used. cycloHexane-1-acetic-2-propionic acid crystallises in small needles, m. p. 106—107°. It is distinguished from the non-hydrogenated acid by its lower solubility in water and complete solubility in cold benzene. The *ethyl ester* is a colourless oil, b. p. 191—192°/15 mm.; the *hydrazide*, which is difficult to crystallise, has m. p. 176°; the *urethane* obtained from the hydrazide is a viscous, colourless oil which could not be crystallised. 1-Amino-methyl-2- β -aminoethylcyclohexane is a strong base; it forms an oil, b. p. 254—255°/731 mm.; its *hydrochloride* is a white salt which liquefies in moist air, and the *picrate* crystallises in yellow needles, m. p. 105°. Decahydroisoquinoline is a strongly basic, colourless oil, b. p. 208—209°/730 mm., distinguished from tetrahydroisoquinoline by its more penetrating odour and by the fact that it does not reduce ammoniacal silver nitrate. The *hydrochloride* crystallises in spangles, m. p. 176°; *picrate*, small, yellow needles, m. p. 144—145°; *chloroplatinate*, small crystals, m. p. 201° (decomp.).

E. H. R.

ω -Trichloro- and ω -Tribromo-quinaldine and the Preparation of Quinaldinic Acid. DALZIEL LLEWELLYN HAMMICK (T., 1923, 123, 2882—2884).

Alkylation and Aralkylation of Carbazole. NATIONAL ANILINE AND CHEMICAL Co., INC. (Brit. Pat. 192376).—Direct alkylation is effected by the interaction of carbazole and alkylating agents, in the presence of a dehydrating or condensing agent (*e.g.*, alkali

hydroxides) and, preferably, of an indifferent organic liquid (*e. g.*, toluene). [Cf. *J.S.C.I.*, 1923, Dec.] W. T. K. B.

The Solubility of the Phenylenediamines and of their Monoacetyl Derivatives. NEVIL VINCENT SIDGWICK and JAMES ACHESON NEILL (*T.*, 1923, **123**, 2813—2819).

The Basic Derivatives of the Ethylbenzene Series. JULIUS VON BRAUN and GEORG BLESSING (*Ber.*, 1923, **56**, [B], 2153—2161). —It has been established that the β -nitrophenylethyl chloride, m. p. 48—49°, prepared from β -phenylethyl alcohol is entirely the para-derivative. The reactions of β -*p*-aminophenylethylamine have been examined in detail.

Bisphenylethylamine is converted into its *benzoyl* derivative, m. p. 61°, which is transformed by fuming nitric acid into the corresponding *dinitro*-compound, $C_{23}H_{21}O_5N_3$, lustrous, pale-yellow leaflets, m. p. 152°. The latter substance is converted by treatment with phosphorus pentachloride and subsequent distillation under diminished pressure into benzonitrile and β -*p*-nitrophenylethyl chloride, m. p. 49°, which is identical with the product obtained from β -phenylethyl chloride. Since it is improbable that the compounds obtained by two widely differing methods would be contaminated to the same degree by the presence of an isomeride they are to be regarded as the pure para-derivative.

p-Nitrophenylacetonitrile dissolved in tetrahydronaphthalene is converted by hydrogen in the presence of a nickel catalyst at 120° into *p*-aminophenylacetonitrile, m. p. 45—46°, the yield attaining 70% of that theoretically possible; the hydrochloride, m. p. 217—220°, and the *picrate*, m. p. 185°, are described. If reduction is effected at 130° the cyano-group is also attacked with the production of the corresponding primary and secondary amines. β -*p*-Aminophenylethylamine, $NH_2 \cdot C_6H_4 \cdot CH_2 \cdot CH_2 \cdot NH_2$, is a colourless liquid, b. p. 140—142°/12 mm.; the *dihydrochloride*, m. p. 270—280°, the *dipicrate*, orange-coloured needles, decomp. 205—210°, the *dibenzoyl* derivative, m. p. 223°, the *diacetyl* compound, m. p. 190—192°, and the *diphenylthiocarbamide*, m. p. 166—167°, are described. The hydrochloride of the base is readily converted by a molecular proportion of sodium nitrite into tyramine, $OH \cdot C_6H_4 \cdot CH_2 \cdot CH_2 \cdot NH_2$, m. p. 159—161°, the yield being 80% of that theoretically possible. *Bis*- β -*p*-aminophenylethyl-amine, $(NH_2 \cdot C_6H_4 \cdot CH_2 \cdot CH_2)_2NH$, is a viscous liquid, b. p. 200—220°/1—2 mm.; the *trihydrochloride*, m. p. 270—275° (decomp.), the *tripicrate*, m. p. 135—140°, the *triacetyl* compound, m. p. 189—191°, and the *dibenzoyl* derivative, m. p. 270—280°, are described. The triamine is converted by two molecular proportions of nitrous acid into bis- β -*p*-hydroxyphenylethylamine (see later).

p-Hydroxyphenylacetonitrile is hydrogenated in tetrahydronaphthalene solution at 120—130° to a mixture of β -*p*-hydroxyphenylethylamine and *bis*- β -*p*-hydroxyphenylethyl-amine. The latter substance forms colourless crystals, m. p. 194°. In comparison with the corresponding primary amine, it is very slightly active pharmaco-

logically. The *hydrochloride*, m. p. 220° , the *sulphate*, the non-crystalline *acetyl* derivative, and the *tribenzoyl* compound, m. p. 102° , are described. Catalytic reduction of *p*-hydroxyphenylacetonitrile dissolved in *cyclohexanol* at 120 – 130° leads to the production of a mixture of the three theoretically possible bases in which *cyclohexyl- β -p-hydroxyphenylethylamine*, $\text{C}_6\text{H}_9\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, predominates. It crystallises in aggregates of needles, m. p. 94° , b. p. 220 – $223^{\circ}/15$ mm.; the *hydrochloride*, m. p. 258 – 260° , the *sulphate*, the *picrate*, m. p. 198° , and the *dibenzoyl* derivative, m. p. 137° , are described. In a similar manner, *cyclohexyl- β -p-amino-phenylethylamine*, a pale yellow, somewhat viscous liquid, b. p. $160^{\circ}/1$ mm., is obtained in 40–45% yield by the reduction of *p*-aminophenylacetonitrile dissolved in *cyclohexanol*. The *dihydrochloride*, the *monopicrate*, m. p. 147° , the *diacetyl* compound, m. p. 129° , the *dibenzoyl* derivative, m. p. 140° , and the diquaternary *iodide*, $\text{C}_{19}\text{H}_{34}\text{N}_2\text{I}_2$, m. p. 186 – 188° , are described.

The complete methylation of *p*-aminophenylethylamine to the compound $\text{NMe}_3\cdot\text{I}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NMe}_3\cdot\text{I}$ appears to be attended by considerable and unexplained uncertainties, so that it is preferable to start from *β -p-dimethylaminophenylethylamine*. For this purpose, *p*-aminophenylacetonitrile is converted successively into the quaternary *iodide*, $\text{CN}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_3\cdot\text{I}$, orange-coloured needles, m. p. 177° , and *p-dimethylaminophenylacetonitrile*, b. p. 162 – $165^{\circ}/11$ mm., m. p. 55 – 56° (*hydrochloride*, m. p. 162° ; *picrate*, m. p. 127°). The nitrile is reduced by sodium and alcohol to *β -p-dimethylaminophenylethylamine*, a colourless liquid, b. p. 120 – $125^{\circ}/11$ mm. (the non-crystalline *hydrochloride* and the *picrate*, m. p. 133 – 135° , are described). The new base is converted into the corresponding diquaternary *iodide*, colourless crystals which do not melt below 300° , from which *p-dimethylaminovinylbenzene*, $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}_2$, is prepared; it is a colourless liquid, b. p. 90 – $91^{\circ}/\text{vacuum}$, which does not appear to become appreciably polymerised when preserved. The non-crystalline *hydrochloride*, the *chloroplatinate*, m. p. 150° , and the *picrate*, yellow leaflets, m. p. 120 – 121° , are described. H. W.

3-Amino- and 3-Hydroxy-quinolines. G. BARGELLINI and M. SETTINI (*Gazzetta*, 1923, **53**, 601–605).—The authors have attempted to prepare 3-hydroxyquinoline and 3-aminoquinoline by the general methods previously described (this vol., i, 482, 847), but without success in either case. The interaction of *o*-aminobenzaldehyde and chloroacetaldehyde in presence of potassium hydroxide yields no trace of 3-hydroxyquinoline, probably owing to resinification of the aldehyde. Potassio-phthalimide could not be induced to condense with either chloroacetaldehyde or chloroacetal to form phthalimidoacetaldehyde, so that condensation of the latter with *o*-aminobenzaldehyde to 3-aminoquinoline could not be effected.

3-Aminoquinoline may, however, be readily prepared by the reduction, by means of stannous chloride and hydrochloric acid, of 3-nitroquinoline, which is easily obtainable from *o*-aminobenzaldehyde and methazonic acid (cf. Badische Anilin- & Soda-Fabrik,

A., 1921, i, 517). Treatment of 3-aminoquinoline with nitrous acid gives 3-hydroxyquinoline. These methods may be used with advantage in place of the tedious methods of preparing these compounds described by Mills and Watson (T., 1910, 97, 741).

3-Hydroxyquinoline picrate forms yellow crystals, m. p. 240—245° (decomp.).
T. H. P.

Synthesis of some Pyridylpyrroles. J. P. WIBAUT and ELISABETH DINGEMANSE (*Proc. K. Akad. Wetensch. Amsterdam*, 1923, 26, 426—435).—An account of preliminary work in connexion with an attempted synthesis of an isomeride of nicotine. By heating 2-aminopyridine with mucic acid at 140°, 1-(2'-pyridyl)pyrrole is obtained as a white, crystalline compound, m. p. 17°, b. p. 140—145°/15 mm., and 260—261°/760 mm., which gives a *picrate*, m. p. 143°, and a *methiodide*, m. p. 141—142°. When 1-(2'-pyridyl)pyrrole is passed over pumice heated at 670—690°, two isomeric C-(2'-pyridyl)pyrroles are formed, one of which is non-volatile in steam, and melts at 132.5°. The other is volatile in steam, melts at 90°, and gives a *picrate*, m. p. 227—228°, and a *methiodide*, m. p. 148°. When the latter isomeride is treated with potassium, and the potassium derivative is heated in a sealed tube with methyl iodide at 100°, C-(2'-pyridyl)-1-methylpyrrole *methiodide*, m. p. 186°, is obtained, from which the free base is liberated by distillation with lime. C-(2'-Pyridyl)-1-methylpyrrole *picrate* was found to melt at 143°.
H. H.

Synthesis of some α -Pyridylpyrroles and a Second Isomer of Nicotyrin. J. P. WIBAUT and ELISABETH DINGEMANSE (*Rec. trav. chim.*, 1923, 42, 1033—1049).—A fuller account of work already abstracted (preceding abstract). The following details are new. Dry hydrogen chloride reacts with an ethereal solution of 1-(2'-pyridyl)pyrrole to give its *hydrochloride*, a greyish-white powder, m. p. 152°, but the pyrrole liberated by the action of alkali on this salt gives a *picrate*, m. p. 180°, which is not identical with that formed directly. 2-Aminopyridine *mucate* melts at 174° (decomp.), but the reaction between ethyl *mucate* and 2-aminopyridine at 105° yields the *diamide* of *diaminopyridylmucic acid*, m. p. 202°. The *picrate* of C-(2'-pyridyl)pyrrole of m. p. 90° is now stated to melt at 222—223° instead of 227—228°. The *hydrochloride* of this C-(2'-pyridyl)pyrrole melts at 179°. The *picrate* (m. p. 211°) and *methiodide* (m. p. 167°) of the isomeric C-(2'-pyridyl)pyrrole, m. p. 132°, are now described. The isomeric bases C-(2-pyridyl)-1-methylpyrrole, isomeric with nicotyrine, are described. That from C-(2'-pyridyl)pyrrole, m. p. 90°, boils at 273°/764 mm., and gives the *methiodide* and *picrate* previously described. That from C-(2'-pyridyl)pyrrole, m. p. 132°, gives a *picrate*, m. p. 197—198°.
H. H.

The Additive Formation of Four-membered Rings. II. The Conditions which confer Stability on the Dimethine-diazidines. CHRISTOPHER KELK INGOLD and HENRY ALFRED PIGGOTT (T., 1923, 123, 2745—2752).

New Investigations with Diazomethane ; Alloxantin. HEINRICH BILTZ and HANS PAETZOLD (*Annalen*, 1923, **433**, 64—87).—The determination of the constitution of alloxantin is rendered difficult by the ease with which it dissociates into alloxan and dialuric acid; even in a saturated aqueous solution, dissociation proceeds to as much as 80% (Billmann and Bentzon, A., 1918, i, 352). Since methylation may be effected in the absence of water by the use of diazomethane, it was hoped that by means of that reagent the structure of alloxantin might be elucidated. But even in the complete absence of water, the products of the action of diazomethane on alloxantin are derived from alloxan and dialuric acid; consequently, the results obtained only contribute to the constitutional problem by providing a further illustration of the ease of dissociation of alloxantin.

Actually it is immaterial whether alloxantin or tetramethylalloxantin is used, and whether water of crystallisation is present or not; the products are 5:6-methylenedioxy-1:3-dimethyluracil, $\text{NMe}\cdot\text{CO}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\cdot\text{O} > \text{CH}_2$ (I), large, flat, rhombic leaflets (possibly monoclinic), m. p. 170°, and 5:6-dimethoxy-1:3-dimethyluracil, $\text{NMe}\cdot\text{CO}-\overset{\text{OMe}}{\underset{\text{OMe}}{\text{C}}}$ (II), slender prisms (apparently monoclinic), m. p. 59°. The compound (I), which has already been obtained as a syrup (Herzig, A., 1922, i, 373), is also produced by the action of diazomethane on alloxan monohydrate, dimethylalloxan monohydrate, or anhydrous dimethylalloxan, but the last named reacts fully only in the presence of water. The dimethoxy-derivative (II) is also obtained by the action of diazomethane on dialuric acid or 1:3-dimethylalialuric acid.

The constitution of the methylene ether (I) follows from its mode of formation and properties. It is unaffected by treatment with concentrated nitric acid, with alcoholic sodium ethoxide, or, in glacial acetic acid solution, with hydrogen peroxide or with sodium amalgam. The ether is dissolved by means of alkali hydroxide solution, but is evidently changed, since it is not recovered by acidifying the solution. The methylenedioxy-ring is broken by the action of cold, or, more rapidly, by means of boiling, water, or by the action of hot, concentrated hydrochloric acid. In the first reaction, formaldehyde is produced; the second leads to the formation of the 6-chloromethyl ether of 1:3-dimethylisodialuric acid, $\text{NMe}\cdot\text{CO}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\cdot\text{O}\cdot\text{CH}_2\text{Cl}$ long prisms, m. p. 92° (corr.), anhydrous, or with H₂O, long prisms, m. p. 88° (corr.). The chloromethoxyl group is probably situated at position 6, rather than at 5, since the molecule of water is apparently held about as firmly as in alloxan monohydrate, and is therefore probably attached to the 5-carbonyl group (see below). The action of warm hydriodic acid, *d* 1.96, on the methylene ether gives the 6-iodomethyl ether, m. p. 83°, or with H₂O, short, compact rhombs, m. p. 123° (corr.). This, and the chloromethyl ether, are stable towards acids, but are decomposed

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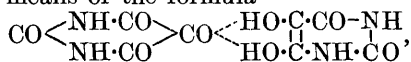
by the action of alkali hydroxide. The action of diazomethane on the chloro-ether gives *5-methoxy-6-chloromethoxy-1:3-dimethyluracil hydrate*, $\begin{array}{c} \text{NMe}\cdot\text{CO}\cdot\text{C}\cdot\text{OMe} \\ | \\ \text{CO}\cdot\text{NMe}\cdot\text{C}\cdot\text{O}\cdot\text{CH}_2\text{Cl} \end{array}\cdot\text{H}_2\text{O}$, long, glistening prisms, m. p. 118.5° , in which the molecule of water is probably attached to the 5:6-double bond, since it is not removed by distillation.

The constitution of the dimethyl ether (II) follows from its synthesis from dialuric acid or its *N:N'*-dimethyl derivative. Moreover, approximately two methyl groups are removed by boiling for about ten minutes with hydriodic acid, although the remaining methyl groups are eliminated by further action of the acid. The dimethyl ether is only decomposed when boiled for a long time with alkali hydroxide solution.

An attempt to prepare the compound (II) by the action of diazomethane on *isodialuric acid*, which could presumably react as 5:6-dihydroxyuracil, was unsuccessful. In the presence of traces of moisture, a gummy product is obtained, whereas when both materials are carefully dried a *compound*, short, compact prisms, m. p. 127° (decomp.), is formed, in which, apparently, two methyl groups are attached to nitrogen, whilst a third molecule of diazomethane has entered into combination without the elimination of nitrogen. Nevertheless, *isobarbituric acid* (5-hydroxyuracil) is readily converted by means of diazomethane into *5-methoxy-1:3-dimethyluracil*, small, slender needles, m. p. 191° (corr.) (slight decomp.).

Neither the methylene ether nor the dimethyl ether of 5:6-dihydroxy-1:3-dimethyluracil could be made to undergo condensation with carbamide.

The extraordinary ease with which alloxantin undergoes fission is expressed by means of the formula



the alloxan-half of which is analogous to the probable structure, $\text{CO} < \begin{array}{c} \text{NH}\cdot\text{CO} \\ \text{NH}\cdot\text{CO} \end{array} > \text{CO} < \begin{array}{c} \text{H} \\ \text{H} \end{array} > \text{O}$, of alloxan monohydrate. In aqueous solution, the dialuric acid half of the molecule simply becomes replaced by water, whereas in ethereal solution it is readily removed by the action of diazomethane, which causes methylation of the reactive hydroxyl groups; but anhydrous alloxan is not acted on by dry diazomethane. The formation of coloured salts containing tervalent carbon (Hantzsch, A., 1921, i, 619) can as readily be explained on the formula now suggested, as on the older pinacone-like formula. It is believed that the hydrate of the chloromethyl ether (above) has a similar structure.

Apparently only one example has been found previously of the production of a methylene ether by the action of diazomethane on a 1:2-diketone; benzil and diazomethane give methylenedioxy-stilbene (v. Pechmann, A., 1895, i, 328). This compound, like the ether (I), is stable towards cold, dilute alkali, or concentrated, and even boiling, acids. By the use of boiling 3% potassium hydroxide solution, formaldehyde is eliminated. Nitration is brought about by the use of fuming nitric acid. The usual reducing and oxidising

agents have no effect, but benzoic acid is produced by the action of hydrogen peroxide in hot glacial acetic acid solution. A similar compound, presumably 9:10-methylenedioxyphenanthrene, which cannot be distilled or made to solidify, is produced by the action of diazomethane on phenanthrenequinone. Oily products are likewise obtained from *p*:*p'*-dibromobenzil, furil, and α -naphthaquinone; anthraquinone also slowly reacts, and benzoquinone (cf. v. Pechmann, *loc. cit.*) gives a yellow, amorphous solid, which blackens at 200° and decomposes at 350°. Diacetyl, acetylacetone, and dimethylparabanic acid do not react with diazomethane; oxalic acid is converted into dimethyl oxalate, which does not undergo any further change. Glyoxal (the solid polymeride) is gradually converted in ethereal solution into diacetyl, yield 85%.

An attempt is made to define the limits of the use of diazomethane for the methylation of nitrogenous or hydroxylic substances, but, although the activating influence which enables a nitrogen atom to become methylated is usually obvious, other examples are quoted, the reason for which remains obscure. W. S. N.

The Constitution of Indophenine. W. SCHLENK and OTTILIE BLUM (*Annalen*, 1923, **433**, 95—103).—The molecular weight of indophenine, or of the other similar condensation products of thiophen with compounds containing the carbonyl group, cannot be determined. It is now shown, however, that the action of ice-cold, concentrated sulphuric acid on a petroleum-ethereal solution containing thiophen and ethyl mesoxalate gives *mesoxophenine* ($C_7H_{10}O_4, C_4H_2S$)₂, small, deep violet tablets, or a powder of coppery lustre, m. p. 159—161°, the molecular weight of which may be determined in chloroform solution. A similar condensation *product*, m. p. 230—232°, is obtained by the use of methyl mesoxalate. By analogy, the empirical formula for indophenine is (C_8H_5ON, C_4H_2S)₂. Liebermann and Krauss (A., 1907, i, 657) have already advanced the formula (I) for indophenine. The residue, $C_6H_4<\begin{smallmatrix} NH \\ CO \end{smallmatrix}>C<$,

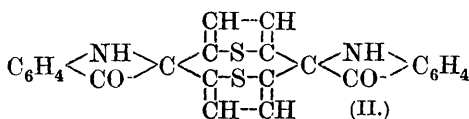
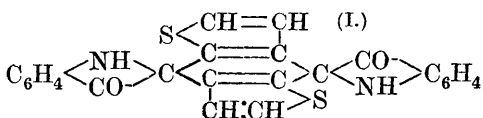
present in this formula is, however, similar to the structure, not of isatin, which contains two conjugated carbonyl groups, but of the colourless, ketonic form of indoxyl; hence, contrary to the view of

Liebermann and Krauss (*loc. cit.*), the formula (I) does not accord with the intense blue colour of indophenine. Moreover, there is no proof that the

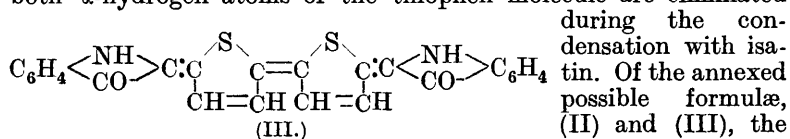
thiophen molecules are linked in the β -position. In fact, it is now shown that only those homologues of thiophen in

which neither α -position is alkylated can give the indophenine reaction. Thus 3-methyl- and 3:4-dimethyl-thiophen react, but not 2-methyl-, 2:5-

dimethyl-, 2:3-dimethyl-, or 2:4-dimethyl-thiophen. Evidently



both α -hydrogen atoms of the thiophen molecule are eliminated

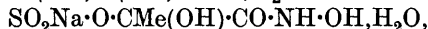


since formula (II) does not account for the intense colour of indophenine. Moreover, either indophenine or mesoxophenine, to which a similar structure is assigned, may be reduced in acetic acid solution by means of zinc dust to a leuco-base, from which the dye is regenerated by making the solution alkaline and shaking in contact with air, this being well expressed by the indigoid structure (III). The direct coupling of two thiophen molecules, as in (III), is actually known to occur, since thiophen is converted into 2 : 2'-dithienyl by the action of concentrated sulphuric acid (Töhl, A., 1894, i, 276).

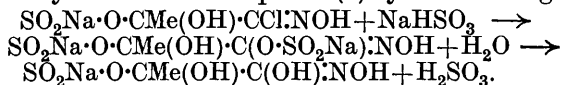
during the condensation with isatin. Of the annexed possible formulæ, (II) and (III), the latter is preferred,

W. S. N.

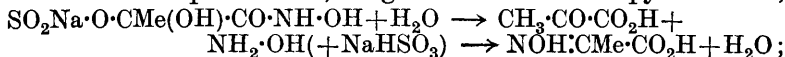
Hydrogen Sulphite Compounds : Hydroxamic Acids and Derivatives of 1 : 2 : 4-Triazole. C. GASTALDI (*Gazzetta*, 1923, 53, 635—645).—The action of sodium hydrogen sulphite on chloroximinoacetone yields (1) the sodium sulphite compound of pyruvylhydroximinic chloride, which has been already considered (A., 1922, i, 626), and (2) the sodium sulphite compound of pyruvylhydroxamic acid, $\text{SO}_2\text{Na}\cdot\text{O}\cdot\text{CMe}(\text{OH})\cdot\text{C}(\text{OH})\cdot\text{NOH}\cdot\text{H}_2\text{O}$ or



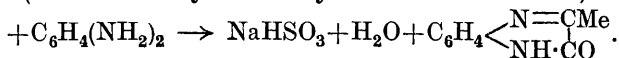
which probably results from compound (1) by the following reactions:



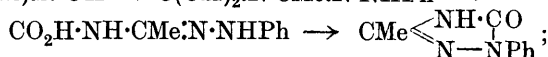
Compound (2) gives the iodoform reaction with iodine and sodium carbonate, and with ferric chloride yields the intense cherry-red coloration characteristic of the hydroxamic acids; when heated with dilute sulphuric acid, it gives the oxime of pyruvic acid,



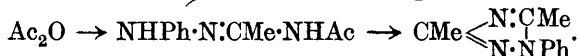
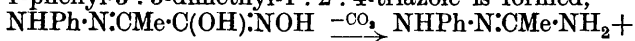
with *o*-phenylenediamine it yields 3-hydroxy-2-methyl-1 : 4-benzodiazine (3-keto-2-methyl-3 : 4-dihydro-1 : 4-benzodiazine) :



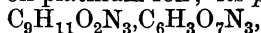
With phenylhydrazine, it gives a compound, $\text{C}_9\text{H}_{11}\text{O}_2\text{N}_3$, which appears to be a phenylhydrazone of pyruvylhydroxamic acid, $\text{NHPh}\cdot\text{N}:\text{CMe}\cdot\text{C}(\text{OH})\cdot\text{NOH}$, since it may readily be converted into 1 : 2 : 4-triazole derivatives. Thus, when this compound or its acetyl derivative is heated, or the latter is treated with sodium ethoxide, 5-hydroxy-1-phenyl-3-methyl-1 : 2 : 4-triazole results, $\text{NHPh}\cdot\text{N}:\text{CMe}\cdot\text{C}(\text{OH})\cdot\text{N}\cdot\text{OH} \rightarrow \text{C}(\text{OH})_2\cdot\text{N}:\text{CMe}\cdot\text{N}\cdot\text{NHPh} \rightarrow$



when, however, the phenylhydrazone is heated with acetic anhydride, 1-phenyl-3 : 5-dimethyl-1 : 2 : 4-triazole is formed,



Pyruvylhydroxamic acid phenylhydrazone forms crystals which, after being dried at 100°, melt and lose carbon dioxide at 178—179°. When reduced in sodium hydroxide solution by means of sodium amalgam, it yields α -phenylhydrazidopropionic acid, m. p. 172—173° (decomp.) (cf. von Miller and Plöchl, A., 1892, 1196), or if the reduction is effected at 0° two compounds, m. p. 124—125° and 144°, respectively. Its sodium salt forms pale yellow prisms, gives an alkaline aqueous solution, and decomposes gradually in the air or violently when heated on platinum foil; its *picrate*,



crystallises in red needles, m. p. 158°, and its *acetyl* derivative forms colourless laminae, m. p. 142° (evolution of gas), gives a brick-red coloration with concentrated sulphuric acid and a brownish-yellow coloration with ferric chloride in alcoholic solution, and exhibits normal cryoscopic behaviour in naphthalene and in acetic acid.

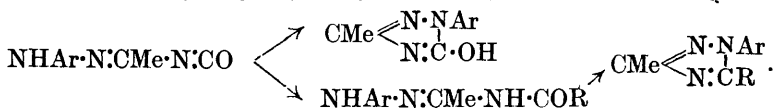
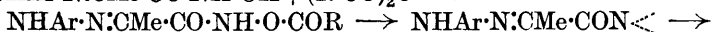
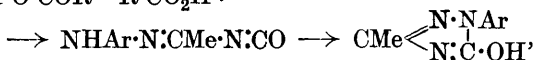
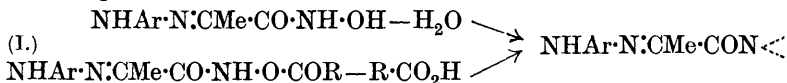
Pyruvylhydroxamic acid phenylmethylhydrazone,

$\text{NMePh}\cdot\text{N}:\text{CMe}\cdot\text{C}(\text{OH})\cdot\text{N}\cdot\text{OH}$ or $\text{NMePh}\cdot\text{N}:\text{CMe}\cdot\text{CO}\cdot\text{NH}\cdot\text{OH}$, prepared similarly to the phenylhydrazone, forms yellow needles, m. p. 126°, gives a deep red coloration with ferric chloride in aqueous or alcoholic solution, is decomposed by concentrated sulphuric acid, and reduces hot Fehling's solution and cold ammoniacal silver nitrate solution. Its *acetyl* derivative crystallises in golden-yellow needles, m. p. 82—83°, has the normal molecular weight in freezing benzene, reduces ammoniacal silver nitrate solution, and gives a brick-red coloration with concentrated sulphuric acid.

T. H. P.

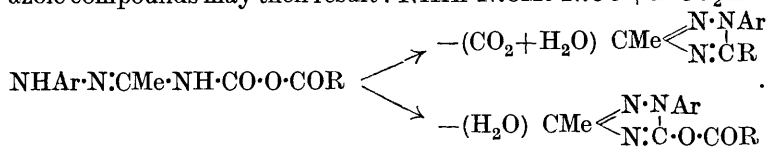
Hydroxamic Acids and Derivatives of 1 : 2 : 4-Triazole.

C. GASTALDI (*Gazzetta*, 1923, 53, 629—634).—According to the views of Stieglitz (A., 1897, i, 43; 1903, i, 235), the formation of derivatives of 1 : 2 : 4-triazole from pyruvylhydroxamic acid arylhydrazones (preceding abstract) may be indicated by the following schemes :



It may be, however, that the carbimide formed unites with a molecule

of the aliphatic acid giving a mixed anhydride from which the two triazole compounds may then result : $\text{NHAr}\cdot\text{N}:\text{CMe}\cdot\text{N}:\text{CO} + \text{R}\cdot\text{CO}_2\text{H} \rightarrow$



The *propionyl* derivative of *pyruvylhydroxamic acid phenylhydrazone*, $\text{NHPh}\cdot\text{N}:\text{CMe}\cdot\text{C}(\text{OH})\cdot\text{NO}\cdot\text{COEt}$, prepared from propionic anhydride on pyruvylhydroxamic acid phenylhydrazone, crystallises in colourless laminae, m. p. 121° , at which temperature it loses propionic acid and yields 5-hydroxy-1-phenyl-3-methyl-1 : 2 : 4-triazole, m. p. 167° .

1-Phenyl-3-methyl-5-ethyl-1 : 2 : 4-triazole, $\text{N} \begin{smallmatrix} \text{CMe}\cdot\text{N} \\ \diagdown \text{CEt}-\text{NPh} \end{smallmatrix}$, prepared, together with the propionyl derivative of 5-hydroxy-1-phenyl-3-methyl-1 : 2 : 4-triazole, from propionic anhydride and pyruvylhydroxamic acid phenylhydrazone, forms a dense, colourless liquid, b. p. $160\text{--}165^\circ/14\text{ mm.}$; its *hydrochloride* forms colourless prisms, m. p. 207° , its *chloroplatinate* orange-yellow prisms, m. p. 190° , and its *picrate* bundles of long, yellow laminae, m. p. 138° .

Pyruvylhydroxamic acid p-bromophenylhydrazone,

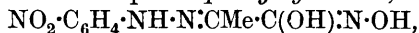


obtained by the action of *p*-bromophenylhydrazine on the bisulphite compound of pyruvylhydroxamic acid, crystallises in colourless prisms, m. p. $185\text{--}186^\circ$, gives a blood-red coloration with concentrated sulphuric acid, and, in alcoholic solution, yields a violet-blue coloration with ferric chloride. Its *sodium* salt was analysed, and its *acetyl* derivative, $\text{C}_{11}\text{H}_{12}\text{O}_3\text{N}_3\text{Br}$, separates in colourless needles, m. p. 155° , and, when heated at its melting point, loses acetic acid and gives 5-hydroxy-1-*p*-bromophenyl-3-methyl-1 : 2 : 4-triazole,

$\text{N} \begin{smallmatrix} \text{CMe}=\text{N} \\ \diagdown \text{C}(\text{OH})\cdot\text{N}\cdot\text{C}_6\text{H}_4\text{Br} \end{smallmatrix}$, which crystallises in colourless needles, m. p. 267° .

1-*p*-Bromophenyl-3 : 5-dimethyl-1 : 2 : 4-triazole, $\text{N} \begin{smallmatrix} \text{CMe}\cdot\text{N} \\ \diagdown \text{CMe}\cdot\text{N}\cdot\text{C}_6\text{H}_4\text{Br} \end{smallmatrix}$, obtained, together with the acetyl derivative of 5-hydroxy-1-*p*-bromophenyl-3-methyl-1 : 2 : 4-triazole, by boiling a mixture of pyruvylhydroxamic acid *p*-bromophenylhydrazone and acetic anhydride, forms a pale yellow, dense liquid, b. p. $225\text{--}230^\circ/45\text{ mm.}$; its *hydrochloride* is obtained in colourless laminae, m. p. 239° .

Pyruvylhydroxamic acid p-nitrophenylhydrazone,



crystallises in chestnut-red prisms, m. p. 224° (decomp.), dissolves in dilute sodium hydroxide solution to a deep violet-red solution, and in alcoholic solution gives a dark green coloration with ferric chloride. Its *acetyl* derivative forms slender, yellow needles, m. p. 170° , and, when heated at its melting point, gives 5-hydroxy-1-*p*-nitrophenyl-3-methyl-1 : 2 : 4-triazole.

T. H. P.

Polypyrroles. ANTONIO PIERONI (*Atti R. Accad. Lincei*, 1923, [v], **32**, ii, 175—179; cf. A., 1922, i, 766).—In accordance with its constitution, Dennstedt's tripyrrole, which is formed of two pyrrole rings united in the 2-position to a pyrrolidine nucleus, yields black compounds only with difficulty, but 2-hydroxydipyrpyl gives such compounds even more readily than pyrrole itself. It hence appears probable that more complex pyrrole derivatives will yield black products still more easily. This conclusion is supported by the results now described.

Ethyl β-pyrrolylpropionate, $\begin{array}{c} \text{CH-CH} \\ | \quad \diagup \\ \text{CH-NH} \end{array} > \text{C} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$, prepared from magnesium pyrpyl iodide and ethyl succinate, crystallises in needles, m. p. 70°, and the free *acid*, $\text{C}_8\text{H}_5\text{O}_3\text{N}$, in white needles, m. p. 140°. When treated in ethereal solution with magnesium pyrpyl iodide, this ethyl ester yields *s*-dipyrroylethane, m. p. 236° (cf. Oddo and Dainotti, A., 1912, i, 721), and the latter, when boiled with ammonium acetate in acetic acid, gives a blue-black powder which has the general properties of the pyrrole-blacks and the composition $\text{C}_{12}\text{H}_8\text{O}_3\text{N}_3$. T. H. P.

Derivatives of Thiosemicarbazides and of Hydrazodithiodicarbonamides. E. FROMM [with E. LAYER and K. NERZ] (*Annalen*, 1923, **433**, 1—17).—3 : 5-Diamino-4 : 1 : 2-thiodiazole, $\text{N}:\text{C}(\text{NH}_2) \text{---} \text{N}:\text{C}(\text{NH}_2) > \text{S}$, has already been obtained (Fromm, Briegleb, and Föhrenbach, A., 1922, i, 377; Busch, Schmidt, and others, A., 1913, i, 907; 1915, i, 317; Freund, Imgart, and Wischewiansky, A., 1894, i, 97; 1895, i, 400) by the action of concentrated hydrochloric acid on hydrazodithiodicarbonamide. A better yield is obtained by oxidising the latter by means of warm, aqueous hydrogen peroxide; the dithienol form of the diamide becomes oxidised to a cyclic disulphide, which undergoes hydrolytic fission, with loss of sulphur, water being then eliminated from the resulting hydroxythienol derivative. The presence of two amino-groups in the product is demonstrated by the formation of a *benzylidene* derivative, pale yellow crystals, m. p. 218°, and of *dibenzoyl* and *diacetyl* derivatives, white, microcrystalline powders, of m. p. above 280°. The latter is also formed, together with phenylthiocarbimide, by the action of boiling acetic anhydride on α -phenyl-β(3 : 5-diamino-4 : 1 : 2-thiodiazolyl)-carbamide, m. p. above 280° (darkens at 210°), which is produced by the action of phenylthiocarbimide on the thiodiamine in boiling, aqueous-alcoholic solution. The action of cyanogen on a warm 50% aqueous-alcoholic solution of the thiodiamine gives a *compound*, small, reddish-brown crystals, m. p. above 280° (blackens at 200°), which has, perhaps, the formula, $\text{CN} \cdot \text{C}(\text{NH}_2) \cdot \text{N} \cdot \text{C} \begin{array}{c} \text{N} \cdot \text{N} \\ \diagup \quad \diagdown \\ \text{S} \cdot \text{C} \cdot \text{NH}_2 \end{array}$, since it gives a *dibenzylidene* derivative, a black or brownish-black, amorphous powder.

Hydrazodithiodicarbonamide is converted by the action of boiling 10% hydrazine hydrate solution into 4-amino-1-thiol-2 : 3 : 5 : 6-tetrazine (or 3 : 4-diamino-5-thiol-1 : 2 : 4-triazole), yellow

needles, m. p. 217°, which gives the following derivatives: *benzyl*, white leaves, m. p. 220°, *benzoylbenzyl*, a microcrystalline powder, m. p. 198°, *acetylbenzyl*, an amorphous powder, m. p. 198—200°, *acetyl*, a white powder, m. p. 265°, *benzylidene*, +2H₂O, m. p. 270°. The latter is oxidised by means of hydrogen peroxide to a *disulphide*, a yellow powder, m. p. 265°; with lead acetate, it gives a *lead* salt.

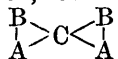
Diphenylhydrazodithiocarbonamide is converted by the action of boiling 10% hydrazine hydrate solution, or of warm dilute sodium hydroxide solution, into 3-anilino-5-thiol-4-phenyl-1:2:4-triazole (Busch and Ulmer, A., 1902, i, 575), which gives a *benzoyl* derivative, m. p. 187°, and a *benzyl* derivative, m. p. 154°, and is converted by the action of cold 50% sulphuric acid, warm aqueous-alcoholic hydrogen peroxide, or faintly acid ferric chloride solution, into a *disulphide*, a yellow, amorphous powder (*diacetate*, +H₂O, lemon-yellow crystals, m. p. 214°). The latter is converted by means of warm alcoholic sodium hydroxide solution into 3-anilino-4-phenyl-1:2:4-triazole (Busch and Bauer, A., 1900, i, 414).

Diphenylhydrazodithiocarbonamide is converted, in boiling alcoholic solution, by means of phenylhydrazine, iodine, or ferric chloride and hydrochloric acid, or, in cold, dilute sodium hydroxide solution, by means of hydrogen peroxide, into 3:5-dianilino-4:1:2-thiodiazole (*dibenzoyl* derivative, m. p. 198—199°) (Freund and Wischewiansky, A., 1894, i, 907; Busch and Schmidt, A., 1913, i, 907). The use of ferric chloride leads also to the formation of 3:5-dithio-4-phenyl-1:2:4-triazole, lemon-yellow needles, m. p. 230°, *dibenzyl* derivative, pale yellow crystals, m. p. 114°.

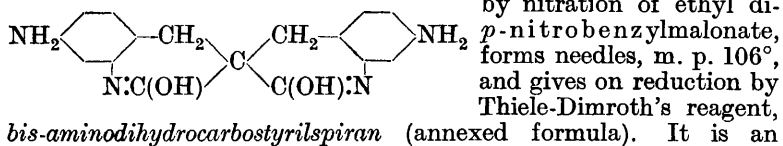
The action of hydrogen chloride, in boiling glacial acetic acid solution, on diphenylhydrazodithiocarbonamide, gives 3-anilino-5-thiol-4:1:2-thiodiazole (Busch and Schmidt, *loc. cit.*; Freund and Imgart, A., 1895, i, 400), which forms a *benzyl* derivative, white needles, m. p. 144°; it is oxidised by means of hydrogen peroxide in warm aqueous alcoholic solution to a *disulphide*, an orange-coloured precipitate, m. p. 227°, which is converted by the action of boiling, alcoholic sodium hydroxide solution into 3-anilino-4:1:2-thiodiazole, m. p. 170°.

W. S. N.

Spirans. X. Ethyl Di-*op*-dinitrobenzylmalonate and its Reduction Products. Synthesis of an Optically Active Spiran without an Asymmetric Carbon Atom. DAN RADULESCU (*Bul. Soc. Științe Cluj*, 1922, 1, 306—310; from *Chem. Zentr.*, 1923, iii, 139—140; cf. this vol., i, 1211).—Spirans of the general formula



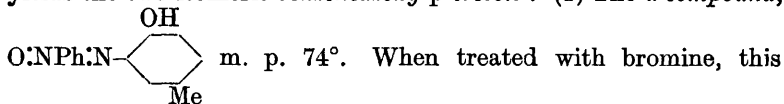
must show molecular asymmetry, although they possess no single asymmetric carbon atom. Such a spiran has been prepared by the author. *Ethyl bis-*op*-dinitrobenzylmalonate*, obtained



amorphous, white substance. The *dihydrochloride* forms flakes. The optically active *base* is obtained by means of silver bromo-camphorsulphonate. It has $[\alpha]_D^{25} - 84^\circ$ and is chemically identical with the racemic base. G. W. R.

Ortho-hydroxyazoxy-compounds. DINO BIGIACI and RAOUL POGGI (*Atti R. Accad. Lincei*, 1923, [v], 32, ii, 168—171).—Two isomeric azoxy-compounds containing a hydroxyl group in the ortho-position to the azo-group are formed as secondary products in the action of alkali and light on nitrosobenzene (Bamberger, A., 1900, i, 531; 1902, i, 505), but the yields are so small that their structures have not been determined.

Oxidation of benzeneazo-*p*-cresol by means of peracetic acid yields the two isomeric *benzeneazoxy-p-cresols*: (1) The α -compound,



yields a *polybromo*-compound, m. p. 164—165°, from which, by reduction, the only base obtained is aniline. (2) The β -isomeride, $\text{NPh:NO}\cdot\text{C}_6\text{H}_4\text{Me}\cdot\text{OH}$, m. p. 125°, which is converted by the action of bromine into a *dibromo*-derivative, m. p. 167°; reduction of the latter yields *p*-bromoaniline.

Certain reactions of the para-hydroxyazoxy-derivatives may be extended to the ortho-compounds. The first products of bromination of the α - and β -benzeneazoxy-*p*-cresols are respectively α -benzeneazoxy-3-bromo-*p*-cresol, m. p. 143°, and β -benzeneazoxy-3-bromo-*p*-cresol, m. p. 117°, each of these giving aniline and 6-amino-2-bromo-*p*-cresol when reduced by means of tin and hydrochloric acid.

In alkaline solution, permanganate oxidises azoxyphenols to *isodiazo*-compounds with diverse velocities, the β -form of *p*-hydroxy-azoxybenzene exhibiting far greater resistance than the α -isomeride (A., 1921, i, 364). Similarly, the oxidation of β -benzeneazoxy-*p*-cresol proceeds to so slight an extent that the normal diazo-compound obtained by acidifying the alkaline solution of the *isodiazo*-compound gives but a feeble red coloration with β -naphthol; contrary to Bamberger's suggestion (A., 1900, i, 531), this reaction cannot be regarded as a means of characterising azoxyphenols. Owing to their different oxidisabilities, the two *o*-hydroxyazoxy-benzenes are to be considered as isomeric and not, as Bamberger at first supposed, as stereoisomeric; the compound, m. p. 78°, will have the α -structure, $\text{O:NPh:N}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, and the isomeride, m. p. 108°, the β -structure $\text{NPh:NO}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$.

It has been shown previously (A., 1922, i, 878) that nitrous acid acts on the grouping $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{N}(\text{C})$, giving rise to a nitro-derivative with the nitro-group in the ortho-position to the hydroxyl, whilst it is without action on the grouping $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}$. In agreement with this, β -benzeneazoxy-*p*-cresol remains unchanged when treated with nitrous acid, whereas the α -isomeride yields α -benzeneazoxy-3-nitro-*p*-cresol, m. p. 122°; further, benzeneazo-

cresol, by virtue of its $\text{:N}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{OH}$ group, yields a nitro-derivative with the nitro-group in the ortho-position to the hydroxyl.

Normal diazo-compounds, such as $\text{NPh}\cdot\text{NH}$, which are analogous to nitrous acid, $\text{NH}\cdot\text{O}$, resemble the latter in reacting with groupings containing a tervalent nitrogen atom and a hydroxyl group, $\text{:N}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$. Thus, benzeneazo-*p*-cresol readily yields the compound $\text{NPh}\cdot\text{N}\cdot\text{C}_6\text{H}_2\text{Me}(\text{OH})\cdot\text{N}\cdot\text{NPh}$, m. p. 180° (cf. Puxeddu and Maccioni, A., 1907, i, 798), and α -benzeneazoxy-*p*-cresol the compound $\text{O}\cdot\text{NPh}\cdot\text{N}\cdot\text{C}_6\text{H}_2\text{Me}(\text{OH})\cdot\text{N}\cdot\text{NPh}$, m. p. 143° .

Although it seems more justifiable to consider the difference between the two *o*-azoxy-compounds to be determined by the position of the oxygen atom in the azo-group, support is furnished to Baudisch's view (A., 1907, i, 356) by the observation that β -*o*-hydroxyazoxybenzene and β -benzeneazoxy-*p*-cresol react with difficulty with benzoyl chloride, acetic anhydride, or ethyl iodide, giving dense, oily products, whereas the corresponding α -compounds readily yield crystalline products with these reagents. T. H. P.

Condensation of Aryldiazonium Salts with Mono-alkylated Malonic Acids. THOMAS KENNEDY WALKER (T., 1923, 123, 2775—2779).

Ring Closure and Intensity of Colour. JULIUS VON BRAUN and JON SEEMAN (*Ber.*, 1923, 56, [B], 2161—2164).—The intensity of the colour reactions given by certain dialkylanilines has been compared with those shown by allied compounds in which the nitrogen atom is present in a ring. The substances investigated include hydrols, $\text{R}\cdot\text{CH}(\text{OH})\cdot\text{R}$, azo-compounds of the formula $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{NR}$, and nitroso-compounds, $\text{R}\cdot\text{NO}$. In general, it appears that the absorption of light is much more marked with cyclic amines than with substituted anilines and that the length of the chain which is closed to a ring is unimportant; the phenomena do not appear to be explicable at the present time.

The following new compounds have been prepared incidentally: *Bis*-1-methyl-1 : 2 : 3 : 4-tetrahydroquinolylmethane (from kairolin and formaldehyde in acid solution), a colourless, viscous liquid, b. p. $235\text{—}240^\circ/1\text{ mm.}$; *bis*-N-methyl- α -methylidihydroindylmethane, $\text{C}_{21}\text{H}_{26}\text{N}_2$, a viscous liquid, b. p. $235\text{—}240^\circ/1\text{ mm.}$; *p'*-nitrobenzene-azo-*o*-anisidine, a brownish-red, microcrystalline powder, m. p. $119\text{—}121^\circ$; *p*-nitrobenzeneazo-1-methyl-1 : 2 : 3 : 4-tetrahydro-6-quinoline, a microcrystalline, brown powder, m. p. 147° ; *p*-nitrobenzene-azo-N-methyl- α -methylidihydroindole, small, dark brown crystals, m. p. 121° ; *p*-nitrobenzeneazo-N-methylphenmorpholine, an almost black, crystalline powder, m. p. 213° . H. W.

The Cyanine Dyes. VII. A New Method of Formation of the Carbocyanines. The Constitution of the Thioisocyanines and of Kryptocyanine. WILLIAM HOBSON MILLS and WALTER THEODORE KARL BRAUNHOLTZ (T., 1923, 123, 2804—2813).

Protein Studies. Crystalline Egg-albumin Salts which are Precipitated by Salts Other than Ammonium Sulphate. S. P. L. SØRENSEN and S. PALITZSCH (*Z. physiol. Chem.*, 1923, **130**, 72—83).—Egg-albumin may be obtained in a crystalline condition by the addition of a mixture of primary and secondary ammonium phosphate. The product resembles in crystalline form that obtained by the use of ammonium sulphate. The values of factor r =(weight of protein [containing water of crystallisation]/weight of protein nitrogen), for different preparations were determined. For protein precipitated at p_H 4.81, r =7.89, and at a p_H 5.48, r =8.12. For protein precipitated by ammonium sulphate, r =7.86. The figures do not decide conclusively whether a different salt is precipitated in the two cases. The solubility of the protein in presence of ammonium sulphate increases rapidly with increase of p_H , i.e., at constant ammonium concentration, the solubility decreases with increase of phosphoric acid. W. O. K.

Hydroxypyrroles in Proteins. N. TROENSEGAARD (*Z. physiol. Chem.*, 1923, **130**, 84—86; cf. this vol., i, 615).—Protein (gliadin) was acetylated (acetyl value, 36.3) and then methylated (methoxyl value, 20.5). The product was reduced with sodium in amyl-alcoholic solution and fractionated. The ether-soluble pyrrole fraction contained the greatest amount of methoxyl. Only about one-third of the total methoxyl survived the reduction. It would appear that there is more hydroxypyrrole in gliadin than is detected by the usual analysis. W. O. K.

The Amino-acids of Zein. H. D. DAKIN (*Z. physiol. Chem.*, 1923, **130**, 159—168).—With the help of the butyl alcohol method (A., 1921, i, 66) an analysis has been made of zein, and the following constituents have been found: alanine, 3.8%; leucine, 25%; phenylalanine, 7.6%; tyrosine, 5.2%; proline, 8.9%; aspartic acid, 1.8%; glutamic acid, 31.3%; β -hydroxyglutamic acid, 2.5%. W. O. K.

Peroxydase. IV. The Peroxydase Activity of Oxyhæmoglobin. RICHARD WILLSTÄTTER and ADOLF POLLINGER (*Z. physiol. Chem.*, 1923, **130**, 281—301).—Systematic investigation has been made of the peroxydase activity of crystalline oxyhæmoglobin, by weighing the amount of purpurogallin produced from pyrogallol in presence of hydrogen peroxide under definite conditions. With a constant quantity of oxyhæmoglobin from horse-blood, the yield of purpurogallin increases with the amount of hydrogen peroxide, and so also with increasing oxyhæmoglobin and constant hydrogen peroxide. In neither case is the relation quite linear. The peroxydase activity does not alter with repeated recrystallisation, but differs from the activity of a simple solution of blood corpuscles, in which the peroxydase is hindered in its action by the catalase. A comparison of the activity of various types of hæmoglobin of various species of animals shows that that from horse-blood is the most active and that the others follow in the following order, dog, ox, and pig. The activity is approximately expressed

xx^*2

by the formula $a = \alpha c^{1/n}$, where $1/n = 0.188, 0.229, 0.214$, and 0.215 , for horse, dog, ox, and pig respectively, for constant hydrogen peroxide and varying hæmoglobin. W. O. K.

Natural Porphyrins. III. Exogenous Porphyrin Formation and Excretion. HANS FISCHER and KARL SCHNELLER (*Z. physiol. Chem.*, 1923, **130**, 302—325).—After the administration of blood, Kammerer's porphyrin has been found in the fæces in addition to the small amounts of coproporphyrin normally present. The adsorption spectra of these spectra has been investigated fully. Kammerer's porphyrin on treatment with ferrous acetate in acetic acid solution combines with iron and Kammerer's hæmin is formed. Exposure to bright sunlight of a person secreting Kammerer's porphyrin as a result of administration of blood gave negative results. Porphyrin is obtained from hæmin by the action of sodium amalgam in alkaline solution. W. O. K.

Analysis of Tuberculinic Acid. ELMER E. BROWN and TREAT B. JOHNSON (*J. Biol. Chem.*, 1923, **57**, 199—208).—On purification, tuberculinic acid (cf. this vol., i, 160, 965) loses guanine, leaving a stable trinucleotide containing adenine, thymine, and cytosine. The absence of uracil from the molecule has been confirmed. E. S.

The Decomposition Products of Gelatin. WL. GULEWITCH (*Z. physiol. Chem.*, 1923, **130**, 152—158).—From the product of the hydrolysis of gelatin by sulphuric acid an amino-acid has been isolated as the nitrate $C_6H_{14}O_2N_4.HNO_3$, m. p. 222° , $[\alpha]_D +0.16^\circ$. The copper salt forms blue rosettes, $(C_6H_{14}O_2N_4)_2.Cu(NO_3)_2$, m. p. 227° (decomp.). The acid is apparently racemic arginine, obtained previously by Kutscher (*Z. physiol. Chem.*, 1898, **26**, 114) by the tryptic decomposition of fibrin. It is considered probable that the racemic form arises by racemisation of *d*-arginine by the acid used in the hydrolysis. W. O. K.

The Combination of Deaminised Gelatin with Hydrochloric Acid. DAVID I. HITCHCOCK (*J. Gen. Physiol.*, 1923, **6**, 95—104).—When prepared without heat, deaminised gelatin, the isoelectric point of which is at $P_H 4.0$, contains 0.0004 equivalent of nitrogen per g. less than the original protein, an amount which is equivalent to the amino-nitrogen present in gelatin as indicated by Van Slyke's method. The difference (0.00045 equivalent) between the maximum combining capacities of gelatin and of deaminised gelatin for hydrochloric acid is practically equivalent to the loss in amino-nitrogen during the deaminising process. This is additional evidence that the combination between protein and acid is a chemical combination. The combining capacity of gelatin for hydrochloric acid (cf. A., 1922, i, 882) has been corrected to 0.00089 mols. per g. of protein. E. S.

Action of Chymosin and Pepsin. IX. The Different Behaviour of the Stomach Enzymes of the Calf and Pig with Acid on Heating. OLOF HAMMARSTEN (*Z. physiol. Chem.*, 1923, **130**, 55—71).—Evidence is brought to show that there is in the stomach of the pig only one enzyme. This is a pepsin and both

coagulates milk and hydrolyses protein. In the stomach of the calf there exist two enzymes, pepsin as before, and also chymosin which only coagulates milk. Whilst pepsin is the less resistant to alkali, as was previously shown (A., 1922, i, 958), it is now demonstrated that chymosin is the less resistant to acid. When heated in presence of 0.2% hydrochloric acid, the milk coagulating action of the extract of calf stomach decreases in the ratio 1 : 11, and the pepsin action only in the ratio 1 : 1.4. In the case of the extract of pig's stomach, the milk coagulating action decreases in the ratio 1 : 1.5, and the pepsin in the ratio 1 : 1.4. W. O. K.

Stoicheiometrical Relationship between Invertase and Silver Nitrate. H. VON EULER and K. MYRBÄCK (*Svensk Kem. Tidskr.*, 1922, 34, 222—231; from *Chem. Zentr.*, 1923, iii, 314; cf. A., 1922, i, 959).—From experiments on the inactivation of invertase by silver nitrate in solutions of varying hydrogen-ion concentration, it is concluded that a stoicheiometrical relationship exists between the enzyme and the silver nitrate which inactivates it. The silver equivalent is calculated as 5400. G. W. R.

Molecular Condition and Stability of Saccharase. H. VON EULER, K. JOSEPHSON, and K. MYRBÄCK (*Z. physiol. Chem.*, 1923, 130, 87—107).—It has been shown previously (this vol., i, 721) that highly purified saccharase can by diffusion be separated from material of high molecular weight associated with it. It is now found that the ratio of the rates of diffusion corresponds with a molecular weight of about 20,000 for the saccharase.

The activity of saccharase is decreased by alcohol, but reversibly, so that the activity returns again when the alcohol is removed. However, alcohol also causes an irreversible destruction of the saccharase. This destruction is a maximum with 60% alcohol and slowly decreases with more concentrated alcohol. The results agree qualitatively but not quantitatively with those of Hudson and Paine (A., 1910, i, 798). Apparently, this irreversible destruction depends to some extent on the degree of purity of the saccharase preparation. Some preparations of saccharase lose their activity on heating according to the law of unimolecular reaction, whereas other preparations of the same activity do not follow this law. Probably two enzymes exist, one of which possesses much greater thermostability than the other. However, the affinities for the substrate of the heated and the unheated enzyme solution are very similar. This would scarcely be expected if two enzymes were present and one was thermolabile. These results may be explained on the hypothesis that the stability of the enzyme is determined by other groups of the enzyme molecule than those which determine the affinity, and that the latter are the same in the two enzymes.

The rate of destruction of the dried enzyme is much less than that of the solution. W. O. K.

The Relation of the Thermolability of Malt Diastase to Acidity. EFR. ERNSTROM (*Biochem. Z.*, 1923, 141, 40—41).—At a p_H of 5.2, the resistance of malt diastase to inactivation, when

exposed for one hour to a temperature of 55°, is at a maximum (cf. Lüers and Lorinser, *Biochem. Z.*, 1922, **133**, 487). J. P.

The Action of Arsenic and Antimony Compounds on the Fermentative Function of the Organism. I. The Action of certain Arsenic and Antimony Preparations on Ptyalin. J. A. SMORODINCEV and FR. E. A. ILIN (*Biochem. Z.*, 1923, **141**, 297—303).—Potassium and sodium arsenites and arsenates, antimony trichloride, and antimonyl potassium tartrate inhibit the action of ptyalin on starch, the antimony compounds being more active than those of arsenic. In great dilutions (0.00004%), antimony trichloride accelerates the action of the enzyme, a result which is ascribed, not to any specific action of the antimony, but to the hydrochloric acid formed from the salt. In higher concentrations, hydrochloric and tartaric acids inhibit ptyalin, the latter exerting much the more marked effect. J. P.

Enzyme Action. XXIV. The Kinetics of the Ester-hydrolysing Actions of some Tissue and Tumor Extracts. KANEMATSU SUGIURA, HELEN MILLER NOYES, and K. GEORGE FALK (*J. Biol. Chem.*, 1923, **56**, 903—920).—Measurements have been made of the reaction velocity of the hydrolysis of glyceryl triacetate by extracts of the Flexner-Jobling rat carcinoma under different conditions of concentration and acidity. The results are similar to those which have been obtained with other enzymes. E. S.

Enzymic Hydrolysis of Hippuric Acid. A. CLEMENTI (*Atti R. Accad. Lincei*, 1923, [v], **32**, ii, 172—174).—The experimental results described confirm (cf. Mutch, A., 1912, ii, 579) the presence in the animal organism of an enzyme, termed hippuricase, which hydrolyses hippuric acid to benzoic acid and glycine and occurs in the kidneys of mammals in general and in pig's liver. Although its amidolytic activity is analogous to that of erepsin or trypsin, hippuricase is biochemically distinct from these enzymes. T. H. P.

Ferments. II. Lability of Soja Urease and the Question of Auxoureaes and Coenzymes. III. Mechanism of the Action of *Robinia* Urease. SATOSU NAKAGAWA (*Mitt. med. Fak. Kais. Univ. Tokyo*, 1922, **28**, 383—427; from *Chem. Zentr.*, 1923, iii, 395).—Soja urease is very labile in dilute solution and its effect at high temperatures is less than that calculated from the time and the amount of enzyme present. The auxoureae described by Jacoby inhibits the decomposition of urease. This inhibition is not shown by sodium nucleate, or the ash constituents of the substances containing the auxoureae. The co-enzyme effect of enzyme solutions inactivated by alkalis, acids, or by heating is explained as a protective action. Whether auxoureaes exert an activating effect can only be decided with preparations free from proteins and their hydrolytic products. Phosphates and acetates have no protective effect on urease, neither do they influence the effect of auxoureaes. It is confirmed that the diminished

activity of urease with increased volume of liquid holds also with constant concentration of urea.

Robinia urease has optimum p_H 7.4. Phosphates have no effect between 0.02 and 0.04 *M*. Urea exerts an inhibitory effect in concentrations above 10%. It is less labile than soja urease.

G. W. R.

Bacterial Tyrosinase. C. STAPP (*Biochem. Z.*, 1923, **141**, 42—69).—A tyrosinase closely resembling that of fungi is present in cultures of the bacteria from the root nodules of *Soja hispida*, various species of *Lupinus*, *Coronilla varia*, *Genista tinctoria*, *Sarothamnus scoparius*, and *Tetragonolobus purpureus*. Soja tyrosinase is capable of oxidising the barium salt of tyrosinesulphonic acid, hydroxyphenylethylamine hydrochloride, and to a less extent β -resorcylic acid. Gentisic acid, 2:4- and 2:5-dinitrobenzoic acids, anthranilic acid, phenylglycine and β -phenylpropionic acid are not oxidised. Bacterial tyrosinase acts more quickly in cultures killed by chloroform than in the presence of the living bacteria. It is regarded as an endocellular enzyme, and does not pass through a porcelain filter. The various tyrosinases investigated were all inactivated at temperatures between 60° and 65°, but they may be reactivated by shaking with oxygen even after subjection to temperatures of 75°. With increasing temperature, the rate of oxidation by bacterial tyrosinase rises, the optimum appearing to be close to the inactivation temperature. The range of action lies between p_H 5 and p_H 10.5, with an optimum at p_H 8. By means of bacterial tyrosinase, the presence of tyrosine in 0.005% concentration may be demonstrated. The intermediate formation of homogentisic acid was not detected during the action of the enzyme on tyrosine.

J. P.

Extraction of Vitamins from Yeast and Rice Polishings with Various Water-miscible Solvents. CASIMIR FUNK, BENJAMIN HARROW, and JULIA B. PATON (*J. Biol. Chem.*, 1923, **57**, 153—162).—When judged by the inactivity of the residues, the best solvents appear to be 70% alcohol in the case of yeast and 60% alcohol in the case of rice polishings. Very active extracts may also be obtained with acetone; moreover, such extracts contain a comparatively small proportion of nitrogenous impurities. The amounts of vitamins-B and -D extracted by different solvents appear to run parallel; no relation appears to exist, however, between these vitamins and the coferment. Extracts of rice polishings have a greater activity on rats than on pigeons. E. S.

Glucokinin. II. J. B. COLLIP (*J. Biol. Chem.*, 1923, **57**, 65—78).—Methods are described for the preparation of extracts of glucokinin (this vol., i, 967) from various plants. Injections of such extracts into normal rabbits produce a marked hypoglycæmia, which, however, may not become evident for some days or even weeks, followed by death. When the blood-serum obtained from such animals immediately prior to, or just after, death is injected into a second rabbit, similar results are produced. A depancreatised

dog has been maintained alive for sixty-six days, only three injections of glucokinin (onion extract) being made during this period.

E. S.

Organic Derivatives of Silicon. XXIX. Preparation, Properties, and Condensation Products of Di-*p*-tolylsilicane-diol. HERBERT SHEPPARD PINK and FREDERICK STANLEY KIPPING (T., 1923, **123**, 2830—2837).

The Preparation and Properties of some Phenylstannanes, $\text{Sn}_n\text{Ph}_{2n+2}$, and the Application of Microchemical Methods to the Determination of their Constants. Tervalent Tin. J. BÖESEKEN and J. J. RUTGERS (*Rec. trav. chim.*, 1923, **42**, 1017—1025).—Magnesium phenyl bromide reacts with stannic chloride to give tin diphenyl, tetraphenylmonostannane, hexaphenyldistannane, dodecaphenylpentastannane, and tin, together with some tin tetraphenyl. The analyses of these compounds were carried out by microchemical means, and their densities determined by flotation. It was found that hexaphenyldistannane in dilute benzene solution has only half the normal molecular weight, and that it will combine with iodine to form triphenylmonostannane iodide. It is therefore considered that tin in this compound is tervalent. Dodecaphenylpentastannane is regarded as having the formula $\text{Sn}(\text{SnPh}_3)_4$.

H. H.

Organic Mercury Mercaptides. GEORG SACHS [with HERBERT ANTOINE, and, in part, LEO SCHLESINGER] (*Annalen*, 1923, **433**, 154—163).—A series of compounds of the type $\text{R}^1\cdot\text{Hg}\cdot\text{S}\cdot\text{R}^2$ has been prepared by the interaction of alkyl- or aryl-mercuric halides and sodium mercaptides, in anhydrous alcoholic or acetone solution. The compounds are white and crystalline, easily soluble in most organic solvents, and volatile in steam. They are somewhat readily hydrolysed by means of dilute acids, giving mercaptans. The lower members of the series possess an unpleasant odour.

Ethylmercuric ethylmercaptide has m. p. 0—3°. *Ethylmercuric phenylmercaptide* has m. p. 61°. *Phenylmercuric ethylmercaptide* forms white, glistening needles, m. p. 56°. *Phenylmercuric phenylmercaptide*, clusters of prismatic needles, has m. p. 105—106°. *Phenylmercuric benzylmercaptide* has m. p. 96°. *Benzylmercuric phenylmercaptide* has m. p. 96°. Phenylmercuric ethylmercaptide reacts with ethyl iodide in boiling absolute alcoholic solution to give a double compound, $\text{Ph}\cdot\text{Hg}\cdot\text{SEt}\cdot\text{SEt}\cdot\text{HgI}$, m. p. 140°, whereas in 96% alcoholic solution, phenylmercuric iodide is formed. If benzyl iodide is used, in anhydrous alcoholic solution, the products are phenylmercuric iodide and benzyl ethyl sulphide. The latter forms the following *additive* compounds by the action of alcoholic mercuric chloride: $\text{EtS}\cdot\text{C}_7\text{H}_7\cdot\text{HgCl}_2$, m. p. 83°, and $\text{EtS}\cdot\text{C}_7\text{H}_7\cdot 2\text{HgCl}_2$, m. p. 142°.

W. S. N.

Physiological Chemistry.

The Significance of the Dual Function of Hæmoglobin in relation to the Mechanism of the Chemical Regulation of Respiration. ROBERT GESELL (*Proc. Amer. Physiol. Soc., Amer. J. Physiol.*, 1923, **63**, 393—394).—In certain conditions there may be a broken co-ordination of the dual function of hæmoglobin (namely, as a carrier of oxygen, and as a source of alkali to the plasma), with abnormal breathing resulting. Response of the respiratory centre to changes in acidity is discussed, as well as the effect of the administration of carbon dioxide on conditions arising from a lack or excess of oxygen. CHEMICAL ABSTRACTS.

Gas and Electrolyte Equilibria in the Blood. V. Factors Controlling the Electrolyte and Water Distribution in the Blood. DONALD D. VAN SLYKE, HSIEN WU, and FRANKLIN C. McLEAN (*J. Biol. Chem.*, 1923, **56**, 765—849).—This paper deals from a physico-chemical point of view with the distribution of electrolytes and water between corpuscles and serum and with the effect of various factors on this distribution. Assuming the applicability to blood of (1) the laws governing the distribution of a base between strong and weak acids, (2) Donnan's law of membrane equilibria, and (3) the laws of osmotic pressure, and making certain simplifying assumptions, expressions have been deduced which indicate the electrolyte and water distribution in blood and the changes which are produced in it by changes in P_H . Measurements of the changes actually produced by variations in the carbon dioxide tension have yielded results in approximate agreement with these expressions. The changes which occur are illustrated in the case of oxygenated blood. Thus, an increased acidity due to an increase in the carbon dioxide tension produces the following changes which are regarded as taking place simultaneously: (1) the transference of base from hæmoglobin to carbonic acid, (2) the migration of Cl' -ions from serum to cells and of HCO_3' -ions in the reverse direction to restore the membrane equilibria, and (3) the migration of water from serum to cells to restore osmotic equilibrium. For the mathematical treatment of the subject and certain deductions therefrom, the original must be consulted.

E. S.

Carbon Dioxide Absorption Curve of Human Blood. III. A Further Discussion of the Form of the Absorption Curve Plotted Logarithmically, with a Convenient Type of Interpolation Chart. JOHN P. PETERS (*J. Biol. Chem.*, 1923, **56**, 745—750).—Absorption curves obtained by plotting $\log(p_{CO_2})$ against $\log(CO_2 \text{ vol.}\%)$ are more nearly straight lines than are those given by the P_H — $MHCO_3$ relation (cf. Peters and Eisenman, *ibid.*, **55**, 709). Hence the former method is superior for the extrapolation or interpolation of points on an absorption curve. Further,

by plotting the carbon dioxide tension against the carbon dioxide content on logarithmic paper, and assuming a constant P_{K_1} value, a chart is obtained in which the P_H values are represented by parallel lines making an angle of 45° with the abscissa. Such charts can only be constructed for plasma, since P_{K_1} is not constant for whole blood.

E. S.

The Oxygen Content of Capillary Blood. F. VERZAR and F. KELLER (*Biochem. Z.*, 1923, **141**, 21—27).—Capillary blood collected from the ball of the finger shows an oxygen content similar to that of arterial blood. The average figure observed in normal individuals was 91% of saturation, falling in a few cases to 85%, but never below 82%. In uncompensated lung affections involving a diminution of respiratory surface values appreciably below normal were obtained. Muscular work in the normal person did not alter the oxygen content of capillary blood.

J. P.

The Ammonia Content of the Blood. V. HENRIQUES (*Z. physiol. Chem.*, 1923, **130**, 39—44).—Estimations show that there is no appreciable difference between the ammonia content of the blood of the renal vein and that of the carotid artery or of the vena cava. This result does not confirm that of Nash and Benedict (A., 1922, i, 191), who found increased ammonia in the renal vein, and suggested on this ground that ammonia is formed in the kidneys.

W. O. K.

The Fatty Acids of Blood Plasma. W. R. BLOOR (*J. Biol. Chem.*, 1923, **56**, 711—724).—Results are given of a large number of analyses of the fatty acid and cholesterol (unsaponifiable matter) content of the blood plasma of fasting animals (pig, ox, sheep, dog). Considerable variations were observed between both the different species and the individuals of the same species. In all species, however, the ratios unsaponifiable matter : fatty acid and liquid fatty acid : total (solid + liquid) fatty acid appeared to be approximately constant, the values being roughly one half and two-thirds, respectively. The liquid fatty acid fractions gave high and relatively constant iodine numbers (110—160), indicating the presence of highly unsaturated acids. These results, together with the constancy in the melting points of the various fatty acid fractions, indicate that the compounds from which the fatty acids are derived have, in the plasma of fasting animals, a constant composition as regards saturated and unsaturated acids, and exist in definitely balanced relation to each other.

E. S.

The Amino-acid Nitrogen of the Blood. I. The Total Free Amino-acid Nitrogen in Blood. II. The Diamino-nitrogen in the Protein-free Blood Filtrate. III. The Occurrence of Peptide Nitrogen in the Blood. NATHAN F. BLAU (*J. Biol. Chem.*, 1923, **56**, 861—866, 867—871, 873—879).—I. Estimations have been made of the amino-nitrogen content of a number of pathological bloods. II. Diamino-nitrogen has been estimated in the protein-free filtrates from pathological bloods. The values obtained, which range from 0.13 to 4.54 mg. per 100 c.c.

of blood, represent the difference in the amino-nitrogen content before and after precipitation of the basic amino-acids with phosphotungstic acid. III. No appreciable amount of peptide nitrogen is present in normal blood. Varying quantities, however, have been found in pathological bloods, but in insufficient amount to account for the undetermined nitrogen. E. S.

Amino-acids of the Blood. III. Influence of Toxic Anæmia and Blood-letting. S. MARINO (*Arch. Farm. speriment. Sci. aff.*, 1923, **36**, 88—96; cf. this vol., i, 1036).—The amino-acid content of the blood of the dog (1) is increased or diminished by repeated blood-letting, according as the repetitions occur at short or long intervals, and (2) under the action of hæmolytic poisons, diminishes during the period of the granules and Heinz bodies, and increases during the regeneration of the blood. In case (1) also the increase is related to the regeneration of the blood.

T. H. P.

The Inter-relationship of Blood-fat and Blood-sugar. T. H. OLIVER and A. HAWORTH (*Lancet*, 1923, II, 114—116).—Evidence is adduced to show that the blood-sugar has a relation to the blood-fat other than that of a mere oxidising agent. Fat properly absorbed into the tissues appears to increase the storage of carbohydrate; if it is not so absorbed, or if it is mobilised by calcium, interference with the storage takes place. Practically all conditions which lead to a hyperglycæmia lead also to a lipæmia, probably owing to diminished oxidation. Injection of adrenaline causes a rise in blood-fat in addition to hyperglycæmia. In this case, since it is difficult to understand why the liberation of a large amount of oxidising material should be accompanied by an increase of the substance to be oxidised, it is suggested that both were stored and liberated together. A. A. E.

Blood Catalase. W. VON MORACZEWSKI (*Biochem. Z.*, 1923, **141**, 471—475).—Blood catalase is diminished in fevers and in shock conditions, and rises after ingestion of proteins and sugar and in diabetes. Phloridzin increases blood catalase although it diminishes the blood-sugar, whilst pilocarpine diminishes both. The enzyme is increased by adrenaline. In certain affections of cardiac and respiratory functions, strychnine lessens the catalase, whilst caffeine increases it. In general a diminution of red blood-corpuscles is associated with an increased catalase activity. J. P.

The Action of Thyroxin. III. The Destruction of the Specific Action of Thyroxin by Blood in Vivo and in Vitro. BENNO ROMEIS (*Biochem. Z.*, 1923, **141**, 500—522).—The blood, liver, bile, and urine of dogs which have been given an intravascular injection of thyroxin in weakly alkaline saline have no effect, even when removed a few minutes after the injection, on the rate of development of tadpoles. The conclusion is drawn that thyroxin is rapidly changed and inactivated in the blood-stream. The activity of a thyroxin solution is lowered by retention for several hours in the body-cavity. By repeated intravenous injection of

thyroxin, the rate of destruction in the blood is lessened. Fresh undiluted blood lowers the activity of thyroxin in vitro and after one to two hours' contact the blood-thyroxin solution becomes toxic to tadpoles. Serum alone and washed erythrocytes inhibit thyroxin, the latter being more active in this respect than the former. It is concluded that a mechanism exists in the blood for the regulation of the amount of thyroxin in response to the tissue requirements. J. P.

Chemical Changes in the Blood under the Influence of Drugs. II. Morphine. H. V. ATKINSON and H. N. ETS (*J. Lab. Clin. Med.*, 1922, 8, 170—175).—Morphine increases the carbon dioxide combining power, and decreases the oxygen combining power of the blood. The content of sugar, creatinine, and total fat is increased, and that of lecithin and cholesterol decreased.

CHEMICAL ABSTRACTS.

The Effect of Buffer Salts on Blood Coagulation. BENJAMIN JABLONS (*J. Lab. Clin. Med.*, 1923, 8, 679—681).—Dipotassium hydrogen phosphate or potassium dihydrogen phosphate causes a striking inhibition of blood coagulation, similar to that produced by sodium citrate. The blood remained incoagulable for forty-eight hours; with the former phosphate, it was bright red, and with the latter, very dark red. The latter salt also increased the viscosity of the blood; hæmolysis was fairly marked, but only slight in the former case.

CHEMICAL ABSTRACTS.

Adsorption of Protein Degradation Products by the Blood-corpuscles in Vivo and in Vitro. II. Adsorption by the Red Blood-corpuscles. B. SBARSKY (*Biochem. Z.*, 1923, 141, 33—36).—It is shown that the adsorption of protein degradation products by blood-corpuscles (this vol., i, 411) is a property of the erythrocytes both in vivo and in vitro. The adsorption does not proceed according to the Freundlich equation. J. P.

Adsorption of Protein Degradation Products by the Blood-corpuscles in Vivo and in Vitro. III. The Adsorption Capacity of the Blood of various Animals. B. SBARSKY and D. MICHLIN (*Biochem. Z.*, 1923, 141, 37—39).—A varying capacity to adsorb foreign proteolytic products (diphtheria-toxin) in the blood is shown by different animals. This increases in the order given: rat < dog < horse < guinea-pig < hen < pigeon. A parallel is drawn between this order and the susceptibility of the animal to the action of the toxin. J. P.

Viscosity of Blood-serum and its Relation to the Content of Albumin and Globulin. S. M. NEUSCHLOSZ and R. A. TRELLIES (*Anal. Asoc. Quím. Argentina*, 1923, 11, 73—77).—Whilst the viscosity of human blood-serum may be correlated with its protein content the data given by the authors for forty sera show that there is no evidence for a correlation with the albumin-globulin ratio. G. W. R.

Study of the Condition of Several Inorganic Constituents of Serum by Means of Ultrafiltration. B. S. NEUHAUSEN and J. B. PINCUS (*J. Biol. Chem.*, 1923, **57**, 99—106).—Analyses of ultrafiltrates of pig's serum indicate that chlorides, phosphates, sodium, and potassium are present entirely in a diffusible form, whilst 30—50% of the calcium is non-diffusible (cf. Cushny, A., 1920, i, 508). E. S.

Relative Precipitating Capacity of certain Salts when Applied to Blood Serum or Plasma and the Influence of the Kation in the Precipitation of Proteins. PAUL E. HOWE (*J. Biol. Chem.*, 1923, **57**, 241—254).—The relative precipitating capacities of a number of salts have been compared, using as criterion of efficiency the increases in concentration which are necessary to precipitate the successive protein fractions. The results are presented in detail in the original, and agree, in general, with those obtained by others. For each particular salt, the increase in concentration required to precipitate succeeding protein fractions is constant, although not necessarily the same for different salts. E. S.

Changes in the Proteins and the Gelafication of Formalised Blood-serum. R. R. HENLEY (*J. Biol. Chem.*, 1923, **57**, 139—151).—Addition of formaldehyde to serum causes the various protein fractions to become progressively less soluble in ammonium sulphate. With high concentrations of formaldehyde, the albumin and ψ -globulin fractions disappear; with low concentrations, an equilibrium is reached. The rate of transformation is, for a given serum, proportional to the concentration of formaldehyde, as also is the rate of gelafication of the serum. With a constant concentration of formaldehyde, the rate of gelafication is proportional to the concentrations of protein and salts in the serum. E. S.

Antipepsin. ERNST STOLZ (*Biochem. Z.*, 1923, **141**, 483—487).—The antipeptic action of blood-serum is ascribed, not to the presence of a specific antipepsin, but to the capacity of serum-albumin to adsorb pepsin and so lower its activity. The absence of the supposed anti-ferment from the alimentary mucous membrane cannot be regarded as a causal factor in gastric or duodenal ulcer. J. P.

The Nature of the Antitryptic Action of Serum and its Biological Significance. A. A. EPSTEIN (*Proc. Soc. Exp. Biol. Med.*, 1922, **20**, 48—50).—The inhibition of tryptic digestion by serum is due slightly to globulin and largely (and proportionately) to the amount of albumin present. Trypsin was quantitatively recovered, after prolonged incubation with serum, by precipitation of the proteins with colloidal iron or ethyl alcohol. After digesting casein, no trypsin was recovered, but the latter was recovered from admixture with serum and casein when digestion did not take place. The action is of the nature of an interference phenomenon.

CHEMICAL ABSTRACTS.

The Diastase Activating Property of Serum. The rôle of the **Pancreas in Carbohydrate Metabolism.** TORAO KOGA (*Biochem. Z.*, 1923, **141**, 410—429).—The activating properties of serum on diastases observed by Wohlgemuth (*Biochem. Z.*, 1911, **33**, 303) have been further investigated. Pancreatic diastase is eight times as active in the presence of serum as it is in pure aqueous solution. An artificial salt solution of the same composition as the serum salts has only half of the activating effect of the serum. It is concluded that a diastase activating substance other than the salts is present in blood-serum. It is regarded as being colloidal in nature, since dialysed serum retains in large part its activity, whilst serum treated with colloidal iron loses most of its activating powers. Adsorption experiments with negatively and positively charged adsorbents on blood-serum show that the active principle has no specific electric charge, but may be to a small extent negatively charged. It is insoluble in ether and light petroleum and is stable to acids and alkalis. Putrefying serum is still active. Washed blood-corpuscles and neutralised urine show a similar activating effect. Dialysed urine loses but little of its activity. The activating substance is also present in milk. In starving dogs, the serum from the pancreatico-duodenal vein increases the action of diastase to a greater extent than that from systemic blood-serum, but this difference is not observed in dogs which have been fed. It is concluded that glycogenolysis in the liver is produced, not by a direct impulse, but indirectly through the pancreas, which is stimulated to produce a hormone (the diastase activating substance of the blood) which then passes to the liver.

J. P.

Inorganic Metabolism. I. The Influence of Cod Liver Oil on Calcium and Phosphorus Metabolism. II. The Influence of Crude Fibre and of Protein on Calcium and Phosphorus Metabolism. B. SJOJLEMA (*J. Biol. Chem.*, 1923, **57**, 255—270, 271—284).—I. Rabbits were used as experimental animals. Administration of cod liver oil produced an increased retention of calcium and phosphorus independently of whether the animals were in positive or negative calcium balance. In the former case, it was mainly the urinary, and in the latter, the faecal, calcium output which was diminished. The total output of phosphorus was independent of the amount of calcium in the food. The amount of calcium excreted in the faeces may exceed considerably that administered in the food.

II. Addition of indigestible material to the diet causes an increased excretion of calcium in the faeces and thus tends to produce a negative calcium balance. A high protein diet favours retention of calcium (cf. this vol., i, 511).

E. S.

Intermediary Metabolism of Carbohydrates. P. A. SHAFFER (*Physiol. Rev.*, 1923, **3**, 394—437).—A comprehensive review with an extensive bibliography. According to the view now prevalent lactic acid represents the main intermediate in dextrose metabolism. There is no obstacle to the belief that glyceraldehyde,

dihydroxyacetone and methylglyoxal (together with the hexose phosphate, "lactacidogen") represent the main intermediates between glycogen or dextrose and lactic acid. The reaction $\text{dextrose} \rightleftharpoons \text{lactic acid}$ is reversible, but the preponderating reaction in the presence of oxygen is $\text{lactic acid} \rightarrow \text{dextrose}$. It is difficult to believe that dextrose is oxidised by way of lactic and pyruvic acids and acetaldehyde. It is not unlikely that it is oxidised to a single molecule of ketolytic substance without previous splitting to triose.

CHEMICAL ABSTRACTS.

Intermediary Protein Metabolism. II. The rôle of the Liver in the Production of Urea. III. The rôle of the Liver in the Metabolism of Amino-acids. IV. The rôle of the Liver in the Intermediary Metabolism of Amino-acids. A. GOTTSCHALK and W. NONNENBRUCH (*Arch. expt. Path. Pharm.*, 1923, **99**, 261—269, 270—299, 300—314).—II. Solutions of pure amino-acids and of mixtures of amino-acids were injected into the dorsal lymph sac of normal frogs, and of frogs from which the liver had been extirpated, and the resulting changes in the concentration of urea nitrogen and residual non-protein nitrogen in the blood were observed. It was found that removal of the liver made no difference to these changes, which consisted in a definite rise in the concentration of urea nitrogen following the administration of the amino-acids. A similar but less pronounced rise in urea concentration followed administration of casein. It was therefore concluded that urea formation is not a special function of the liver in the frog.

III. In the case of rabbits and dogs, a rise in both urea and non-urea fractions of the non-protein nitrogen of the blood was observed to follow intra-duodenal administration of amino-acids, and this rise is quantitatively the same in blood from all parts of the circulation, except where an increased autolysis of the liver cells brought about by the conditions of the experiment may cause an increase of nitrogenous products in the hepatic vein. The feeding of casein and the slow, continuous administration of amino-acids bring about little change in the nitrogen of the blood. It is concluded that the part played by the liver in the metabolism of the amino-acids which are absorbed into the blood-stream is not a predominant one, but that every cell in the body may share in this process to an extent which is determined by its individual needs at the moment.

IV. The fourth paper deals with the extension of these results to man.

C. R. H.

Nuclein Metabolism. I. Adenine Nucleotide in Human Blood. HENRY JACKSON, jun. (*J. Biol. Chem.*, 1923, **57**, 121—128).—Adenine has been isolated from human blood in the form of its picrate under conditions which indicate that it was originally present as adenine nucleotide. Normal whole blood appears to contain 15—25 mg. of adenine nucleotide per 100 c.c.; this accounts for a considerable portion of the undetermined nitrogen. E. S.

To What Extent is Cetyl Alcohol Absorbable (by Animals)?

K. THOMAS and B. FLASCHENTRÄGER (*Skand. Arch. Physiol.*, 1923, **43**, 1—5; from *Chem. Zentr.*, 1923, iii, 266).—Feeding experiments with dogs showed that cetyl alcohol is absorbed only to a very slight extent. As the m. p. of the alcohol is 49.5° and therefore above body temperature, experiments were carried out with *cetyl acetate*, m. p. 19°. This also was utilised to an insignificant extent and it is concluded to be of no value as a food material.

G. W. R.

Nutritive Values of Starch and Sucrose. GEORG VON WENDT (*Skand. Arch. Physiol.*, 1923, **43**, 264—274; from *Chem. Zentr.*, 1923, iii, 266).—For fat production in cattle and pigs sucrose has only 75 to 80% of the value of starch. For maintenance, however, the two substances are equal, whilst for energy production sucrose is superior to starch by at least 10%. This is probably due to the fact that starch is absorbed as dextrose, whilst sucrose yields lævulose as well as dextrose. Fat synthesis from dextrose probably begins by way of acetaldehyde, whereby two carbon atoms are lost as carbon dioxide. The keto-group in lævulose is easily broken down. Two mols. of lævulose are necessary for the formation of aldol. Thus only two carbon atoms from lævulose as against four carbon atoms from dextrose are utilised for fat synthesis. Lævulose will also be less efficient than dextrose for glycogen synthesis. For the production of mechanical energy lævulose may be more efficient than dextrose.

G. W. R.

Age and Chemical Development in Mammals. C. R. MOULTON (*J. Biol. Chem.*, 1923, **57**, 79—97).—A large amount of data on the composition of animals at various stages of development has been collected. When this is recalculated on a fat-free basis, it is found that the relative water content of mammals decreases, and the relative protein and ash content increases, from earliest life until chemical maturity is reached, following which a fairly constant composition is shown. The ratio, age at which chemical maturity is reached/total life cycle, is fairly constant for mammals. The relative water content of mammals at birth is smaller the greater the maturity.

E. S.

Influence of the Positive Nitrogen Balance on Creatinuria during Growth. VICTOR JOHN HARDING and OLIVER HENRY GAEBLER (*J. Biol. Chem.*, 1923, **57**, 25—45).—The total creatine production in growing dogs increases with the protein content of the diet until a maximum, which corresponds with the maximum positive nitrogen balance, is reached. With a constant nitrogen intake, the creatine excretion varies inversely as the nitrogen gain. The total creatine coefficient (cf. this vol., i, 169) of puppies is more than twice the creatinine coefficient of the adult dog.

E. S.

Is Cystine Synthesised in the Animal Body? J. A. MULDOON, G. J. SHIPLE, and C. P. SHERWIN (*Proc. Soc. Exp. Biol. Med.*, 1922, **20**, 46—47).—Bromobenzene, which in the case of

dogs can be detoxicated by combination with cystine, the amino-group of which is then acetylated, was fed to dogs in conjunction with a carbohydrate diet, and with sodium sulphate, taurine, calcium sulphate, sodium thiocyanate, and aminoethyl mercaptan; detoxication by cystine did not result. The addition of nitrogen in the form of ammonium acetate or gelatin also gave negative results.

CHEMICAL ABSTRACTS.

Weight of Microscopic Objects. [Herring Spermatozoon.] H. STEUDEL (*Z. physiol. Chem.*, 1923, **130**, 136—143).—The following values are arrived at. Weight of one herring spermatozoon, 0.53×10^{-11} mg. Dry weight, 0.29×10^{-11} mg. Nucleic acid content, 0.12×10^{-11} mg. Average weight of herring ovum, 0.923 mg., containing approximately 71.7% of water and 28.3% of dry matter.

W. O. K.

The Hormone of the Placenta and of the Corpus Luteum and the Lipoids of the Corpus Luteum. SIGMUND FRÄNKEL and MARIA FONDA (*Biochem. Z.*, 1923, **141**, 379—393).—The active substance promoting sexual development in young dogs found by Herrmann (*Monatsh. Geburts. und Gynäkol.*, 1915, **41**, 1) in the placenta has been isolated both from the placenta and corpus luteum, and the lipoids of the latter have been investigated. The active principle was obtained from the acetone extract of the ether-soluble portion of the finely minced dry tissues, and distilled in a high vacuum. It was isolated as a viscous, light yellow syrup boiling at $194^{\circ}/0.064$ mm. Elementary analyses and molecular weight determinations indicate the formula $C_{32}H_{52}O_2$. It forms a tetrabromide, $C_{32}H_{52}O_2Br_4$, when treated with a solution of bromine in glacial acetic acid. The phenylhydrazone, $C_{38}H_{58}ON_2$, a dark orange-red syrup; the acetylphenylhydrazone, $C_{40}H_{60}O_2N_2$, a reddish-brown syrup; the oxime, $C_{32}H_{53}O_2N$; the benzenesulphonate of the tetrabromide, $C_{38}H_{56}O_4Br_4S$; the benzoate, $C_{39}H_{56}O_3$, and the barium derivative, $(C_{32}H_{51}O_2)_2Ba$, are also described, but none was obtained in a crystalline condition. It is concluded that two unsaturated linkings, a hydroxyl and a carbonyl grouping are present. The distilled product was optically inactive in methyl alcohol and lost some of its activity during distillation. In the product from the chloroform extract of the corpus luteum, there were found, in addition to the active substance, kephalin, lecithin, the ester of dilignoceryl-*N*-diglucosaminomonophosphoric acid, cholesterol, cholesterol ester, glyceryl tripalmitate, free myristic acid, and a galactoside containing nitrogen and phosphorus.

J. P.

The Ferments of the Hen's Egg. TORAO KOGA (*Biochem. Z.*, 1923, **141**, 430—446).—Egg-yolk is richer in diastase than is egg-white, but both yolk and white diastase increase in quantity during the development of the embryo chick. Egg diastase shows an increased activity in the presence of sodium chloride and, more especially, of blood-serum. Lipases are represented by monobutyrase in the yolk and to a much less extent in the white, and

by tributyrase in a reverse distribution. The latter is unstable to quinine but stable to atoxyl, and diminishes in amount during development whilst the former remains constant. In addition to autolytic enzymes, egg-white contains an erepsin and a fibrin-splitting enzyme. In the yolk, salicylase and histozym are present, but both disappear during development. An oxydase is present in the white which does not act on tyrosine, but forms a brown pigment with pyrocatechol, adrenaline, and dihydroxyphenyl-alanine.
J. P.

The Proteolytic Enzyme in the Mucous Membrane of the Small Intestine of the Ox. S. G. HEDIN (*Z. physiol. Chem.*, 1923, **130**, 45—54).—If the mucous membrane of the small intestine of the ox is treated at 37° with weak acetic acid of p_H 5.1, a solution is obtained which hydrolyses genuine protein (except unheated serum-albumin), and peptone best in alkaline solution, *e.g.*, it hydrolyses casein best at p_H 9. As the action of this enzyme on casein or peptone is not inhibited appreciably by serum-albumin it must be practically free from trypsin. No enzyme acting best in acid solution appeared to be present, nor could the presence of erepsin be detected.
W. O. K.

The Chemical Regulation of the Activities of the Human Kidney. E. F. ADOLPH (*Proc. Amer. Physiol. Soc., Amer. J. Physiol.*, 1923, **63**, 432—433).—Hypertonic solutions of substances not changed in metabolism (*e.g.*, sucrose) caused excessive excretion of water by the kidneys, but only the substance ingested was excreted in this excess of water at a rate much above the normal; little but water was excreted at an abnormal rate in water diuresis. Slight but prolonged augmentation of water excretion was caused by Locke's solution and isotonic sodium chloride; rapid diuresis by isotonic potassium chloride and urea; and no increment by isotonic calcium chloride.
CHEMICAL ABSTRACTS.

The Action of Quinine and Atoxyl on the Lipase of the Kidney. P. RONA and H. E. HAAS (*Biochem. Z.*, 1923, **141**, 222—235).—A Ringer extract of fresh kidney contains a non-dialysable lipase, with an optimum range of action lying between p_H 7 and 8, which in its general properties is identical with blood lipase. Its lipolytic action on tributyrin proceeds as a unimolecular reaction. Kidney lipase is not affected by quinine, but is very susceptible to inhibition by atoxyl. If the logarithm of the atoxyl concentration be plotted against that of the hydrolysis constant, a curve similar to that of a dissociation curve is obtained. The atoxyl inactivation is reversible. Unlike liver lipase, kidney lipase is not protected against atoxyl by the presence of blood-serum. The reactions of the new lipase to quinine and atoxyl therefore serve to differentiate it from all other lipases.
J. P.

The Chemistry of the Pancreas. LUDWIG PETSCHACHER (*Biochem. Z.*, 1923, **141**, 109—120).—Two kg. of horse pancreas were freed from fat, finely divided, and put through a lengthy series of fractional alcoholic and aqueous extractions and pre-

cipitations, for the exact details of which the original must be consulted. The examination of the various fractions has been only partly completed, and the present results are concerned with two of these. 0.5 G. of a substance, of the formula $C_{14}H_{31}O_5N_3$, was obtained in the form of fine, short, white prisms, m. p. 265° , and was slightly levorotatory. It was neutral to litmus and gave negative Millon, xanthoproteic, Mörner, and glyoxylic acid reactions. Injected intravenously into dogs, it produced, in from two to four hours, an increase in blood-sugar. This effect was most marked with small doses. From another fraction *l*-leucine was isolated in an impure condition. Its intravenous injection produced a lowering of blood-sugar amounting to 30%. Control injections of pure *l*-leucine (Grübler) had a marked effect in increasing the blood-sugar. It is concluded that the leucine isolated from the pancreas contained as impurity a substance capable of lowering the blood-sugar. The injection of the two fractions investigated had no effect on the animal other than the alteration of the blood-sugar.

J. P.

Is the Pentose of the Nucleotides Formed under the Action of Insulin? C. BERKELEY (*Nature*, 1923, **112**, 724—725).—Winter and Smith (this vol., i, 727) having observed that the blood and certain tissues of the rabbit contain, after injection of insulin, a substance which reacts as a carbohydrate with α -naphthol, but has no reducing action on copper salts even after acid hydrolysis, suggest in effect that this unidentified carbohydrate substance is formed from glucose under the influence of insulin. If this is so, it should be present in normal blood but absent from that of diabetics. It is suggested that the substance may be a pentose nucleotide, such as have been found to be distributed through a wide range of animal tissues; nucleotides give the α -naphthol reaction, and unsuitable conditions of hydrolysis may cause the pentose to be overlooked. From experiments on the islet gland in a typical teleost fish, the author infers that the general high pentose content of the pancreas in mammals is due mainly to the presence of the isles of Langerhans. An hypothesis indicating a connexion between the production of insulin and the high concentration of pentose compounds in the islet tissue is outlined.

A. A. E.

Relation between Innervation and Chemical Composition of Striped Muscle. I. Creatine Content in Hyperinnervation. J. G. DUSSER DE BARENNE, and D. G. COHEN TERVAERT. (*Pflüger's Archiv*, 1922, **195**, 370—389; from *Chem. Zentr.*, 1923, iii, 321).—The creatine content of the muscle of cats is unchanged in rigor due to removal of the brain. Increase in creatine content occurs in phasal innervation superimposed on rigor due to removal of the brain.

G. W. R.

Hydrolysis of the Muscle Protein of *Cryptobranchus japonicus*, Hœv. I. SHIGEO SUGA (*J. Pharm. Soc. Japan*, 1923, No. 497, 588—592).—The muscle protein of *Cryptobranchus*

japonicus, Hoev., was hydrolysed by boiling with ten times its weight of 33% sulphuric acid for fourteen hours and the amino-acids formed were separated and determined by the methods of Kossel and of Kutscher. One hundred g. of the water-insoluble dried flesh (nitrogen content 13.65%) gave 6.69 g. of arginine, 2.29 g. of histidine, and 7.41 g. of lysine. K. K.

Composition of the Cartilage of an Invertebrate Animal, *Limulus*. A. P. MATHEWS (*Z. physiol. Chem.*, 1923, **130**, 169—175).—The entosternite of the cartilage of *Limulus* is a mixture of cartilaginous and fibrous connective cells, as shown by its chemical composition. It is a typical protein, with very little prosthetic substance, containing no gelatin and only a small quantity, 1—2%, of chondroitinsulphuric acid. W. O. K.

The Concentration of Protein in Tissues. E. J. COHN (*Proc. Amer. Physiol. Soc., Amer. J. Physiol.*, 1923, **63**, 430—431).—The relationship of water, electrolytes, and proteins in animal tissues is discussed from the point of view of physical chemistry. The variations among species of these cell constituents agree with the theories of Donnan and of Loeb on membrane equilibrium. The concentration of such dissociable, non-diffusible contents of cells as the proteins must lead not only to the loss of water, but also to the loss of diffusible electrolytes with which the proteins are in equilibrium. CHEMICAL ABSTRACTS.

The Normal Content of Arsenic in the Human Body. O. BILLETER and E. MARFURT (*Helv. Chim. Acta*, 1923, **6**, 780—784).—Using the method already described (this vol., ii, 786), the normal content of arsenic in different parts of the human body in subjects of different ages was determined. An appreciable, fairly constant quantity of arsenic was always found, the mean value being about 0.0103 mg. per 100 g., with an excess of 0.0032 mg. in the thyroid gland and a deficit of 0.0019 mg. in the spleen. In the newly-born, the proportion is considerably less, but in elderly people it is above the average, and a specially high amount was found in the nails of an old man. E. H. R.

The Nitrogen Compounds of Skimmed Milk Cheese. E. WINTERSTEIN and O. HUPPERT (*Biochem. Z.*, 1923, **141**, 193—221).—Details are given of the qualitative and quantitative distribution of the nitrogen present in skimmed milk cheeses of various ages, and these are compared with fatty cheeses (Emmentaler, Cheddar). The former are found to have a higher water, ash, and ammonia content than the latter. The skimmed milk cheeses do not ripen so rapidly as the fatty varieties, which is reflected in the higher amino-acid content of the latter (100 to 150% greater) as compared with the former. The total nitrogen of the skimmed milk cheeses, freed from water and fat and exclusive of the ash, varied between 13.4 and 13.9% and the total protein nitrogen between 11.4 and 12.5%. The basic and amino-acid nitrogen, although low, was very variable, and, in general, the nitrogen precipitable by phosphotungstic acid variable inversely as that of the amino-acids. In both fatty and

skimmed milk cheeses, the ripening process is accompanied by the formation of valine, leucine, isoleucine, glycine, alanine, phenylalanine, proline, aspartic acid, and glutamic acid. Notably the hexone bases are absent or present only in minimal amount in the skimmed milk cheeses, but they contain considerable quantities of polypeptides yielding bases on hydrolysis. Caseoglobulin, tyroalbumin, and tyrocasein are also present. The xanthhydrol reaction failed to reveal the presence of urea.

J. P.

Excretion of Lactic Acid in Urine. F. KNOOP and H. JOST (*Z. physiol. Chem.*, 1923, **130**, 338—349).—Lactic acid is excreted in the urine of dogs after ingestion of propionic acid, butyric acid, hydroxybutyric acid, and, to a small extent, malonic acid. The mechanism of the formation of lactic acid under these conditions is discussed.

W. O. K.

Synthesis of Hippuric Acid in the Animal Organism. V. The Influence of Amino-acids and Related Substances on the Synthesis and Rate of Elimination of Hippuric Acid after the Administration of Benzoate. WENDELL H. GRIFFITH and HOWARD B. LEWIS (*J. Biol. Chem.*, 1923, **57**, 1—24).—The rate of excretion of hippuric acid following the oral administration of sodium benzoate is decidedly increased when glycine is administered simultaneously with the benzoate, thus indicating an increased rate of synthesis of hippuric acid in the presence of large amounts of glycine. No increased rate of elimination was observed when other amino-acids, glycollic acid, glycollaldehyde, dextrose, urea, or sodium acetate were used in place of glycine. Apparently none of these substances is a readily available precursor of glycine.

E. S.

Can Aliphatic Diamines be Obtained from Normal and Nephritic Urine by Means of Picric Acid and Sodium Chloride? R. SCHÜLER and F. THIELMANN (*Z. Biol.*, 1923, **79**, 139—144).—The precipitate produced in normal urines by 1% aqueous picric acid and saturated sodium chloride, and supposed by Bergell (this vol., i, 1155) to contain uripicric acid (1 mol. of uric acid+1 mol. of picric acid) and aliphatic diamines, is found to consist of sodium picrate, creatinine, uric acid, and pigments. The precipitate produced by substituting saturated potassium chloride for sodium chloride consists of potassium picrate and creatinine, which is quantitatively precipitated, together with small quantities of uric acid. Precipitates of similar composition varying only in quantity are obtained from various nephritic urines.

J. P.

A Special Group of Enteroliths from Man; Choleic Acid Stones. CARL TH. MORNER (*Z. physiol. Chem.*, 1923, **130**, 24—33).—A large enterolith was found to have the following composition: organic material soluble in alcohol, 76.34%; organic material insoluble in alcohol, 8.46%; mineral matter, 2.42%; water, 12.78%. The organic material did not contain cholesterol, glycocholic acid, cholic acid, or lithocholic acid, but consisted essentially

of choleic acid, $C_{24}H_{40}O_4$. The following derivatives were prepared: acetylcholeic acid, m. p. 142—143°, xylene-choleic acid, m. p. 181°, and stearin-choleic acid, m. p. 188°. W. O. K.

Fat Metabolism in Avitaminosis. I. The Total Fat and Cholesterol Contents of the Body on Normal and Vitamin-free Diets. KAZUO ASADA (*Biochem. Z.*, 1923, **141**, 166—186).—Rats kept on vitamin-free diets showed a diminution of total and neutral body fat when compared with normal controls. The fat content in vitamin-fed animals kept on various diets diminished in the order of dieting given: fat > carbohydrate > mixed > protein, whilst in the avitaminosed animals the order was: mixed > carbohydrate > fat > protein. In avitaminosis, the total cholesterol underwent less diminution than did the fat. The order of diminution for the various diets employed was: in the vitamin-fed animal, fat > mixed > carbohydrate > protein; in the avitaminosed animal, mixed > carbohydrate > fat > protein. The order of the length of life on various vitamin-free diets was: mixed > carbohydrate > fat > protein. Under normal dietetic conditions, no diminution of life period was observed except when the rats were kept on a starch or protein diet. In general, avitaminosis is associated with an increased blood-fat content, a diminished capacity to store fat, and an increase in its rate of oxidation. J. P.

The Fat Content of the Blood in Avitaminosis. J. A. COLLAZO and GOMEZ BOSCH (*Biochem. Z.*, 1923, **141**, 370—378).—In avitaminosed dogs the total blood-fat and cholesterol undergo a marked increase, but again fall in the later stages without returning to normal values before death. The blood phosphatides show little alteration, but may diminish slightly in the late stages of avitaminosis. On doubling the amount of fat in the diet of avitaminosed dogs, the period of increased blood-fat is of longer duration than that produced in normal animals by similar methods. The hyperlipæmia in avitaminosis is associated with a diminution in the total body fat (cf. Asada, preceding abstract). J. P.

Glycolysis in Diabetic and Non-diabetic Blood. W. DENIS and UPTON GILES (*J. Biol. Chem.*, 1923, **56**, 739—744).—Glycolysis is much more active in normal blood than in blood from patients with severe diabetes. It is suggested in explanation that the glycolytic enzyme attacks γ -glucose, which is present in normal, and practically absent from diabetic, blood, but is without action on α - β -glucose (cf. Forrest, Smith, and Winter, this vol., i, 513).

E. S.

The Behaviour of the Urea and Non-urea Fraction of the Residual Nitrogen in Heart and Kidney Affections. HUGO PRIBRAM and OTTO KLEIN (*Biochem. Z.*, 1923, **141**, 488—499).—The urea-nitrogen, the non-urea-nitrogen, and the "double nitrogen" (difference in the nitrogen of the filtrates after precipitation with trichloroacetic and with phosphomolybdic acids) of blood, have been determined as ratios of the total residual nitrogen in cases of heart and kidney affections and in normals. The "double

nitrogen" of the non-urea fraction is a measure of the protein breakdown and may vary markedly with regard to the residual nitrogen. In the conditions studied, increased degradation of tissue proteins produces a high "double nitrogen" value and the ratio of the urea nitrogen to the residual nitrogen is lessened. In kidney and heart affections, oliguria and œdema are associated with an increase in urea nitrogen, whilst in polyuria and œdema drainage the urea fraction is diminished and the non-urea and double nitrogen fraction increases. The ratio of the urea nitrogen to the residual nitrogen is increased in renal insufficiency, but in the late stages the other fractions increase whilst the urea diminishes. The fractional examination of the residual nitrogen must be modified according to the protein content of the serum. J. P.

Syphilis. IV. The Arsenic Content of the Blood at Various Intervals after Intravenous Injection of Salvarsan. J. A. FORDYCE, ISADORE ROSEN, and C. N. MYERS (*Amer. J. Syphilis*, 1923, 7, 225—286).—Immediately after the injection, 60% of the arsenic has been localised outside of the blood-stream, and this is the time of maximum concentration of arsenic in the blood, 4.21 mg. of elementary arsenic being present in 100 g. of dried material. The rate of division of arsenic between blood and tissues varies in different individuals. Persons with an arsenic idiosyncrasy show abnormal values for the arsenic in the blood.

CHEMICAL ABSTRACTS.

Neurosyphilis. I. Arsenic Content of the Spinal Fluid after the Intravenous Administration of Silver Salvarsan. L. H. CORNWALL and C. N. MYERS (*Amer. J. Syphilis*, 1923, 7, 287—317).—Within two hours of the intravenous injection of silver salvarsan, arsenic may be found in the spinal fluid in amounts as large as 143 mg. per 100 g. of dried material. Usually the amount present decreases after the first two hours, rises slightly between twenty-four and forty-eight hours, and reaches a new high point at seventy-two hours, when as much as 192 mg. per 100 g. of material may be present.

CHEMICAL ABSTRACTS.

Alkalosis versus Abnormal Sodium-ion Concentration as a Cause of Tetany. W. DENIS and L. VON MEYSENBUG [with JULIA GODDARD] (*J. Biol. Chem.*, 1923, 57, 47—63).—The tetany produced in dogs by excessive injections of sodium hydrogen carbonate is due to an abnormal $\text{H}_2\text{CO}_3/\text{NaHCO}_3$ ratio rather than to poisoning by sodium-ions. Injections of sodium chloride or sodium sulphate, whilst producing convulsions, do not increase the irritability of the nerves; with sodium hydrogen carbonate, on the other hand, both these effects are produced. E. S.

The Fate of Sodium Thiosulphate in the Organism. WILHELM NYIRI (*Biochem. Z.*, 1923, 141, 160—165).—That portion of sodium thiosulphate, administered intravenously or orally, which is not excreted unchanged by the kidney, is oxidised completely to sulphuric acid and is present in the urine as sodium sulphate.

J. P.

A Pharmacological Comparison of Six Alcohols, Singly and in Admixture, on *Paramæcium*. CHARLES E. BILLS (*J. Pharm. Exp. Ther.*, 1923, **22**, 49—57).—The narcotising and toxic effect on *Paramæcium caudatum* of methyl, ethyl, propyl, isopropyl, butyl, and isobutyl alcohols was examined. The criterion of narcotisation adopted was the inability of the organisms to rise to the surface of the liquid. It was found that both toxicity and narcotising power increase progressively with the molecular weight. The margin between narcotising and toxic concentrations is greater in the case of propyl alcohol than in the case of either ethyl or butyl alcohols. *iso*Propyl and *isobutyl* alcohols are less toxic than their normal isomerides, although *isobutyl* alcohol is more narcotic than *n*-butyl alcohol. When mixed the alcohols antagonise each other in narcotising effect. C. R. H.

Formation of Dextrose from Alanine and from Lactic and Pyruvic Acids. E. AUBEL and R. WURMSER (*Compt. rend.*, 1923, **177**, 836—837).—Since, with phloridzinised dogs, alanine and lactic acid give their own weight of extra dextrose, whilst pyruvic acid gives less than its own weight, the latter substance, in preventing acetonuria in dogs by formation of dextrose, should be required in a larger proportion than the two former substances. It is actually found that 92% of alanine or of lactic acid, but only 80% of pyruvic acid, is thus converted into dextrose, this being due to the greater ease with which pyruvic acid is oxidised in the animal organism. It is concluded that alanine and the above acids are not transformed directly into dextrose, but that intermediate compounds are not only formed, but also should be discoverable. E. E. T.

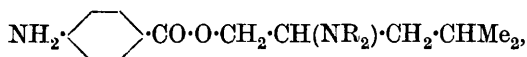
The Behaviour of Fatty Aromatic Ketones in the Animal Body. H. THEIRFELDER and K. DAIBER (*Z. physiol. Chem.*, 1923, **133**, 380—396).—After subcutaneous injection of acetophenone into rabbits, 35.7% is reduced to the carbinol and excreted as the paired glycuronic acid, whilst 24.3% is oxidised to benzoic acid and excreted as hippuric acid. Forty % is completely decomposed. Ethylbenzene is eliminated as hippuric acid, phenylmethylcarbinol and mandelic acid (isolated as the cadmium salt). Various alkyl ketones investigated, propiophenone, butyrophenone, benzyl propyl ketone, and benzyl isopropyl ketone, are reduced to the carbinol and also are oxidised; benzyl isopropyl ketone yields phenylacetic acid. W. O. K.

The Supposed Colloidal Character of Solutions of Chloroform and Some of its Related Compounds. PANCHANAN BOSE (*Biochem. Z.*, 1923, **141**, 269—273).—By subjecting aqueous solutions of chloroform, dichloromethane, tetrachloromethane, ethylene dichloride, and *s*-tetrachloroethane to the Tyndall test, to ultra-microscopic examination and to ultra-filtration, and by measuring their depression of freezing point and rates of diffusion into gelatin and through membranes, it is shown that these halogen derivatives are present in a state of molecular dispersal and not in the colloidal condition as supposed in Traube's theory of narcosis. J. P.

The Physiological Action of Proteinogenic Amines. VIII. The Local Anæsthetic and Narcotic Action of Phenylethylamine and Some of its Derivatives. J. ABELIN (*Biochem. Z.*, 1923, **141**, 458—470).—Phenylethylamine has a strong local anæsthetic action on muscle-nerve preparations, and in concentrations of $M/200$ to $M/500$ acts as a narcotic on frog larvæ. The introduction of a para-hydroxyl group, as in tyramine, increases both actions. Hordenine has but slight narcotic properties. The activity of phenylethylamine derivatives varies with the p_H , being most marked at p_H 8·4 to 8·5 and much less in acid solutions. The increased imbibition of water by gelatin in the presence of phenylethylamine is greatly diminished in neutral and acid solutions.

J. P.

The Relationship between Chemical Constitution and Local Anæsthetic Action in the Case of *N*-Alkyl Derivatives of the Leucinol Ester of *p*-Aminobenzoic Acid. HANS GRAF (*Arch. exp. Path. Pharm.*, 1923, **99**, 315—345).—The first part of the paper is a theoretical discussion of the relationship between chemical constitution and local anæsthetic action with special reference to the cocaine group. The experimental part deals with the investigation of the *N*-dialkyl derivatives of the *p*-aminobenzoic ester of isobutylaminoethyl alcohol ("leucinol"), being substances of the type



and also of the *N*-piperidyl derivative. Of the whole series investigated, the *N*-diethyl derivative was the only one which seemed promising from the practical point of view. Its anæsthetic power approximates to that of cocaine, whilst its toxicity is intermediate between those of cocaine and novocaine.

C. R. H.

The Central Influence of Atropine and Hyoscine on the Heart Rate. W. J. R. HEINEKAMP (*J. Lab. Clin. Med.*, 1922, **8**, 104—111).—Small doses of atropine (0·0003 g. in dogs and 0·001 g. in man) produce inhibition of the heart owing to direct stimulation of the cardio-inhibitory centre. Hyoscine exerts a similar action to that of atropine on the medulla of *Pseudomys troostii*, except that the primary stimulation is followed by depression.

CHEMICAL ABSTRACTS.

Difference in Activity of Optical Isomerides (*l*-Cocaine and *d*-Cocaine). R. GOTTLIEB (*Z. physiol. Chem.*, 1923, **130**, 374—379).—On subcutaneous injection, *d*- ψ -cocaine is at most only one-half as poisonous as *l*- ψ -cocaine for the central nervous system of the frog, mouse, or cat. 0·15—0·18 Mg. of *l*-cocaine is toxic per 1 g. mouse whilst at least 2 mg. of the *d*-cocaine are required. It is considered that detoxication of the *d*-form occurs more quickly.

W. O. K.

The Action of Morphine, Codeine, and apoMorphine as Shown by Perfusion of the Medulla of the Terrapin (*Pseudomys troosti*). W. J. R. HEINEKAMP (*J. Lab. Clin. Med.*, 1923, **8**, 165—169).—Morphine sulphate when perfused through the medulla of the terrapin produces inhibition of the heart, owing to its products of oxidation, since morphine oxidised in vitro with nitric acid when perfused exerts a quicker and more powerful stimulating action than morphine itself. Codeine exerts no influence on the medulla, probably because of the presence of a methoxyl group. However, when oxidised it too has a powerful stimulating effect. apoMorphine first stimulates and then paralyses the medulla. Solutions which have been exposed to air and hence oxidised are ineffective. CHEMICAL ABSTRACTS.

Increase in the Toxic Action of Carbon Disulphide-Hydrogen Sulphide Gaseous Mixtures. RICHARD FISCHER (*Biochem. Z.*, 1923, **141**, 540—544).—With the view of determining if a mixture of two toxic gases has a greater toxicity than that of the sum of its separate components, dogs were subjected to the action of varying concentrations of hydrogen sulphide, carbon disulphide, and a mixture of both gases. In general, no increased toxicity was noted, the effects being those produced by each component in corresponding concentration. J. P.

The Mechanism of the Action of Arsenic on Protoplasm. C. VOEGTLIN, H. A. DYER, and C. S. LEONARD (*U.S. Pub. Health Reps.*, 1923, **38**, 1882—1912).—Reduced glutathione, thioglycollic acid, α -thiolactic acid, glycylcysteine, and thiosalicylic acid counteract the toxic action of arsenic compounds of the structure $RAs\cdot O$ on trypanosomes in vitro and in the blood of rats, whilst disulphides, $R\cdot S\cdot S\cdot R$, are much less, if at all, effective. The amount of the compound (possibly glutathione) containing an $\cdot SH$ group, present in all cells, is thereby prevented from falling below the physiological requirement owing to its chemical interaction with the arsenic compound. Glutathione and some other analogous compounds are concerned in certain biological oxidations and reductions.

3-Amino-4-hydroxyphenylarsino-bismonothioglycollic acid is prepared in 94.2% purity by heating on a water-bath a mixture of 7 g. of 3-amino-4-hydroxyphenylarsenious oxide hydrochloride and 11 g. of thioglycollic acid, drying the gummy mass in a desiccator, washing it with ethyl ether, and dissolving in absolute ethyl alcohol. After removal of the alcohol in a vacuum, the residue is again washed with ethyl ether, dried in a desiccator, and pulverised. The above theory of the action of arsenic is supported by the fact that in equimolecular doses it shows a marked delay in parasiticial action as compared with arsenoxide. CHEMICAL ABSTRACTS.

Chemistry of Vegetable Physiology and Agriculture.

Reducing Action of Micro-organisms on Ammonium Molybdate. V. E. LEVINE and H. M. JAHR (*Abstracts Bact.*, 1921, 5, 4—5).—Bacteria growing in peptone broth containing ammonium molybdate reduce that compound with the production of an intense blue colour. Sterile dextrose peptone broth produces this reduction at a temperature of 37·5° but not at room temperature. Peptone broth containing 1% of lactose and 1% of ammonium molybdate is reduced only in the presence of micro-organisms. No relationship exists between reduction and fermentation. Living yeast-cells also produce the reduction. Both bacteria and yeast secrete reductase as an endocellular enzyme; the reduction is due partly to this enzyme and partly to the metabolic products of the organisms. Low concentrations of ammonium molybdate do not retard bacterial growth; the degree of retardation, or even complete inhibition, produced by a relatively high concentration (1%) varies with the species.

CHEMICAL ABSTRACTS.

The Minimum Concentration of Oxygen for Luminescence by Luminous Bacteria. E. NEWTON HARVEY and THOMAS F. MORRISON (*J. Gen. Physiol.*, 1923, 6, 13—19).—A method is described for estimating the minimum concentration of oxygen which is necessary to produce a perceptible luminescence in luminous bacteria. Using this method, a value equivalent to an oxygen pressure of about 0·005 mm. of mercury was found. E. S.

The Formation of Acetaldehyde during the Fermentation of Lævulose, Galactose, Sucrose, Maltose, and Lactose by *Bacillus coli* and *B. lactis aerogenes*. K. NAGAI (*Biochem. Z.*, 1923, 141, 261—265).—Lævulose, galactose, sucrose, maltose, and lactose all yield acetaldehyde when fermented at 37° by cultures of *B. coli* and *B. lactis aerogenes* in the presence of yeast-water, peptone, and calcium carbonate. Variable yields from 0·5% to 7% of aldehyde, isolated as the bisulphite compound, were obtained.

J. P.

The Formation of Acetaldehyde during the Bacterial Degradation of Carbohydrate Acids and Related Acids. K. NAGAI (*Biochem. Z.*, 1923, 141, 266—268).—Malic, *dl*-lactic, *d*-tartaric, *d*-glyceric, and *d*-gluconic acids, fermented by cultures of *Bacillus coli* and *B. lactis aerogenes*, yield appreciable quantities of acetaldehyde in the presence of yeast-water, ammonium sulphate, and calcium carbonate. The presence of sodium sulphite in the culture is necessary. In its absence no aldehyde was detected.

J. P.

Butylene Glycol Fermentation of Calcium Lactate by Bacteria of the *B. subtilis* group. M. LEMOIGNE (*Compt. rend.*, 1923, 177, 652—654).—Lactic acid, like sugar, is decomposed by bacilli of the *Bacillus subtilis* group, with formation of butylene

glycol ($\beta\gamma$ -dihydroxybutane) and γ -hydroxybutan- β -one (acetyl-methylcarbinol). Owing to the great stability of lactic acid, these products are formed only slowly, so that they are only detectable in old cultures in which oxidative and synthetic processes (which cause their disappearance as soon as they are formed) are reduced to a minimum.

E. E. T.

Influence of Concentration of Sugar in Media on Activity of Nitrogen-fixing Bacteria. G. TRUFFAUT and N. BEZSSONOFF (*Compt. rend.*, 1923, **177**, 649—652).—In a nitrogen-free medium (Hutchinson liquid), the development of aërobic soil bacteria is favoured by concentrations of sugar of the order of 1 : 1000, rather than by higher concentrations, the converse being true of the corresponding anaërobic bacilli. The aërobic nitrogen-fixing bacilli (*Bacillus Truffauti* and *B. azotobacter agile*) act best with feebler concentrations of sugar than have usually been employed. In the case, however, of the anaërobe *Clostridium Pastorianum*, though cultivated in symbiotic union with the (aërobic) β -bacillus, the fixation of nitrogen is not appreciably affected by the concentration of sugar.

E. E. T.

The rôle of Vitamins and Avitaminosis in Microbiology. Avitaminosis and Increase of Virulence. ALBERTO ASCOLI (*Z. physiol. Chem.*, 1923, **130**, 259—269).—Pathogenic bacteria grown in a vitamin-free medium increase in virulence. A similar increase in virulence in vivo explains the increased virulence of infection in animals suffering from avitaminosis. The effective agent, "exaltin," appears to be a dialysable substance.

W. O. K.

The Influence of Oxygen on the Assimilatory and Dis-assimilatory Activity of Yeast. I. The Behaviour of Dextrose. II. The Behaviour of the Monosaccharides. HARRY LUNDIN (*Biochem. Z.*, 1923, **141**, 310—341, 342—369).—A detailed investigation of the course of the fermentative action of yeast on dextrose, lævulose, and galactose at temperatures varying from 16° to 20°, and in the absence of a source of nitrogen in the fermentation mixtures. The experiments were conducted both under conditions assuring excess of oxygen (by shaking with the gas) and under normal conditions with access of air only. Under these conditions galactose was only slightly fermented, and in general the results given by dextrose and lævulose, which are both rapidly fermented, were similar. No increase in the number of yeast-cells was observed, but the total cell mass underwent a 60% increase as estimated from the dried cell residue. This increase did not affect the cell proteins. None of the usual by-products of alcoholic fermentation was formed nor was the production of fat or acetaldehyde noted. Both in the presence and in the absence of excess of oxygen assimilation of the sugar to higher carbohydrates occurred, and evidence is available to show that this process takes place with the intermediate formation of alcohol and involves the liberation of one-third of the total energy of the

assimilated sugar, the remaining two-thirds being utilised by the complex assimilatory products. These are solely of a carbohydrate nature and consist in part of a readily hydrolysable form—glycogen, and a form soluble to a large extent in 3% hydrochloric acid, but not hydrolysed by this strength of acid. The two forms are produced in equal proportions, but the easily hydrolysable glycogen alone may be subsequently utilised by the yeast-cells as a source of energy when the fermentable sugar in the solution is exhausted. This utilisation of assimilated glycogen is markedly increased in the presence of excess of oxygen. The assimilatory processes are independent of the rate of fermentation. The author regards his results as opposing the glycogen fermentation theory of Grüss (*Zeit. ges. Brauwesen*, 1904, 27) and as favouring Laquer's views (*A.*, 1922, i, 1089) on the oxidation of dextrose through preliminary transformation into a readily oxidisable form. J. P.

The Action of Metallic Salts on the Course of Alcoholic Fermentation. ALBERT VON MAY (*Biochem. Z.*, 1923, 141, 447—457).—The observations of Kostytschev (*A.*, 1912, ii, 589; 1921, i, 149), that during the fermentation of sugar by yeast in the presence of cadmium and zinc salts a large proportion of the sugar disappears without forming known condensation or degradation products, are due to the difficulty of estimating sugar by reduction methods in the presence of yeast-proteins. If these be precipitated, the presence of the unchanged sugar may be demonstrated both polarimetrically and by reduction methods. The increased aldehyde formation also observed by Kostytschev is produced by the addition of other salts, notably those of barium, calcium, glucinum, magnesium, and iron, and to a less extent by nickel, tin, lead, aluminium, and thallium salts. J. P.

The Specific Action of Ferments. Is it Possible by Means of Ferments to Determine whether Amino-acids of Known Configuration are Present in Nature, Particularly as Constituents of Protein? EMIL ABDERHALDEN (*Z. physiol. Chem.*, 1923, 130, 205—207).—Polypeptides have been synthesised containing α -*dl*-aminoheptonic acid, α -*dl*-amino-octonic acid, and α -*dl*-amino-myristic acid. These amino-acids are not known to occur naturally. The racemic polypeptides are hydrolysed asymmetrically by yeast-cells, indicating that it is not the whole structure of the protein but only a particular group that determines whether it will be attacked by the enzymes. W. O. K.

The Behaviour of Pyrimidine Derivatives in the Organism.
I. The Action of Yeast on Pyrimidine Derivatives. AMANDUS HAHN and WOLFGANG LINTZEL (*Z. Biol.*, 1923, 79, 179—190).—Living yeast-cells in the presence of sucrose, and cell-free yeast extracts deaminise cytosine at room temperature with formation of uracil. In the former case, the liberated ammonia serves the cells as a source of nitrogen, and in the latter case the deamination, which is quantitative, causes the solution to become alkaline,

Uracil and thymine are not affected by yeast or by yeast extracts even when the solutions are aërated. The deaminising action of yeast extracts on cytosine is lost on boiling. It is concluded that a cytosine deaminase is present in yeast. J. P.

Biochemistry of the Germination of Cereal Grains. HANS LOIBL (*Z. ges. Brauwesen*, 1923, **46**, 30—35, 37—41, 45—48, 53—56, 61—67, 69—72; from *Chem. Zentr.*, 1923, iii, 396—397).—The increase in soluble substances in the endosperm of germinating cereal seeds is the result of degradation of reserve materials. The starch content decreases partly through respiration and partly through the formation of soluble carbohydrates. An increase in soluble carbohydrates, reducing sugars, and sucrose occurs. The increase in soluble pentosans during germination is due to hydrolysis of the hemicelluloses of the cell-walls. There is no appreciable increase in total pentosans and total crude fibre. Total nitrogen, coagulable nitrogen, and nitrogen titratable by formaldehyde all increase. The notable increase in total titratable acidity is mainly due to the change of organic phosphates to inorganic phosphates. There is, however, a slight decrease in hydrogen-ion concentration. Amylase, catalase, peptase, cytase, and phytase show increases, whilst urease shows a decrease. G. W. R.

A Method of Simultaneously Studying the Absorption of Oxygen and the Discharge of Carbon Dioxide in Respiration. D. S. FERNANDES (*Proc. K. Akad. Wetensch. Amsterdam*, 1923, **26**, 408—419).—A detailed description is given of a thermostatic apparatus for the study of respiratory exchange in plants. The respiratory gases are pumped round a closed circuit; a known quantity of oxygen can be introduced by an electrolytic method, and the carbon dioxide may be estimated by means of baryta. H. H.

Comparative Studies on Respiration. XVIII. Respiration and Antagonism in *Elodea canadensis*. C. J. LYON (*Amer. J. Bot.*, 1921, **8**, 458—463).—Working with *Elodea canadensis* it was found that solutions of sodium chloride (0.1M) caused an initial increase in respiration followed by a decrease. Calcium chloride solution (0.07M) caused a decrease in respiration. Respiration remains normal in the presence of sodium chloride and calcium chloride when these salts are present in the molar ratio 99.65 : 0.35. The curve showing the rate of respiration with mixtures of sodium chloride and calcium chloride in varying proportions is unique in that it shows two maxima, one at 99.65 : 0.35, as above, and the other at 98.62 : 1.38. At the latter maximum, respiration is very much increased above normal. G. W. R.

Comparative Studies on Respiration. XXII. The Effect of Lactic Acid on the Respiration of Wheat. EDITH PHILIP SMITH (*Amer. J. Bot.*, 1922, **9**, 307—310).—In high dilutions such as 0.0025M, lactic acid first increases and then depresses the

rate of production of carbon dioxide of wheat seedlings. With more concentrated solutions the maximum becomes less marked, until finally only a decrease is observed. Recovery occurs even after the rate of respiration has been reduced to 25% of normal by a 2*M*-solution of lactic acid. The effects are believed to be due to a specific action of lactic acid. It is concluded that lactic acid is not an intermediate substance in the metabolism of wheat seedlings.

G. W. R.

New Method of Proceeding from Carbonic Acid to Formaldehyde. Theory of the Assimilation of Carbon Dioxide. T. THUNBERG (*Z. physikal. Chem.*, 1923, **106**, 306—312).—When basic lead carbonate, preferably in the presence of boric acid, is boiled with hydrogen peroxide and the resulting mixture distilled, the distillate is found to contain formaldehyde. The reaction is carried out by mixing 5 g. of basic lead carbonate with 100 c.c. of distilled water and heating to boiling in a 250 c.c. distilling flask. When 10 c.c. of liquid had distilled over, 50 c.c. of 6% hydrogen peroxide was added slowly and further portions of 10 c.c. of distillate collected in each of which formaldehyde was found. Other carbonates gave negative results. On the basis of this experiment, the author puts forward an hypothesis for the assimilation of carbon dioxide, according to which sunlight decomposes water with the formation of hydrogen and hydrogen peroxide, $2\text{H}_2\text{O}=\text{H}_2\text{O}_2+\text{H}_2$. Then carbon dioxide reacts with hydrogen peroxide and hydrogen to form methylene glycol, $\text{CO}_2+\text{H}_2+\text{H}_2\text{O}_2=\text{H}_4\text{CO}_2+\text{O}_2$, and this compound loses a molecule of water with the formation of formaldehyde, $\text{H}_4\text{CO}_2=\text{H}_2\text{O}+\text{HCHO}$.

J. F. S.

Theory of the Assimilation of Carbon Dioxide. FRITZ WEIGERT (*Z. physikal. Chem.*, 1923, **106**, 313—323).—A theoretical paper in which the author discusses the hypothesis put forward by Thunberg for the assimilation of carbon dioxide (preceding abstract). The author puts forward the following scheme to represent the mechanism of the assimilation of carbon dioxide. $2\text{Chlorophyll}+2h\nu+2\text{O}_2=2\text{Chl}^++2\text{O}_2^-$; $2\text{O}_2^-+2\text{H}_2\text{O}=2\text{H}+2\text{OH}^-+2\text{O}_2$; $2\text{H}+2\text{OH}^-+2\text{Chl}^+=\text{H}_2+\text{H}_2\text{O}_2+2\text{Chl}$. These lead to the total equation $2\text{H}_2\text{O}+2h\nu=\text{H}_2+\text{H}_2\text{O}_2$ (1) which is followed by $\text{CO}_2+\text{H}_2+\text{H}_2\text{O}_2=\text{H}\cdot\text{COH}+\text{H}_2\text{O}+\text{O}_2$ (2). The sum of (1) and (2) give the final equation $\text{CO}_2+\text{H}_2\text{O}+2h\nu=\text{HCHO}+\text{O}_2$. The reactions are both endothermic, $2\text{H}_2\text{O}=\text{H}_2+\text{H}_2\text{O}_2-92,000$ cal. $\text{CO}_2+\text{H}_2+\text{H}_2\text{O}_2=\text{HCOH}+\text{H}_2\text{O}+\text{O}_2-18,000$, consequently the light energy $2Nh\nu$ must furnish this energy. Calculation shows that this can be done by wave-lengths of $517\text{ }\mu\mu$. At this wave-length, the radiation is transformed completely into chemical energy in this reaction.

J. F. S.

A Factor Causing the Assimilation of Calcium. CHAS. H. HUNT and A. R. WINTER (*Science*, 1923, **57**, 717—718).—It is assumed that most of the calcium, however combined, in the cells of green plants is in a highly dispersed form, and is hence better

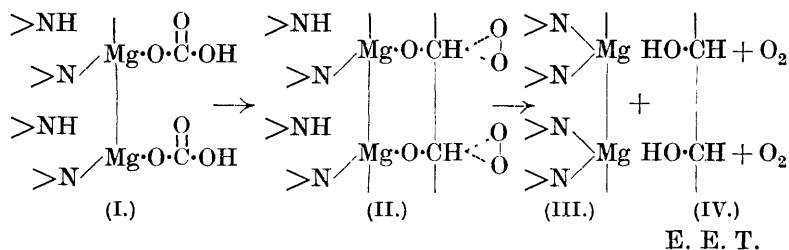
assimilated than the calcium in the dry plant. The cell contents were roughly imitated by a solution containing calcium chloride, sodium phosphate, and starch paste, and fed, with grain and dry timothy hay, to goats. The results are, however, so far inconclusive.

A. A. E.

The Absorption of Ions by Plants, including Observations on the Effect of Light. D. R. HOAGLAND and A. R. DAVIS (*J. Gen. Physiol.*, 1923, **6**, 47—62).—The absorption of inorganic ions by the fresh-water alga *Nitella* (this vol., i, 882) is favoured by illumination. It is concluded that light supplies the energy necessary for the transference of the ions from a dilute solution into the more concentrated cell sap. The absorption of one ion may be influenced by the presence of another.

E. S.

Theory of Chlorophyllic Synthesis. L. MAQUENNE (*Compt. rend.*, 1923, **177**, 853—857).—The theories hitherto put forward to account for the synthesis of carbohydrates in plants are unsatisfactory, mainly because they assume formaldehyde to be formed intermediately, whereas its presence in plants has never been indubitably proved. It is now suggested that photosynthesis of carbohydrates is effected through the agency of colloidal chlorophyll, which is assumed to be a polymerised chlorophyll possessing the grouping III, that is, containing quadrivalent magnesium, associated with weakened attachment of metal to nitrogen. Carbonic acid is assumed to combine with III, giving I, which then undergoes isomeric change to give II, this complex losing the oxygen which is characteristic of photosynthesis, being at the same time converted into polymerised (colloidal) chlorophyll (III) and a carbohydrate (IV). The complexity of the latter is determined by the complexity of the polymerised chlorophyll, and this is obviously capable of considerable variation. Thus, if six mono-magnesium complexes are polymerised to give a ring, inositols will result.



The Effect on Permeability of Multivalent Kations in Combination with Multivalent Anions. O. L. RABER (*Amer. J. Bot.*, 1921, **8**, 382—385; from *Physiol. Abstr.*, 1923, **8**, 315).—Bivalent and trivalent kations in combination with univalent anions produce an initial increase in the electrical resistance of *Laminaria*, but when combined with bivalent or trivalent anions the increase is reduced and may be zero.

W. O. K.

The Effect on Permeability of (I) the Same Substance as Kation and Anion and (II) Changing the Valency of the Same Ion. O. L. RABER (*Amer. J. Bot.*, 1921, 8, 464—470; from *Physiol. Abstr.*, 1923, 8, 315).—The change in the electrical resistance of the thallus of *Lamaria Agardhii* was followed when the tissue was immersed in (a) a mixture of 0.61*M*-chromous chloride and 0.52*M*-sodium chloride in equal proportions, and (b) a mixture of 0.22*M*-sodium chromate and 0.52*M*-sodium chromate in equal proportions with enough chromic acid to make the p_H equal to that of the mixture (a). In the former case the tissue first undergoes an increase in resistance, in the latter a decrease. Ferric chloride brings about a greater increase in resistance than ferrous chloride. This is independent of the hydrogen-ion concentration. W. O. K.

Permeability of the Cell to Electrolytes. O. RABER (*The Botan. Gazette*, 1923, 75, 298—308; from *Physiol. Abstr.*, 1923, 8, 314—315).—Neutral salt solutions of the same osmotic pressure and conductivity as sea-water cause an initial decrease in permeability of *Laminaria* cells, followed by an increase if the valency of the kation is greater than that of the anion, whereas they cause an increase of valency from the start if the valency of the kation is less than that of the anion. If the two are of the same valency, the effect will depend on the relative size of the anions and the density of the accompanying electric charges. A hypothesis, based on consideration of the charge on the membrane is suggested to explain the observed phenomena. W. O. K.

The Permeability of Living and Dead Cells. MATILDA MOLDENHAUER BROOKS (*Proc. Soc. Exp. Biol. Med.*, 1922, 20, 39—40; 384—385; *U.S. Public Health Reports*, 1923, 1449—1470; 1470—1477).—The penetration of arsenic from “atoxyl” solutions into the cell sap of *Nitella* increase with p_H up to p_H 7.5, the most alkaline solution used. The arsenic content of the cell sap of living cells is always less than that of the external solution. With dead cells, the internal and external concentrations are approximately equal. The effect of p_H on the penetration of arsenic may be due either to its effect on the dissociation of “atoxyl” or to changes in cell permeability. In a series of experiments with *Valonia ventricosa*, it was found that the p_H of the cell sap is unaffected by acids and remains at 5.2 until all the hydrogen carbonates present have been decomposed. Acids which decompose hydrogen carbonates penetrate slowly, whilst other acids which do not decompose hydrogen carbonates penetrate rapidly. It is inferred from the similarity in the behaviour of live and dead cells that protoplasm is not the only agency regulating the penetration of acids. The cells of *Valonia* are very permeable to carbon dioxide dissolved in sea-water. In the presence of alkali hydrogen carbonates, an increase in the alkalinity of the cell-sap freed from carbon dioxide takes place. The entrance of carbon dioxide and the increase in alkalinity is more marked with potassium

hydrogen carbonate than with sodium hydrogen carbonate. With alkali citrates, acetates, and chlorides, increases in the alkalinity of the cell-sap freed from carbon dioxide are less marked, but the greater influence of the potassium-ion in producing alkalinity is also shown. The above processes do not occur in dead cells.

G. W. R.

The Synergetic Action of Electrolytes. O. L. RABER (*Proc. Nat. Acad. Sci.*, 1917, **3**, 682—685; from *Physiol. Abstr.*, 1923, **8**, 315).—*Laminaria* tissue was immersed in solutions of sodium chloride, sodium citrate, and in mixtures of both. The presence of the two ions increases the action of both, so that the resistance of the tissue is lower than would be expected if the effect were additive.

W. O. K.

Chemistry of Japanese Plants. II. Composition of Fossil Wood. SHIGERU KOMATSU and HIDENOSUKE UEDA (*Mem. Coll. Sci. Kyoto Imp. Univ.*, 1923, **7**, 7—13).—Umoregi, a fossil wood, contains more sulphur and nitrogen than coal and has a carbon and hydrogen content similar to that of peat. It contains: resin, 5—6%, water 17—18%, ash 1%, methylpentosan 1·8%, total polysaccharides 5·1%, lignin 56%, and cellulose 28—30%. By comparing these figures with similar ones for the analysis of the red wood (*Sequoia sempervirens*) from which the umoregi was formed, it is concluded that during fossilisation the wood lost 20% as cellulose and 4% as polysaccharides, gaining, at the same time, 25% as lignin and 2% as resin.

E. E. T.

Lævulosans in Cereals. H. COLIN and H. BELVAL (*Compt. rend.*, 1923, **177**, 973—975: cf. this vol., i, 1044).—Rye is the cereal with which lævulosans are to be associated, since they constitute 40% of the dried material in the case of very young grains, and are even present in the ripe grains and in rye flour. Wheat and barley contain smaller quantities (than rye) of lævulosans, but the distribution is similar from the point of view of age of the plant. Lævulosans are present in the stem and immature grains of oats, but not in the ripe grains, or in oatmeal, whilst maize and buckwheat do not contain lævulosans at any stage in their development.

E. E. T.

Effect of Boric Acid and Borax on the Broad Bean and certain other Plants. KATHERINE WARINGTON (*Ann. Bot.*, 1923, **37**, 629—672).—In water-cultures, a continual supply of boric acid was found to be essential for the healthy growth of broad bean plants. Beneficial effects were produced at concentrations of 1:12,500,000 to 1:25,000. With higher concentrations, toxic effects were observed. In the absence of boron, death ultimately occurs, but the small amounts of boron shown to be present in the cotyledons of the plant enable it to survive for a short period. Whilst barley does not appear to require boron, certain other plants of the *Leguminosæ* were found to resemble the broad bean. The

function of boron is held to be nutritive rather than catalytic. Application of boric acid under ordinary field conditions is, as a rule, unlikely to be required since small quantities of boron commonly occur in ordinary soils. G. W. R.

The Occurrence of Urease. HENRY E. ARMSTRONG (*Nature*, 1923, 112, 620—621; cf. Werner, this vol., i, 1046; Beijerinck, this vol., i, 1157).—Quotations demonstrate that, contrary to Werner's belief, the existence of urease in the root-nodules of leguminous plants was recognised previously to the publication of the papers cited. The relation of the occurrence of urease to the use of carbamide as a fertiliser is emphasised. A. A. F.

Composition of *Monotropa hypopitys*. L. Isolation of a New Methyl Salicylate Glucoside, Monotropitin. MARC BRIDEL (*Compt. rend.*, 1923, 177, 642—644; cf. this vol., i, 820).—Bourquelot (A., 1896, ii, 540), who showed that *Monotropa hypopitys*, L., contained a glucoside derived from methyl salicylate, conjectured its identity with gaultherin (Schneegans and Gerock, A., 1895, i, 109). This is incorrect, the glucoside present in *Monotropa hypopitys* being now named *monotropitin*. It forms odourless needles, possessing a bitter taste, is non-reducing, has $[\alpha]_D -57.05^\circ$, and, after drying in a vacuum at 50° (a process accompanied by a loss of weight of 5.67%), has m. p. $91.5-92^\circ$ (shrinking at 88°). Dilute sulphuric acid at 100° affords methyl salicylate and a reducing sugar (possibly an equimolecular mixture of xylose and dextrose).

E. E. T.

The Cyanogenic Glucosides. N. WATTIEZ (*Ann. bull. Soc. roy. Sciences med. natur. Bruxelles*, 1922, 70—77; *Ber. ges. Physiol.*, 16, 211—212; from *Chem. Zentr.*, 1923, iii, 159).—Direct estimation of hydrocyanic acid by distillation always gives smaller results than those obtained from estimating the amount of glucoside (Bourquelot). This is regarded as evidence that in the plants examined, *Prunus laurocerasus*, *P. persicaria*, and *Sambucus nigra*, hydrocyanic acid does not occur in the uncombined state.

G. W. R.

Essential Oil of *Stirlingia latifolia* from Western Australia. (*Bull. Imp. Inst.*, 1923, 21, 318—320).—The yield obtained from fresh plants by distillation with steam was 0.75%, but from dried shoots sent to England the yield was only 0.35%. The oil consists almost entirely of acetophenone. S. I. L.

Acidity of Highly Basic Soils. W. T. McGEORGE (*Soil Sci.*, 1923, 16, 195—206).—A study of the behaviour of a number of Hawaiian soils of high basicity, as shown by gross analysis, but of varying actual acidity with different tests for lime requirement. [See, further, *J.S.C.I.*, 1923, 1142A.] G. W. R.

Manganese, Aluminium, and Iron Ratio as Related to Soil Toxicity. R. H. CARR and P. H. BREWER (*Ind. Eng. Chem.*, 1923, 15, 634—637).—Manganese, aluminium, and iron are present as

soluble salts in many soils and in quantities sufficient to be toxic to vegetation; they are readily soluble in 5% potassium thiocyanate solution (cf. A., 1922, ii, 172), yielding a red coloration when iron is present and a green coloration when manganese is present in the manganic form and the solution has been sufficiently basic (p_H 5.5) to remove the red coloration of the ferric thiocyanate. Aluminium, ferric and ferrous iron, manganese, calcium hydrogen carbonate (as calcium carbonate), and magnesium are precipitated as hydroxides in the order mentioned, and range in reaction from p_H 4.0 to p_H 10.0; different amounts of limestone added to a soil appear to precipitate some of these elements in the same order. There is but little evidence of toxicity or of a green coloration when 0.006 to 0.008% of manganese is present in the potassium thiocyanate extract of a soil, but 0.015 to 0.03% exhibits distinct toxicity. When a considerable quantity of manganese is present in a soil, as indicated by the formation of a green coloration in the potassium thiocyanate solution, from 40 to 50 c.c. of $N/10$ -alkali solution per 50 g. of soil are required to precipitate the manganese as hydroxide.

W. P. S.

Native Ferromanganese Ore as a Catalytic Fertiliser. E. PICADO and E. VICENTE (*Ann. Inst. Pasteur*, 1923, 37, 891—899).—Application of finely ground ferromanganese ore gave increases in the yield of carrots, oats, haricot beans, potatoes, and maize. The optimum application varied from 2 kg. per hectare in the case of maize to 74 kg. per hectare in the case of potatoes. The increase for optimum application varied from 12.56% for maize to 68% for oats. Negative results were obtained with radish and mustard. It is also shown that the alcoholic fermentation of molasses is accelerated by the presence of small quantities of ferromanganese.

G. W. R.

Organic Phosphorus in Soils. J. T. AUTEN (*Soil Sci.*, 1923, 16, 281—294).—The Potter and Benton method (A., 1917, i, 76) for the estimation of organic phosphorus is held by the author to give fairly accurate results. Considerable amounts of organic phosphorus were found in the soils examined. The mode of occurrence of organic phosphorus in soils is discussed. It is concluded that it does not exist in appreciable amounts as nucleic acid, phytin, lecithin, or pyrimidine nucleotides. Organic phosphorus added to soils is probably hydrolysed and combined as a calcium-magnesium or other metallic salt of an amphoteric organic complex.

G. W. R.

Estimation of the Relative Solubility of Phosphoric Acid in Soils. O. LEMMERMANN and L. FRESENIUS (*Z. Pflanz. Düng.*, 1923, 2, 363—369).—From a comparison of different soils, some of which respond and others of which do not respond to phosphatic fertilisers, it is concluded that the relative solubility of the phosphoric acid of soils, *i.e.* the proportion of the total phosphoric acid, soluble in 1% citric acid, can give information as to the need or otherwise for phosphatic applications.

G. W. R.

JOURNAL
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ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN
BRITISH AND FOREIGN JOURNALS.

PART II.

General and Physical Chemistry.

The Molecular Scattering of Light in *n*-Pentane. RAMA-
VENKATASUBBA VENKATESWARAN (T., 1922, 121, 2655—2663).

The Calculation of the Hydrogen Dissimilar Spectra from the Inner Movements of the Electrons. I. E. FUES (Z. *Physik*, 1922, 11, 364—378).—A theoretical paper in which the general type of the potential function in the inner field of the atom has been elucidated, and methods are outlined of determining the true series constants from the course of this function. The calculation of the spectrum of an idealised cubic sodium atom gives a quantum relationship of the sodium terms which is in agreement with the new Bohr assumptions. A consistent quantitative interpretation of the sodium spectrum will be given in the second part of this paper.
W. E. G.

New Spectra of Water-vapour, Air, and Hydrogen in the extreme Ultra-violet. J. J. HOPFIELD (*Nature*, 1922, 110, 732—733).—In an investigation of the Lyman series of hydrogen, three new members were found. On the same spectrogram there appeared a line λ 243.2 \pm 0.2, of which the wave-length agrees within limits of experimental error with the equivalent wave-length (λ 248) for the *L* critical potential of oxygen. The conditions of the observation of this line indicate the transparency of

hydrogen in this region, and the termination on the long wave-length side of λ 243 of the great absorption band of hydrogen which begins at about λ 850. Water-vapour gives a spectrum in the ultra-violet extending to about λ 900, and consisting of oxygen lines, hydrogen series lines, the secondary spectrum of hydrogen, and some bands probably not due to hydrogen. For air, a spectrum was obtained to λ 350.

A. A. E.

Effect of Pressure on the Band Spectra of Nitrogen. JEAN HUDDLESTON (*Physical Rev.*, 1921, **18**, 327).—An investigation of the negative pole bands and the second group of positive bands produced by nitrogen or air at pressures ranging from one to six atmospheres by means of a spark discharge, using a transformer or small induction coil. In nitrogen at one atmosphere pressure, the positive and negative bands were of about the same strength, whilst as the pressure increased there was gradual formation of a continuous spectrum, the positive and negative bands being similarly affected. With air, the negative bands were stronger than the positive. In the region of the first group of positive bands, which was observed visually, there was no evidence of any band structure at or above one atmosphere pressure.

A. A. E.

Determination of the Wave-lengths of 118 Titanium Lines by means of the Interferometer. FREDERICK L. BROWN (*Astrophys. J.*, 1922, **56**, 53—70).—By the use of a Fabry-Perot interferometer and a Hilger spectrograph of the constant-deviation prism type, a number of titanium lines between λ 4263.134 and λ 6261.097 have been measured in comparison with the cadmium line λ 6438.4696.

A. A. E.

The Ultra-violet Absorption Spectra of Pyridine and isoquinoline. H. FISCHER and P. STEINER (*Compt. rend.*, 1922, **175**, 882—884; cf. Henri and Steiner, A., 1922, i, 928).—A quantitative study of the absorption spectra of pyridine and isoquinoline in hexane solution has given new results. In the case of pyridine, the bands which correspond with those of benzene are replaced by a single band, whilst five new bands were observed in the region of greater wave-length. The curve obtained for isoquinoline resembles that given by naphthalene, but is situated as a whole towards the region of shorter wave-length. Certain general similarities are also found between the spectra of pyridine and isoquinoline.

H. J. E.

Luminescence of Zinc Oxide above Red Heat. E. L. NICHOLS (*Physical Rev.*, 1921, **17**, 429—430).—Zinc oxide, whilst not photoluminescent or responsive to X-rays, is susceptible to excitation by the hydrogen flame (cf. Nichols and Wilber, A., 1922, ii, 105, 806) with the development of (a) a red band which appears when the oxide is heated at 568° ; at 700° it is displaced by a yellowish-green band, (b) a yellowish-green band which disappears at about 940° . The point of maximum brightness, somewhat above 800° , may indicate the occurrence of some molecular transformation.

A. A. E.

Chemi-luminescence and the Thermochemical Behaviour of Organo-magnesium Compounds. I. LIFSCHITZ and OTTO E. KALBERER (*Z. physikal. Chem.*, 1922, **102**, 393—415).—An investigation on the mechanism of the luminescence brought about by chemical reactions. It is shown that ethereal solutions of magnesium phenyl, *p*-bromophenyl, *o*-tolyl, *p*-tolyl, *p*-diphenyl, and α -naphthyl bromides in the presence of air all give rise to a white luminescence, whilst in the presence of oxygen a blue luminescence varying in shade is observed. On the other hand, magnesium ethyl, benzyl, *n*-propyl, and camphor bromides, magnesium ethyl, *n*-propyl, and isoamyl iodides, magnesium *n*-propyl and triphenylmethyl chlorides, and all compounds in which the magnesium is directly linked with an aliphatic carbon atom, do not give rise to luminescence under the influence of air or oxygen in ethereal solution. The luminescence gains in intensity in the above-named compounds with increasing molecular weight, and the light gives a continuous spectrum which extends from the green to the blue, and in no case does it correspond with the absorption spectrum of the ethereal solution. The dry magnesium halogen derivatives, irrespective of whether they are aliphatic or aromatic, give a much more intense light when in contact with air or oxygen than the ethereal solutions; here the light is of a green colour and gives a continuous spectrum. Among other reactions which are accompanied by luminescence, the authors note the action of nitrous oxide and ethyl nitrite, nitric oxide and ethyl nitrate, nitrogen dioxide and acetyl chloride, carbon dioxide and water, carbon monoxide and benzene triozonide in benzene solution, and chloropicrin and magnesium phenyl bromide. It is shown that a high velocity of reaction is not a necessary cause of luminescence; large heat changes or active masses are also not at all determinative of luminescence. The heat of formation of a number of additive compounds of ethyl ether and Grignard compounds and the heat of reaction of these substances with water have been determined calorimetrically. In the case of the Grignard compounds, the authors are of the opinion that either the Grignard compound (I) or the mono-ether derivative (II) is the seat of the luminescence, $R \cdot Mg \cdot X$ (I) + n mols. ether $\rightleftharpoons R \cdot Mg \cdot X$, ether (II) + n mols. ether $\rightleftharpoons R \cdot Mg \cdot X$, 2 ether.

J. F. S.

Theory of Radiation Transformation. I. General Mechanism of Photochemical Processes. FRITZ WEIGERT (*Z. physikal. Chem.*, 1922, **102**, 416—437).—A theoretical paper in which the mechanism of the absorption of light and its conversion, when absorbed, into such a form that it can bring about a chemical reaction is discussed.

J. F. S.

The Photochemistry of Hydrogen-Chlorine Mixtures. FRITZ WEIGERT (*Z. Elektrochem.*, 1922, **28**, 456—458).—A study of the Draper effect, and the changes in density which occur on illumination of mixtures of chlorine and hydrogen with light of short wave-length. On exposure of the gaseous mixture to light from an electric spark, a wave of cloud spread out from the illumi-

nated region which synchronised with a movement of the surface of a water manometer in contact with the gas. The initial stages in the propagation of the wave and its mode of formation were examined by a photographic method. No appreciable change was observable until 1/160 second after illumination, when bright regions appeared in the tube near the point of entrance of the light. This brightness reached a maximum in 1/40 second, and had entirely disappeared in 1/10 second. The rate of combination between hydrogen and chlorine thus appears to reach a maximum 1/40 of a second after illumination. The chain-like mechanism postulated by Bodenstein and Nernst for this reaction provides the most convenient interpretation of this time interval. If 10^6 molecules be converted one after the other by one energy quantum, it can be shown that each element in the chain takes 10^{-8} seconds to be completed. This interval of time occurs frequently in the modern atomic theory of chemical action. W. E. G.

Effect of X-Rays on Chemical Reactions. O. R. OLSON (*Science*, 1922, 56, 231).—Exposure to X-rays of cyclohexanol contained in a brass cell, resulted in the dissolution to a greenish-blue solution of about 0.1 g. of copper. Calculations based on the conditions of the experiment indicate that the X-rays produced some kind of trigger action. Mesitylene showed a similar behaviour. On account of the large effect produced by relatively small amounts of energy, the possible preparation of organic compounds by the use of X-rays is indicated. A. A. E.

Adsorption of Radium-B and Radium-C by Ferric Hydroxide. JOHN ARNOLD CRANSTON and ROBERT HUTTON (T., 1922, 121, 2843—2849).

The Ionisation Potential of Selenium Vapour. A. D. UDDEN (*Physical Rev.*, 1921, 18, 385—388).—The ionisation potential of selenium vapour is found to be 12.7 ± 0.4 volts. If this potential is substituted for V in the equation $\nu = Ve/h$, the limiting frequency of the spectrum of selenium vapour is about 980 Å. A. A. E.

The Ionisation of Abnormal Helium Atoms by Low Voltage Electronic Bombardment. FRANK HORTON and ANN CATHERINE DAVIES (*Phil. Mag.*, 1922, [vi], 44, 1140—1146).—The formation and maintenance of an arc in helium with alternating E.M.F. at about 5 volts has been described by Kannenstine (*Astrophys. J.*, 1922, 55, 345). This occurs only if the helium contains abnormal helium atoms activated by voltages above 20.4. This result indicates the possibility of ionising abnormal helium atoms by electrons having 4.8 volts energy. In the present paper, abnormal atoms are produced by the action of radiation from an auxiliary side-tube of the apparatus, and the effect of bombarding these with a stream of electrons is investigated. Ionisation commenced at about 4.5 volts. Below this voltage the ionisation was very slight. Thus no abnormal atoms could have been present which had absorbed radiation corresponding with voltages greater

than 21·2 volts. The abnormal atoms responsible for the maintenance of low-voltage arcs must correspond therefore with 20·4 and 21·2 volts. There is no necessity to assume the existence of metastable helium atoms.

W. E. G.

The Temperature Ionisation of Elements of the Higher Groups in the Periodic Classification. MEGH NAD SAHA (*Phil. Mag.*, 1922, [vi], **44**, 1128—1139).—The degree of ionisation of the alkaline-earth metals, as measured by the intensity of the spectrum lines in the sun, is greater than that of the alkali metals with similar ionisation potentials. This is due to differences in the rates of loss of the outer electrons under the influence of external forces, and in the speeds of recombination of the displaced electron with the positively charged atoms. The two outer electrons in bivalent elements will be displaced with equal ease by bombarding electrons, and, for elements with the same ionisation potentials, the number of successful hits by the collision of an electron with a bivalent atom will be twice as great as with a univalent atom. A steric factor also operates in the same direction. Owing to the protective action of the remaining electron, the recombination of the displaced electron with the positively charged bivalent atom will be slower than in the case of a univalent atom. The equation deduced by Boltzmann for the steric factor in the formation of diatomic gases is applied to the case of the combination between an ionised atom and an electron, and it is shown that the effective ionisation potential $I_e = I - 2 \cdot 3 RT \log (n_a n_b) / 23,000$ volts. The variation in the effective ionisation potential of the elements with temperature is calculated from this equation, and the results are in agreement with the intensities of the lines in the stellar spectra for uni-, bi-, ter-, quadri-, and quinque-valent elements. The successive stages in the ionisation of a multivalent element are shown to follow in quick succession as the temperature rises.

W. E. G.

Inelastic Collisions of Electrons in Vapours of certain Compound Molecules. PAUL D. FOOTE and F. L. MOHLER (*Physical Rev.*, 1921, **17**, 394).—The ionisation potential of zinc ethyl is 12 volts and the resonance potential about 7 volts. The ionisation potentials of zinc chloride and mercuric chloride are 12·9 volts and 12·1 volts, respectively. In the case of carbon monoxide, there are two ionisation potentials, namely, 10·1 and 14·3 volts. Besides these inelastic collisions, electrons undergo the following velocity losses without producing ionisation: 6·4, 12·1, 13·6, 19·1, 21·9, and 24·6 volts. There is a marked contrast in the behaviour of sodium and potassium chlorides on the one hand and calcium on the other; vapours of the former are highly ionised at 2 mm. pressure, preventing measurements of the ionisation potential, whilst calcium vapour is not appreciably ionised at 700°.

A. A. E.

Solubility of Barium Selenate. JULIUS MEYER and WALTER FRIEDRICH (*Z. physikal. Chem.*, 1922, **102**, 369—387; cf. A., 1922, ii, 70).—The equivalent conductivity of sodium and potassium

selenate has been determined at 0°, 5°, 18°, 25°, 35°, and 50° for concentrations between $v=2$ and $v=2048$. From the conductivity values the mobility of the selenate-ion has been calculated for various concentrations for 18° and 25°. Among the data obtained, the following values of the ionic conductivity of the selenate-ion at infinite dilution are quoted, $\lambda^{18^\circ}=64.01$ and $\lambda^{25^\circ}=73.68$ from sodium selenate and $\lambda^{18^\circ}=65.12$ and $\lambda^{25^\circ}=74.80$ from measurements with potassium selenate, the mean values accepted being 64.57 and 74.24, respectively. The temperature coefficient of the ionic conductivity of the selenate-ion at infinite dilution is obtained from the formula $x_h = x_h[1 + c(t_1 - t_2) + c'(t_1 - t_2)^2]$, in which $c=210 \times 10^{-4}$ and $c'=49 \times 10^{-6}$. The transport numbers of the anions of sodium, potassium, and barium selenate have been calculated. In every case the value decreases with increasing concentration. From the conductivity measurements, the solubility of barium selenate at 25° is calculated to 82.5 mg. per litre of water, whilst the direct determination of this quantity gives the values 79.2 and 82.0 mg. per litre.

J. F. S.

Conductivity of Aqueous Solutions of Iodic Acid and the Limiting Value of the Equivalent Conductivity of the Hydrogen-ion. CHARLES A. KRAUS and HENRY C. PARKER (*J. Amer. Chem. Soc.*, 1922, **44**, 2429—2449).—The apparatus employed and the precautions observed in carrying out conductivity measurements with iodic acid at concentrations down to $5 \times 10^{-5}N$ are described. The measurements were carried out in glass and quartz cells to determine the influence of impurities on the conductivity of acid solutions at low concentrations. It was found that the conductivity curve exhibits a maximum due to impurities with water having a specific conductivity above $0.1\text{--}0.2 \times 10^{-6}$. The influence of alkali derived from the glass is, if anything, greater than that of the impurities present in the water having a specific conductivity of 0.8×10^{-6} . Conductivity measurements with iodic acid in quartz cells with water having a specific conductivity 0.1×10^{-6} were carried to concentrations as low as 0.5×10^{-6} with a relative precision of a few hundredths per cent. Extrapolating on the assumption that the law of mass action is followed as a limiting law at low concentrations, the value 389.55 is found for Λ_∞ at 25°, which may be accepted as a lower limit to the possible value of this constant. The mass-action constant corresponding with the extrapolation has a value 0.0717. Iodic acid is thus a much stronger electrolyte than potassium chloride. The conductivity of the iodate-ion has been deduced for 25° on the assumption that the Λ_∞ value between 18° and 25° changes in the same proportion as the conductivity of a 0.0015*N*-solution of the acid. The value 39.62 was thus found for the conductivity of the iodate-ion. For the conductivity of the hydrogen-ion at 25°, the value 349.93 is obtained. Assuming that the limiting value of the equivalent conductivity of iodic acid between 18° and 25° varies in the same way as that of a 0.001*N*-solution of the same acid, 349.62 is found for the value of Λ_∞ of iodic acid at 18°. Assuming the value

34.0 for the equivalent conductivity of the iodate-ion at 18°, there is obtained the value 315.62 for the conductivity of the hydrogen-ion at 18°.

J. F. S.

Conductivity of Solutions of Salts in Phenol. CHARLES A. KRAUS and HERMAN F. KURTZ (*J. Amer. Chem. Soc.*, 1922, **44**, 2463—2468).—The electrical conductivity of solutions of tetramethylammonium iodide in phenol has been determined at 50° for concentrations from 0.07*N* to $1 \times 10^{-4}N$. The conductivity curve is accounted for by Kraus and Bray's equation $(c\gamma)^2/c(1-\gamma) = D(c\gamma)^m + K$, in which $D=0.70$, $m=1.28$, and $K=2.25 \times 10^{-4}$. The equivalent conductivity at infinite dilution is 16.67. The conductivity of sodium iodide solutions in phenol has been measured at the same temperature for concentrations between $1 \times 10^{-4}N$ and $1.6 \times 10^{-3}N$. It is shown that sodium iodide is much less ionised than tetramethylammonium iodide in phenol solution. Solutions of tetramethylammonium iodide in phenol are not appreciably hydrolysed.

J. F. S.

Calibration of Cells for Conductivity Measurements. CHARLES A. KRAUS and HENRY C. PARKER (*J. Amer. Chem. Soc.*, 1922, **44**, 2422—2428).—The necessary data for making up standard potassium chloride solutions according to the weight method for calibrating conductivity cells are correctly given by Kohlrausch and Holborn for 1.0*N*-solutions only; their directions for making up standard solutions of concentrations 0.1, 0.02, and 0.01*N* are in error. In the case of the 0.1*N*-solution, the error is 0.10% and for the 0.01*N*-solution 0.54%. The conductivity data as given by Kohlrausch and Holborn are not sufficiently precise for present-day purposes, and it is suggested that the values obtained by Kohlrausch and Maltby (*A.*, 1900, ii, 61) be employed. The necessary data are given in the present paper for making up 1.0, 0.1, and 0.01*N*-solutions of potassium chloride by the weight method. The specific conductivity of 0.1*N* (at 18°) potassium chloride has been determined at 25° in terms of its value at 18°. Assuming for the specific conductivity at 18°, the value 0.011203, as determined by Kohlrausch and Maltby, the specific conductivity at 25° is found to be 0.0128988. This value may serve for the purpose of calibrating cells at 25°, thus avoiding the necessity of making determinations at 18°.

J. F. S.

Free Energy of Dilution of Alcoholic Solutions of Lithium Chloride and the Effect of the Solvent on the Activity of the Ions. J. M. PEARCE and H. B. HART (*J. Amer. Chem. Soc.*, 1922, **44**, 2411—2419).—The *E.M.F.* of concentration cells, both with and without ion transport, containing alcoholic solutions of lithium chloride have been measured at 25°, 30°, and 35°. From the data thus obtained the authors have calculated the transport number of the lithium-ion in ethyl and methyl alcohols at various dilutions and find a value of about the same size as that for aqueous solutions. The transport number increases with dilution and with increase in temperature. The decrease in free energy and in the

heat content accompanying the dilution has been calculated. The *E.M.F.* of cells containing two solvents in which an alcohol solution of various concentrations is opposed to an 0.1*N*-solution of lithium chloride in water have also been measured at the same temperatures. The decrease in free energy and in heat content accompanying the transport of 1 gram-molecule of lithium chloride from its solution in alcohol to an 0.1*N*-solution in water has been calculated. Using the values of free energy decrease obtained for these cells, the free energy of dilution of lithium chloride in ethyl and methyl alcohols from any concentration to a concentration of 1 gram-molecule in 10,000 gram-molecules of solvent has been calculated. The apparent geometric mean activities of the ions of lithium chloride have been calculated for a series of concentrations expressed in gram-molecules per 100 gram-molecules of solvent. J. F. S.

The Electromotive Behaviour of Silver-Cadmium Alloys.

ERLING SCHREINER, IVAR BULL SIMONSEN, and OLE H. KRAG (*Z. anorg. Chem.*, 1922, **125**, 173—184).—The *E.M.F.* of the cell Ag-Cd alloy| $\text{N}\text{CdSO}_4(\text{Ag})$ |Cd was determined. As the amount of cadmium was increased to 30%, the potential gradually decreased, indicating a solid solution of the metals. A sudden change of potential occurs when the amount of cadmium reaches 60 atom. %, indicating the formation of the compound Ag_2Cd_3 ; similarly, another sudden change occurs at 80 atom. % of cadmium, indicating the compound AgCd_4 . Between 93 and 100 atom. % of cadmium, the results are again in harmony with the assumption of a solid solution. Very few measurements were carried out for alloys with 75—80 atom. % of cadmium, and therefore the formation of the compound AgCd_3 was not detected. On keeping the alloy for some time (three to four months), a new compound, AgCd , is indicated. The temperature coefficient of the *E.M.F.* of the alloys was also determined, and was found to vary with the composition of the alloy. The authors point out the difficulty of getting trustworthy results on account of changes at the surface of the electrode, and also show that the heat of formation of the alloy cannot be calculated from the electrical measurements. W. T.

The Hydrogen Electrode under High Pressures. W. R. HAINSWORTH (*Science*, 1921, **53**, 578).—From a study of the variation of the *E.M.F.* of the cell $\text{H}_2|\text{HCl}(0.1\text{N-HCl})|\text{HgCl}|\text{Hg}$ with pressure, it is concluded (a) that the "thermodynamic environment" is not appreciably changed by the molecular hydrogen in solution, or by compression, and (b) that the fugacity (or effective pressure) of hydrogen can be calculated up to 400 atmospheres from the equation of state developed by Keyes. A. A. E.

The Behaviour of Metals on Cathodic Polarisation. G. TAMMANN and W. WIEDERHOLT (*Z. anorg. Chem.*, 1922, **125**, 67—85).—The authors have investigated the recovery after short circuiting of a cell composed of two metals immersed in a solution of a salt of the less noble metal. If the *E.M.F.* is plotted against the logarithm of the time, three straight lines are obtained; these

three curves being represented by expressions of the following form: $E = E_1 + (E_1 \log .t) / \log a_1$. The value of the constant for two of the curves depends on the external conditions; the constant for the third curve depends only on the nature of the electrode and the polarising ion. Partial covering of the surface of the more noble metal by the less noble increases the potential almost to the value for the less noble.

W. T.

Theory of Electrolytic Ions. Simple Method of Determining the Limiting Molecular Conductivity of Strong Electrolytes. RICHARD LORENZ and A. LANDÉ (*Z. anorg. Chem.*, 1922, **125**, 59—66).—The authors assume that strong electrolytes are completely ionised, and that the increase in conductivity on dilution is due to an increase in the mobility of the ions. Thus, instead of the expression $\mu = \alpha(u_0 + v_0)$, the expressions $\mu = (u + v)$ and for the limiting value $\mu_0 = (u_0 + v_0)$ are obtained. The rate of increase of the mobility with dilution, i.e., $u/u_0 = x$ and $v/v_0 = y$, is characteristic for each ion. The authors have, however, found that, for example, $1 - x_K / 1 - y_{Cl} = \text{constant} = a$, similarly $1 - x_{Na} / 1 - y_{Cl} = \text{constant} = b$, and $1 - x_{Na} / 1 - x_K = \text{constant} = c$. These values are given as $a = 1.079$, $b = 1.396$, and $c = 1.292$. These values are easily determined for such salts as potassium chloride and sodium chloride, which are therefore defined as normal electrolytes; hence, to find the limiting conductivity of an acid, the sodium or potassium salt is prepared, and in the case of a base, the chloride. Thus in the case of the anion A^- , the conductivity of the potassium salt is determined in at least two concentrations, e.g., at $C_1 \mu_1 = K^+ + v_1$ and at $C_2 \mu_2 = K^+ + v_2$ (K^+ = ionic mobility of the potassium ion). If $y = v/v_0$; then from the above $1 - x_1 / 1 - y_1 = 1 - x_2 / 1 - y_2 = \text{constant}$; hence v_0 , i.e., the limiting conductivity of the anion, can be determined.

W. T.

Free and Total Energy Changes in the Reduction of Quinones. JAMES B. CONANT and LOUIS F. FIESER (*J. Amer. Chem. Soc.*, 1922, **44**, 2480—2493; cf. A., 1922, ii, 547).—A continuation of previous work. The temperature coefficients of the oxidation-reduction potentials of a number of derivatives of *p*-benzoquinone, naphthoquinone, and anthraquinone have been measured by two methods. The free energy, total energy, and latent heat of reduction in aqueous solution have been calculated from the potentials and the temperature coefficients. The free and total energy are shown to vary greatly with the different types of quinones measured. The total energy change, in aqueous solution, agrees with the total heat change for the solids as measured calorimetrically, since the heats of solution are small. A method is developed for measuring the free energy of reduction of quinones in alcoholic solutions. By means of this method, a number of substances have been investigated which are too insoluble to measure in aqueous solution. The oxidation-reduction potential of a given quinone is slightly greater in alcoholic than in aqueous solution. It is practically identical in 50, 75, and 95% alcoholic

solutions. Preliminary measurements indicate that the temperature coefficient is greater than in aqueous solution. An equation has been developed which relates the free energy change referred to the solids to the potential in a given solution and the solubilities of the quinone and quinol. The differences in the oxidation potential as measured in two different solvents can thus be calculated from solubilities. The discrepancy between the present value for *p*-benzoquinone and the value obtained by Haber and Russ (A., 1904, ii, 309), is shown to be due to an assumption made by these authors which is invalid.

J. F. S.

The Specific Resistance and its Temperature Coefficient and the Thermo-electromotive Force of Ternary Mixed Crystals. KURT FISCHBECK (*Z. anorg. Chem.*, 1922, 125, 1—27).—The specific resistances and their temperature coefficients of ternary alloys of gold, silver, and copper were measured. The thermo-electromotive force of the alloys against copper were also determined, the ends of the wires being kept at 100° and 0°. The paper also contains a *résumé* of the literature on the specific resistance, its temperature coefficient, and the thermo-electromotive force of ternary mixed crystals.

W. T.

Effect of Absorbed Hydrogen on the Thermo-electric Properties of Palladium. R. M. HOLMES (*Science*, 1922, 56, 201—202).—Strip palladium which had been heated at 700° in a vacuum and cooled in hydrogen was found to possess a thermo-electric power of 73% of that of the gas-free metal, whilst saturation of the strip by electrolysis resulted in a reduction to as little as 28%. The effect of absorbed hydrogen is to increase the effective electron density in palladium, since $e = K \log(n_a/n_b)$, where e is the thermo-electric power of a couple, K is a constant, n_a and n_b are the effective electron densities in the two materials forming the circuit.

A. A. E.

Specific Heats. III. Specific Heats of Isomerides and of Aromatic Hydrocarbons in the Solid State. M. PADOA (*Gazzetta*, 1922, 52, ii, 202—207; cf. A., 1921, ii, 15; 1922, ii, 348).—Measurements have been made of the specific heats of dihydroxybenzenes, succinic, maleic, and fumaric acids, methyl oxalate, trihydroxybenzenes, and various hexose sugars. The results show that the specific heats of solid isomeric compounds often differ and are sometimes less for those containing the more energy. The values for maleic and fumaric acids at various temperatures indicate inversion of the stability relations of the acids as the temperature rises. The specific heats of optical antipodes are identical. For polynuclear benzenoid hydrocarbons the mean atomic heat varies, the differences depending on the different arrangement of the linkings in the molecules and in the crystals. The mean atomic heat has the same value in the isomeric compounds, anthracene and phenanthrene, the numbers, directions, and energies of the linkings being the same in the two cases.

T. H. P.

A Modification of van der Waals's Equation. W. P. BOYNTON and ARTHUR BRAMLEY (*Physical Rev.*, 1922, 20, 46—50).—The equation $(p + a/v^2)(v - b) = RT(1 + \psi^2/T^2)$, where ψ is a characteristic temperature, is proposed as a modification of that of van der Waals; it is claimed to represent more closely the behaviour of carbon dioxide and other substances, and to give better values for the ratio $T_c/p_c v_c$. It is shown that not only the energy but also the specific heat and entropy derived from this equation approach zero values at the absolute zero, in agreement with conclusions drawn from Nernst's investigations. Theoretical formulæ for specific heat (c_v), internal energy, and entropy as functions of T and v are derived.

A. A. E.

A New Formula for the Internal Pressure of Liquids. Criterion of Molecular Association in a Liquid. N. VASILESCU KARPEN (*Bull. Acad. Sci. Roumaine*, 1922, 8, 22—26).—The internal pressure K of a liquid can be calculated from the formula $K = T\alpha/\mu - p$, where α is the coefficient of expansion and μ the coefficient of compression of the liquid. The following values of K have been calculated: ethyl ether, at 168°, 1900; ethyl alcohol, at 90°, 3300; water, at 200°, 10,300; ethyl chloride, at 8°, 2700; methyl alcohol, at 20°, 3900. In each case, the ratio K/p_c , where p_c is the critical pressure, is approximately equal to 50. The values of K found by van der Waals for these liquids were about 25% lower except in the case of water, for which the value found was 10,700. For most liquids, it is found that at lower temperatures the value of K/p_c is higher than normal, indicating association. If dq is the heat absorbed by dissociation of the molecules and K is the internal pressure of the non-associated liquid, the above equation can be modified into the form $J.dq/dv = T.\alpha/\mu - K - p$. The heat dq is generally positive, but in the case of water is negative. It is concluded that water is associated at all temperatures below 200° and that dissociation of the complexes is exothermic.

E. H. R.

The Determination of Temperatures of Combustion of Gases. F. POLITZER (*Z. angew. Chem.*, 1922, 35, 683—684).—The theoretical maximum temperature attainable by the combustion of any gas or mixture of gases can be calculated graphically as follows. The increase in energy content in calories of 1 gram-molecule of the different gases considered, at constant pressure above the energy content at 0°, is plotted against the temperature in degrees C. Thus the molecular heat at constant pressure $C_p = dI/dT$. Such curves are identical for gases of the same molecular complexity. Considering, for example, the combustion of carbon monoxide with its exact equivalent of oxygen to carbon dioxide, the heat of reaction is 68,000 cal. The point where the carbon dioxide curve cuts this abscissa gives the theoretical maximum temperature of the reaction (under adiabatic conditions) reading from the x -axis, of 4850°. Cases in which there is an excess of one reagent, or indifferent gases are present, can be dealt with by curves in which the energy contents of the different components

of the burnt mixture are added together. Such curves will, of course, be steeper indicating lower flame temperatures. A correction is necessary for the dissociation of carbon dioxide and water vapour which takes place to a marked extent at temperatures above 2000°. At 4850°, the dissociation of carbon dioxide is no less than 99%. The proportion of dissociated gaseous product must be considered as if it were an addition of an indifferent gas. If x is the degree of dissociation of carbon dioxide and y that of water vapour, and if m molecules of water vapour are present to 1 mol. of carbon dioxide, then the number of molecules of diatomic gases present in the burnt mixture to each molecule of carbon dioxide or water vapour is $1.5(x+my)+a/1+m-(x+my)$, a being the dilution with indifferent gas. Corrected values for flame temperatures can be obtained from equations thus developed by methods of trial and error. Figures so obtained for the combustion of different gases with their equivalents of air are: hydrogen 2130°, carbon monoxide 2095°, acetylene 2200°, illuminating gas 1975°. The latter compares with Berkenbusch's experimental result of 1800° with a bunsen burner. C. I.

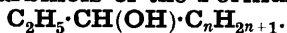
Application of the Nernst Heat Theorem to Dilute Solutions. KARL F. HERZFELD (*Z. Elektrochem.*, 1922, 28, 460—463).—An attempt to calculate the bound energy, G , of molar solutions from the normal potentials, and the solubility of sparingly soluble salts. The value $1/\gamma(G_X - G_{Ag})$ is derived for a number of ions, where G_X is the bound energy of the ion X . The greater the heat of hydration of this ion, the greater is the value of G_X . From these values, the solubilities of a number of sparingly soluble salts are calculated. The statistical meaning of G is discussed.

W. E. G.

Air Thermostat Regulated Electrically. HAJIME ISOBE (*J. Chem. Soc. Japan*, 1922, 43, 650—653).—A description with diagram of an air thermostat regulated electrically, using as the source of heat an electric lamp, with Ikeda's regulator and relay. It is suitable for rather high temperatures (even above 80°), its accuracy being 0.05°.

K. K.

Boundary Lubrication and Chemical Constitution. The Optically Active Carbinols of the Formula



IDA DOUBLEDAY (*T.*, 1922, 121, 2875—2879).

Surface Tension of Solid Substances. G. N. ANTONOFF (*Z. physikal. Chem.*, 1922, 102, 388—392; cf. A., 1918, ii, 437).—In a previous paper (*loc. cit.*), the author has shown that the surface tension of a liquid may be deduced from a knowledge of the internal pressure by means of the equation $P = 2\alpha\{(d-d_2)/M\}^{\frac{1}{3}}$, where P is the internal pressure, α the surface tension, d the density of the liquid, d_2 that of the saturated vapour, and M the molecular weight. In the present paper, on similar hypotheses, the author determines the vapour tension of solid substances. The weight required to cut through a piece of a solid is determined and from

this quantity the internal pressure is ascertained. A piece of rock salt is prepared 15 sq. mm. in cross section and 2—3 cm. long, and cut through by a wire to which a suitable load is attached. It is found that the force required to cut the crystal is a measure of the internal pressure and is the same in all three axial directions, and the surface tension has the value 3500 dyne/cm. This value is of the same order as that found by Ostwald (A., 1900, ii, 712) and Hulett (A., 1901, ii, 493) for barium and calcium salts. The above result is in accordance with some aspects of Bragg's symmetrical structure for this substance, but from other aspects a value about one thousand times as large might be anticipated.

J. F. S.

Adsorption and the Corresponding States. RICHARD LORENZ and A. LANDE (*Z. anorg. Chem.*, 1922, 125, 47—58).—A theoretical paper in which the conclusions of Eucken (A., 1914, ii, 433; 1922, ii, 262) are discussed. The present authors claim that adsorption phenomena can be employed to calculate the dipolar moment of the adsorbed molecules. They explain the apparent independence of the adsorption potential on the temperature by assuming that the bulk of the adsorbed substance is concentrated on the adsorbing surface and that the orientating tendency of the adsorption force is much greater than the kinetic force produced by a higher temperature. In the regions where Henry's Law is obeyed, it is shown that the amount of gas adsorbed divided by its critical temperature is the same for all gases except hydrogen. The constant is equal to about 13; this is a strong argument for the identity of adsorption and molecular cohesion forces.

W. T.

Adsorption on Metal Surfaces. H. VON EULER [with E. G. RUDBERG] (*Z. Elektrochem.*, 1922, 28, 446—449; cf. A., 1922, ii, 822).—Measurements have been made of the adsorption of the silver-ion from solutions of silver nitrate by gold and silver foil. Typical adsorption isotherms are obtained giving a maximum adsorption on a gold surface of 5.5 mg. silver per m²., and on silver 8.5 to 9.0 mg. silver per m². Polished and etched surfaces gave the same amount of adsorption. Assuming the formation of a unimolecular layer, the atomic diameter of the adsorbed silver-ions was found to range from 1.4 to 1.8×10^{-8} cm. These values are smaller than that of Lorenz for the diameter of the silver-ion (2.8×10^{-8} cm.), and that of Vegard from crystal measurements (4.06×10^{-8} cm.). These divergences may be due to irregularities of the metal surface, and, on this view, the amount of adsorbed silver-ion can be used as a measure of the degree of roughness of the metal surface.

W. E. G.

Dissociation of Iodine Vapour and the Chemical Constant of Monatomic Iodine. H. BRAUNE and H. RAMSTETTER (*Z. physikal. Chem.*, 1922, 102, 480—503).—With the object of bringing the experimentally determined chemical constant of iodine into

line with that calculated by means of the formula $C = -1.59 + 1.5 \log A$, the authors have redetermined the dissociation of iodine over the temperature range 600—1000°. The measurements were effected in a quartz flask and the pressure measurements were made by means of a new quartz thread manometer, which is capable of reading to 0.001 mm. The following values of the degree of dissociation are recorded for the given temperatures, which are expressed in absolute degrees: 945.8°, 0.2047; 991.0°, 0.2879; 1096.8°, 0.5228; 1226.8°, 0.7679; and 1343.8°, 0.8808. The results do not effect the experimental chemical constant as was hoped, and it is shown that an agreement between the theoretical value and the experimental value can only be brought about by the discovery of an unexpectedly large error in the heat of vaporisation of iodine and in the value, $\beta\nu=106$, which represents the change of the specific heat of solid iodine with temperature. J. F. S.

Dissociation of Hydrogen Sulphide, Sodium Sulphide, and Sodium Hydrosulphide in Aqueous Solution. KARL JELLINEK and JOHANNES CZERWINSKI (*Z. physikal. Chem.*, 1922, 102, 438—479).—The depression of the freezing point, the electrical conductivity, and the *E.M.F.* of solutions of hydrogen sulphide, sodium sulphide, and sodium hydrosulphide have been measured at 0°, 18°, and 25° over a wide range of concentrations. The concentration of the various ions in the hydrolysis equilibrium of sodium sulphide and sodium hydrosulphide has been evaluated, and the following quantities have been obtained: Sodium sulphide, 0.1*N* contains Na_2S , 0.0003, NaS' , 0.002, Na^+ , 0.08, S'' , 0.006, OH' , 0.035; SH' , 0.033, H^+ 30×10^{-15} , NaOH , 0.004, NaSH , 0.0055; sodium hydrosulphide 0.1*N*, NaSH , 0.085, S'' , 3.2×10^{-6} ; H^+ , 6.3×10^{-11} ; $\text{OH}' = \text{H}_2\text{S}$ 8.0×10^{-5} , all expressed in normality. The degree of hydrolysis of the same substances has been calculated for various concentrations at 0°, and the following values have been obtained: Sodium sulphide 0.1*N*, 0.805, 0.21*N*, 0.754, 0.53*N*, 0.655, 1.06*N*, 0.585, 1.59*N*, 0.535, 2.12*N*, 0.50, and 2.85*N*, 0.46; sodium hydrosulphide 0.1*N* 0.15% at 0° and 0.08% at 10°. It is shown to be probable that the temperature coefficient of the hydrolysis of sodium sulphide and of the heat of hydrolysis are small and the heat of dissociation of HS' is large, about 13,000 cal. The first dissociation constant of hydrogen sulphide at 0° is found to be 1×10^{-7} , and the second dissociation constant 2×10^{-15} . From the great difference between the two dissociation constants and the heat of dissociation, it is shown that hydrogen sulphide must possess a strongly asymmetric structure. The dissociation of sodium hydrosulphide has been investigated at a number of temperatures. The mobility of the ions HS' and S'' and their dependence on temperature have been ascertained. The following values are recorded: SH' ; 0°, 42.5, 18°, 56.5°, and 25°, 64 all at infinite dilution. The solubility product of copper sulphide, silver sulphide, and lead sulphide have been determined, and the values Ag_2S , 3×10^{-50} , CuS , 3×10^{-42} , and PbS , 3×10^{-13} obtained. It is also shown that a more soluble form of lead sulphide exists. J. F. S.

The Diffusion of Acids in Aqueous Solution. L. W. OHOLM (*Finske Kemistamfundets Medd.*, 1921, **30**, 69—78).—From experiments conducted at 18—20° ($\pm 0.25^\circ$), the following values of the diffusion coefficient, k , corrected to 20°, are calculated. For nitric acid, 2*N*, 2.150; 1.5*N*, 2.141; *N*, 2.164; 0.5*N*, 2.227; 0.1*N*, 2.246; 0.05*N*, 2.266. For sulphuric acid, 2*N*, 1.297; 1.5*N*, 1.350; *N*, 1.369; 0.5*N*, 1.399; 0.1*N*, 1.498. For phosphoric acid, 3*N*, 0.644; 2*N*, 0.656; *N*, 0.692; 0.25*N*, 0.772. For boric acid, 1.5*N*, 0.813; *N*, 0.816; 0.5*N*, 0.826; 0.1*N*, 0.876; 0.05*N*, 0.954. For oxalic acid, 2*N*, 0.790; *N*, 0.875; 0.5*N*, 0.987; 0.1*N*, 1.215. For succinic acid, *N*, 0.604; 0.5*N*, 0.654; 0.1*N*, 0.708.

CHEMICAL ABSTRACTS.

The Influence of Salts on the Rate of Diffusion of Acid through Collodion Membranes. JACQUES LOEB (*J. Gen. Physiol.*, 1922, **5**, 255—262).—If a collodion membrane separate two solutions of hydrochloric acid of the same P_H , one of which contains a salt, for example, sodium chloride, there is observed along with the diffusion of the sodium chloride a temporary increase in the P_H of the liquid which originally contained no salt. This is explained as due to hydrogen-ions being carried along with the chlorine-ions in preference to the more slowly moving sodium-ions. This view is verified by the fact that the rate of diffusion of hydrochloric acid is increased by a salt. W. O. K.

Separation of Crystalloids by Dialysis. LOUIS KAHLENBERG (*Science*, 1921, **53**, 143).—Separation of the following pairs of substances was effected by dialysis, using pyridine as the solvent, and vulcanised caoutchouc membranes as the septa: (1) sucrose and sulphur, (2) silver nitrate and naphthalene, (3) silver nitrate and camphor, (4) silver nitrate and sulphur, (5) sucrose and camphor, (6) sucrose and naphthalene, (7) lithium chloride and sulphur, (8) lithium chloride and camphor, (9) lithium chloride and naphthalene, the first-named substance remaining in each case in the solution in the dialyser. It has also even been found possible to separate crystalloids from colloids by causing the latter to pass through the membrane. A. A. E.

Complex Compounds. A. MAGNUS (*Z. anorg. Chem.*, 1922, **124**, 289—321).—A theoretical paper (cf. A., 1922, ii, 559). Since the most stable complex is the one formed from its components with the greatest liberation of energy, the author shows that comparatively small central atoms have generally a low co-ordination number. The solubility of an inorganic compound is shown to depend on the dielectric constant and the dipolar moment of the molecules of the solvent. The author discusses qualitatively the solubility of a series of compounds from this point of view (cf. Fajans, *Naturwiss.*, 1921, **37**, 2). W. T.

The Significance of Crystal Structure. A Lecture delivered before the Chemical Society on October 26th, 1922. SIR WILLIAM H. BRAGG (*T.*, 1922, **121**, 2766—2787).

Crystal Structure and Chemical Constitution. W. GRAHMANN (*Z. Kryst. Min.*, 1922, **57**, 48—93; from *Chem. Zentr.*, 1922, iii, 689—690).—Theoretical. It is maintained that the distinction between atom-lattices and molecule-lattices is purely formal, since the geometrical resolution of molecules in the crystal lattice does not involve a loosening of chemical valencies. Crystal structure is determined by the arrangement of atoms in the lattice and by the atom symmetry deduced from the total symmetry. Atomic symmetry is understood, not as a definite geometrical property of the atom, but as differing according to the arrangement of the valency electrons from compound to compound. The structure of the sodium chloride lattice and the influence of valency on the crystal structure of elements are discussed. The structure of typical metals is held to be mainly governed by the tendency to spherical packing, and not by valency electrons. Valency electron linking is correlated with anisotropy and electrical conductivity.

G. W. R.

Lattice Energy and Work of Ionisation of Inorganic Compounds. H. G. GRIMM (*Z. physikal. Chem.*, 1922, **102**, 504—506; cf. A., 1922, ii, 690).—On the basis of some new wave-length measurements of Lyman (A., 1922, ii, 674) in which it appears that all helium terms are 0.8 volt=18.4 Cal. too large, the author has recalculated many of his results recently published. A list of the essential corrections to be applied to the previous values (*loc. cit.*) is given.

J. F. S.

Valencies which Stabilise the Crystal Lattices of Elementary Substances and of Compounds between Metals. M. PADOA (*Gazzetta*, 1922, **52**, ii, 189—202).—The author discusses the evidence bearing on the nature of the valencies by means of which crystals of metals and metalloids are constructed. The suggestion that these valencies have the significance of primary chemical valencies is open to serious objection. The behaviour of metals during anodic attack indicates that, in their crystalline space lattices, metals either exhibit a diminished valency or, more probably, are non-valent, like the rare gases. The peculiar position of carbon among the elements is maintained also in this respect, as it crystallises by means of its principal valencies (cf. A., 1919, ii, 96). As regards elements such as selenium, antimony, and arsenic, which are both non-metallic and metallic in character, it may be assumed that, in the non-metallic forms, the molecules are formed by means of principal valencies and are polarised, whereas in the metallic modifications these elements are non-valent and are united in the lattices by secondary valencies; the hypothesis that the non-metallic forms contain ions is supported by the fact that molecules like Cl₂, Br₂, and I₂ are auto-dissociated, although in small measure, and hence conduct electrolytically in the liquid state.

Isomorphism between metallic elements of one and the same group is regarded as due to the analogies between the non-valent

forms of these elements dependent on equality of the numbers and directions of the secondary valencies causing the stability of the crystal lattices. The formation of compounds between metals is capable of explanation on similar lines, the secondary valencies utilised in the construction of the crystal lattices being employed here also. The variation in the properties of alloys without corresponding variation in the composition is regarded as dependent on the existence of isomerism in the crystal lattices.

The question of the terminal elements of the lattices and their influence on stoichiometric relations and on surface affinity is also discussed. In colloidal precipitates which are often ultra-microscopic but of crystalline structure, stoichiometric relationships hold exactly, as is shown by the fact that copper, zinc, mercury, etc., may be estimated as sulphides. The external zone of the lattice, completed by the number of atoms of a given kind to yield simple, rational relations, exhibits secondary valencies which may serve to explain the phenomena of absorption and catalysis. Various crystallised substances exist which may be regarded as compounds of variable composition. Thus the compositions of minerals of the pyrrhotite group correspond with formulæ lying between Fe_5S_6 and $\text{Fe}_{16}\text{S}_{17}$. The excess of sulphur has been attributed to the formation of solid solutions of pyrites in ferrous sulphide, but it may depend on a microcrystalline structure with a granulation varying in different specimens and with incomplete polygons.

[With B. ZANELLA.]—The results of experiments on the anodic attack of mineral arsenides and sulpho-arsenides, of copper arsenides of the formulæ As_2Cu_5 and AsCu_3 , and of copper-zinc alloys, are given in confirmation of the above views. T. H. P.

The Absolute Sizes of certain Univalent Ions. WHEELER P. DAVEY (*Physical Rev.*, 1921, **18**, 102—104).—Bragg's results, although consistent among themselves, are not in accord with experimental investigations on the crystals. In agreement with Langmuir's deductions (A., 1919, ii, 328), it is assumed that potassium, rubidium, and cæsium ions are equal in size to those of chlorine, bromine, and iodine, respectively, the values obtained being 1.56 Å., 1.73 Å., and 1.98 Å. The figures for sodium and fluorine ions are 1.25 Å. and 1.13 Å., respectively. A. A. E.

Quantitative Experiments on the Coagulation of Colloids. RAY V. MURPHY and J. H. MATHEWS (*Science*, 1921, **53**, 581).—Determinations of the lowest concentration (limiting concentration) of electrolytes necessary to coagulate hydrous ferric oxide sol show (1) that the limiting concentration decreases with increasing purity in the case of chloride-, chromate-, and ferricyanide-ions, the mechanism of the process being evidently similar for the three ions, (2) that the limiting concentration decreases markedly with decreasing concentration of the sol in the case of all three ions. The relation indicated by Burton and Bishop (A., 1921, ii, 176) for mastic, arsenious sulphide, and copper sols holds for ferric oxide hydrosol only in the case of the tervalent ion. A. A. E.

Silver Soap Gels. G. STAFFORD WHITBY (*Science*, 1921, **53**, 580—581).—Silver salts of the fatty acids are capable of giving reversible gels in organic liquids, particularly in homologues of benzene, and in the halogenated derivatives of benzene and its homologues. The silver salts form gels at a lower point in the series of saturated fatty acids than do the alkali metal salts. The silver salts of the higher members of the saturated fatty acid series show a greater solvation capacity than those of the lower ones. Silver oleate gives a gel in benzene. In the case of solvents of the same general chemical character, the higher the boiling point of the solvent, the greater appeared to be the solvation capacity of a given salt, and the smaller the extent to which the gel from a given salt suffered syneresis. A. A. E.

Esterification by Silica Gel. C. H. MILLIGAN and E. EMMET REID (*Science*, 1921, **53**, 576).—Silica gel is more than twice as active as titanium oxide as a catalyst for esterification. A mixture of acetic acid and ethyl alcohol, when passed slowly at 150°, gives a percentage esterification of 75—80, instead of 67, which was previously regarded as the limit. A. A. E.

The Preparation of Active Nickel for Organic Catalysis. ANDRÉ BROCHET (*Compt. rend.*, 1922, **175**, 816—819).—Three different methods of preparation of catalytic nickel for hydrogenation are described, and it is stated that the three varieties obtained have sensibly the same catalytic properties (see *J.S.C.I.*, 1923, Jan.). H. J. E.

Catalytic Decomposition of Hydrogen Peroxide by Ferric Salts. J. DUCLAUX (*Bull. Soc. chim.*, 1922, [iv], **31**, 961—966).—The work corroborates and complements that of von Bertalan (A., 1920, ii, 614) and Bohnson (A., 1921, ii, 250). For a constant concentration of iron, the reaction constant is found to be proportional to the hydrogen-ion concentration, provided that the latter has a value of 0.003*N* and upwards. The inference is drawn that hydrogen peroxide behaves as a weak acid; its dissociation is thus reversed in presence of strong acid, and so the proportionality found would be expected on theoretical grounds. The lesser catalytic activity of ferric sulphate is explicable on the grounds of its smaller electrolytic dissociation and the results obtained on the addition of other ionogens (Bohnson, *loc. cit.*) are consistent with this explanation. The limiting value of hydrogen-ion concentration below which the reaction constant decreases is due to hydrolysis of the ferric salt in solutions where the value is lower with consequent diminution of its activity (cf. Tian, A., 1921, ii, 439). The general conclusion is drawn that all the experimental evidence tends to show that the reaction takes place between ferric-ions and HO₂-ions derived from the peroxide. H. J. E.

Catalytic Effect in the Reaction between Ketones and Halogens in Aqueous Solution. F. O. RICE (*Science*, 1921, **53**, 581).—Since higher ketones have the same velocity constant as acetone, and since, contrary to Lapworth, the reaction is accel-

erated by neutral salts, Lapworth's views (T., 1904, 85, 30) on the mechanism of the reaction are considered to be probably incorrect. A. A. E.

Forces within a Static Atom. IRVING LANGMUIR (*Physical Rev.*, 1921, 18, 104).—If in addition to the Coulomb forces between charged particles the existence is assumed of another force (quantum force) $Fq = (1/mr^3)(nh/2\pi)^2$ acting between an electron and a nucleus, it is found that when a stationary electron is in stable equilibrium its distance from a nucleus, and its total energy, are in accord with Bohr's theory, and its frequency of oscillation about the position of equilibrium is identical with the frequency of revolution of the electron in the Bohr atom. Thus the Rydberg constant and the Balmer series can be deduced without the assumption of moving electrons. For the construction of models of the helium atom and hydrogen molecule, it is assumed that each electron acts towards the nucleus like a dipole acting on a charge, whilst the quantum action between electrons is like that between dipoles. The forces therefore depend on the orientation of the electrons as well as on their distance. It may be that each change in the quantum number associated with an electron corresponds with a change in the structure of the electron. A. A. E.

Atomic Systems based on Free Electrons, Positive and Negative, and their Stability. R. HARGREAVES (*Phil. Mag.*, 1922, [vi], 44, 1065—1105).—A theoretical paper suggesting an atomic scheme of which the characteristic feature is a structure consisting of two concentric rings, one of positive and the other of negative electrons. W. E. G.

Missing Elements in the Periodic Table. F. H. LORING (*Chem. News*, 1922, 125, 309—311).—Certain features of the periodic table may be accounted for by assuming that atomic number differences are represented by one or two types of mathematical series. It follows that missing elements only exist in minute quantities, if at all. The table to which reference is made is a development of that constructed by Langmuir. H. J. E.

The Nature of the Multiple Carbon Linking. H. J. PRINS (*Ber.*, 1922, 55, [B], 3437—3439).—Mainly a re-statement of the author's views (cf. A., 1914, i, 648; 1917, i, 685; 1918, i, 261) consequent on the recent publications of Fajans (A., 1922, ii, 818).

The energy of a substance containing a double carbon linking is considered to comprise (i) energy of linking which causes the double bond to be "stronger" than the single bond, and (ii) atomic energy which conditions the activity of the carbon atoms and the greater amount of which renders them more active than similar atoms in saturated compounds. H. W.

Determination of the Velocity of Filtration. ANNA STEINER (*Kolloid Z.*, 1922, 31, 204—209).—The velocity of filtration of suspensions and colloidal solutions may be measured by the following method. The top of a burette is widened so that it

will take a cork through which the stem of a filter funnel passes, and a side tube is attached near to the top but just above the graduation. The side tube is connected through a manometer and safety flask with a water pump and a definite volume of the suspension placed in the filter-paper. The volume of liquid collected in the burette is read at intervals and a filtration curve drawn. For quantitative work, the pressure of the filtration must be kept constant. The velocity of filtration is shown to change markedly with changes of hydration of the suspension and also with the presence of electrolytes.

J. F. S.

Inorganic Chemistry.

The [Suggested] Formation of Helium and Neon in Geissler Tubes containing Hydrogen. ARNALDO PIUTTI (*Z. Elektrochem.*, 1922, 28, 452—453).—The author has varied the experimental conditions operating in Geissler tubes with a view to the production of helium and neon from hydrogen. In all, 70 different experiments were carried out, and variations were made in the size of the electrodes, their difference apart, the nature of the current, etc. In no case was found any trace of the D_3 line of helium, or of the D_5 line of neon, or any evidence of the conversion of hydrogen into neon or helium (cf. A., 1920, ii, 311). W. E. G.

Hydrogen as a Halogen in Metallic Hydrides. DWIGHT C. BARDWELL (*J. Amer. Chem. Soc.* 1922, 44, 2499—2504).—A new method is described for the preparation of pure sodium and potassium hydrides. Pure sodium or potassium was placed in a steel test-tube and heated to 400° by immersing in a eutectic bath of sodium and potassium nitrates. Pure hydrogen, made by passing electrolytic hydrogen through a tube containing platinised asbestos at 400° , two tubes containing phosphoric oxide, and finally bubbling through sodium potassium eutectic alloy, was passed into the molten metal by a steel tube, when the hydride formed in fine, white crystals higher up the test tube where it was scraped into glass side tubes and sealed up. Calcium hydride free from metallic calcium was similarly prepared in the form of white crystals. The absence of free metal in the above-named compounds was demonstrated by leaching with liquid ammonia, which remained quite colourless. Solutions of the hydrides in a molten eutectic mixture of potassium and lithium chloride were electrolysed, when it was found, chiefly in the case of calcium hydride, that hydrogen was liberated at the anode in quantities strictly in keeping with Faraday's law, whilst no gas was liberated at the cathode. J. F. S.

Improved Still for Producing Pure Water. CHARLES A. KRAUS and WILBUR B. DEXTER (*J. Amer. Chem. Soc.*, 1922, 44, 2468—2471).—Water having a specific conductivity of 0.12×10^{-6}

ohms⁻¹ may be obtained in large quantities by the use of a still constructed as follows. A copper boiler of 90 litres capacity is connected at the top with a block tin tube, which leads to a tinned copper chamber containing a filter of asbestos fibre or glass wool between two pieces of nickel gauze. The steam passes through the filter and a portion condenses and runs off through a drip tube. The residue of the steam passes into a settling chamber, also of tinned copper, and thence to a block tin worm in which the water is condensed. Water having a specific conductivity 0.05×10^{-6} ohms⁻¹ at 18° may also be prepared in quantity. The principle on which the preparation depends consists in allowing about 20% of the steam to pass away uncondensed. This carries with it practically all the carbon dioxide and other volatile impurities present in the water. The still used in this case is a copper boiler as before, connected directly by a block tin pipe to the settling chamber. From this the steam passes through a block tin pipe, which at its lower end is surrounded by a condenser jacket, to a separating chamber where a large fraction about 70–80% of the water condenses and runs away; the residual 20% of the steam carrying all the volatile impurities escapes from the top of the separating chamber. In both the above cases ordinary distilled water is placed in the boiler and this is made alkaline with sodium hydroxide and a little potassium permanganate is added. When not in use, the water in the boiler is kept near to the boiling point so that air is not dissolved in it to any large extent. J. F. S.

Structure of Molecules of Water. IRVING LANGMUIR (*Science*, 1921, **53**, 580).—In view of Dennison's demonstration (*Physical Rev.*, 1921, **17**, 20) that ice consists of molecules of the formula H_4O_2 , a structure is proposed in which the four hydrogen nuclei bind the two oxygen atoms. The duplet held by each hydrogen nucleus has one of its electrons in each of the oxygen octets, instead of the more usual arrangement in which both electrons of a duplet form part of the same octet. A. A. E.

Properties of Pure Hydrogen Peroxide. III. O. MAASS and W. H. HATCHER (*J. Amer. Chem. Soc.*, 1922, **44**, 2472–2480; cf. A., 1921, ii, 106).—A continuation of previous work in which the properties of pure hydrogen peroxide have been investigated. It is shown that hydrogen peroxide is diamagnetic and has a susceptibility of 8.8×10^{-7} , a value which is larger than that of water. This may be taken as evidence in favour of a structure for hydrogen peroxide in which the oxygen atoms are not connected in the same way as in the oxygen molecule. The solubility of anhydrous hydrogen peroxide has been measured in a number of organic solvents with the following results at 0°. Benzene is quite immiscible, alcohol completely miscible, and ether partly miscible. The solubility curves of sodium chloride, sodium nitrate, sodium sulphate, and sucrose in anhydrous hydrogen peroxide have been determined, and it is shown that the degree of dissociation is of the same order as in water. The tendency toward the formation of molecular compounds is less than in the case of water, there

being evidence of only one compound, namely, $\text{Na}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}_2$. The action of the halogen hydrides on pure hydrogen peroxide and its aqueous solutions has been examined and the conditions have been determined under which the oxidation of the haloid occurs. These are to form the subject of a future paper. The halogens are found to be less soluble in hydrogen peroxide than in water. Ammonia dissolves in pure hydrogen peroxide, with the formation of a crystalline compound which melts at 24.5° and is stable in the absence of water. This compound is slightly soluble in ether, and may be formed by passing ammonia into an anhydrous solution of the peroxide in ether. A compound of the formula $2\text{NH}_3 \cdot \text{H}_2\text{O}_2$ was not obtained. The stability of the compound $\text{NH}_3 \cdot \text{H}_2\text{O}_2$ shows that it is the hydroxyl-ion which causes the decomposition of hydrogen peroxide. Water dissociates or possibly hydrolyses it, and, with the consequent formation of hydroxyl-ions, the decomposition is cumulative. Whether or no this compound is an ammonium salt, $\text{NH}_4\text{O}_2\text{H}$, is not certain. The vapour pressure, dielectric constant, and conductivity of salts in hydrogen peroxide are under investigation, and the results will be published shortly.

J. F. S.

Activation of Chlorine. GERALD L. WENDT, ROBERT S. LANDAUER, and W. W. EWING (*J. Amer. Chem. Soc.*, 1922, **44**, 2377—2382).—A number of methods have been used in an attempt to activate chlorine, but neither the light from a 3000-watt Bovie mercury lamp nor a high potential electric discharge was found capable of converting chlorine into an active form such that it would react with hydrogen in the dark. The experiments described by Draper (*Phil. Mag.*, 1843, [iii], **23**, 491; 1848, **25**, 9, 1845; **26**, 473; **27**, 327) have been repeated and confirmed. It is shown that the fact that the latent period in the hydrogen-chlorine reaction can be destroyed by previous insolation of the chlorine must be attributed to the destruction of substances which inhibit the reaction rather than to any activation of the chlorine itself.

J. F. S.

Preparation of Pure Ozone and Determination of its Molecular Weight. SEBASTIAN KARRER and OLIVER R. WULF (*J. Amer. Chem. Soc.*, 1922, **44**, 2391—2397).—Pure ozone may be prepared by leading the gas issuing from an ozoniser into a bulb condenser cooled with liquid air until the bulb in which the liquid mixture is collected is about one-half to three parts filled with the deep blue liquid mixture of ozone and oxygen. In this process, a considerable concentration may be obtained by periodically lifting the condenser from the liquid air and so effecting a partial condensation only. The mixture is then distilled at -182° , when for a long period oxygen containing only 0.8% of ozone passes off, that is, the distillation proceeds as though liquid oxygen and liquid ozone were immiscible. At the temperature stated, liquid ozone has a vapour pressure of 6 mm. After distillation has been carried on for some while and most of the liquid has passed off and the residue is very small in volume, the temperature rises slowly to -119° , and then a blue gas, practically pure ozone, commences

to distil over. At this stage of the operations extreme care is necessary if explosions are to be avoided. After the blue gas has distilled over for some time, it becomes much darker in colour and this gas, which is pure ozone, was collected in a globe of known volume. The pressure of the gas in the bulb, the weight, and the pressure after decomposing the ozone by heating to ordinary temperature were determined and the molecular weight was calculated. As a mean of many experiments, the value 47.3 was obtained. It is shown that there is no evidence to confirm the existence of tetratomic and hexatomic allotropes of oxygen.

J. F. S.

The Polythionic Acids. F. FOERSTER and A. HORNIG (*Z. anorg. Chem.*, 1922, 125, 86—146).—The reaction between sulphurous acid and hydrogen sulphide can be represented by the equilibrium $\text{H}_2\text{S} + \text{H}_2\text{SO}_3 \rightleftharpoons \text{H}_2\text{S}_2\text{O}_2 + \text{H}_2\text{O}$. Further reaction with hydrogen sulphide produces sulphur, whereas excess of sulphurous acid leads to the formation of pentathionic acid. Of the polythionic acids and their alkali salts, the tetrathionates are the most stable, and the trithionates the most unstable; the pentathionates occupy a mean position. None of these compounds is completely stable in aqueous solution, the following decompositions taking place: $\text{S}_5\text{O}_6'' \rightleftharpoons \text{S}_4\text{O}_6'' + \text{S}$, $\text{S}_4\text{O}_6'' \rightleftharpoons \text{S}_3\text{O}_6'' + \text{S}$, $\text{S}_3\text{O}_6'' + \text{H}_2\text{O} = \text{SO}_4'' + \text{S}_2\text{O}_3'' + 2\text{H}^+$, $\text{S}_2\text{O}_3'' + \text{H}^+ \rightleftharpoons \text{HSO}_3' + \text{S}$. The insolubility of sulphur removes it from the equilibrium, and at boiling temperature the sulphur dioxide is removed and SO_4'' is alone left in solution; side reactions were also found to take place. The more sulphur dioxide and sulphur there remains in the solution, the greater is the tendency of thiosulphuric acid to polymerise, *e.g.*, $\text{S}_3\text{O}_6'' + \text{S}_2\text{O}_3''\text{H}^+ \rightleftharpoons \text{S}_4\text{O}_6'' + \text{HSO}_3'$, $\text{S}_4\text{O}_6'' + \text{S}_2\text{O}_3'' + \text{H}^+ \rightleftharpoons \text{S}_5\text{O}_6'' + \text{HSO}_3'$. A high concentration of hydrogen-ion retards the decomposition of tetra- and penta-thionic acids, but not of trithionic acid.

W. T.

Specific Volume of Liquid Ammonia. C. S. CRAGOE and D. R. HARPER (*U.S. Bur. Standards, Sci. Papers*, 1921, 420, 287—315).—The apparatus used in the determination of the specific volume of saturated liquid ammonia is described and the results obtained for every degree from -70° to 100° are tabulated. These may be expressed by the equation: $\mu = [4.2830 + 0.813055\sqrt{133 - \theta} - 0.0082861(133 - \theta)]/[1 + 0.424805\sqrt{133 - \theta} + 0.015938(133 - \theta)]$ where μ is expressed in c.c. per g. and θ in $^\circ\text{C}$.

A. R. P.

Oxidation of Nitrogen Tetroxide by Ozone. OLIVER R. WULF, FARRINGTON DANIELS, and SEBASTIAN KARRER (*J. Amer. Chem. Soc.*, 1922, 44, 2398—2401).—The oxidation of nitrogen tetroxide to nitrogen pentoxide by ozone has been investigated at 25° . The oxidation occurs almost instantaneously and in consequence a piece of apparatus has been constructed whereby the oxidation can be followed titrimetrically, using the disappearance of brown fumes as an indication of the end-point, thus carrying out a true titration in the gaseous phase. The results show that

one molecule of ozone is required to oxidise one molecule of nitrogen tetroxide at 25° , thus only one atom of the ozone molecule is available in the oxidation at this temperature. This result is in striking contrast to the oxidation of sulphur dioxide to the trioxide by ozone at temperatures below 40° in which one molecule of ozone oxidises three molecules of sulphur dioxide, all three atoms of the ozone molecule being available for oxidation. J. F. S.

Decomposition of Nitrogen Pentoxide in the Presence of Ozone. FARRINGTON DANIELS, OLIVER R. WULF, and SEBASTIAN KARRER (*J. Amer. Chem. Soc.*, 1922, **44**, 2402—2404).—According to the experiments of Daniels and Johnston (A., 1921, ii, 249), nitrogen pentoxide decomposes rapidly at the ordinary temperature. It is shown that in the experiments on the oxidation of nitrogen tetroxide by ozone (preceding abstract) in which a trace of ozone in excess was present, a very long period of time elapsed before any visible decomposition of the pentoxide was observed. Calculations from Daniels and Johnston's results show that the brown colour ought to have returned to the gas in 15.3 minutes, but actually it was found that this did not happen until the gas had been kept at 80° for 195 minutes. It follows, therefore, that a trace of ozone retards the decomposition of nitrogen pentoxide. If traces of the decomposition products are added to the system the decomposition takes place with its normal velocity. J. F. S.

Cryoscopy of Boron Trifluoride Solutions. V. Systems with Methyl Ether and with Methyl Chloride. A. F. O. GERMANN and MARION CLEAVELAND (*Science*, 1921, **53**, 582).—The melting-point curve of boron trifluoride and methyl ether shows a eutectic at 3 mol. % of boron trifluoride, and a maximum at 50 mol. %, corresponding with the formation of the compound $\text{BF}_3 \cdot (\text{CH}_3)_2\text{O}$, previously prepared by Gasselin. The melting-point curve of boron trifluoride and methyl chloride shows two maxima, at 15 mol. % and 33 mol. %, respectively, of boron trifluoride, and an angular point in the curve at 50%. The form of the maximum at 15% is identical with that at 50% for methyl ether, and the mixture yields a compound having the same f. p. and b. p. as the compound $\text{BF}_3 \cdot (\text{CH}_3)_2\text{O}$. It appears that methyl ether may be present as an impurity in methyl chloride as a constant boiling mixture. The use of boron trifluoride for its detection is suggested. A. A. E.

Catalysis in the Interaction of Carbon with Steam and Carbon Dioxide. H. A. NEVILLE and H. S. TAYLOR (*Science*, 1921, **53**, 577).—Potassium carbonate and other salts accelerate the interaction of carbon and steam, and carbon and carbon dioxide. Reduced nickel also markedly promotes interaction of carbon and carbon dioxide. It has been shown that adsorption of carbon dioxide by carbon at 445° is increased by addition to the carbon of such accelerating agents, although the latter themselves show no adsorptive property for the gas. A. A. E.

Vapour Density of Technical Phosgene. A. F. O. GERMANN and VERNON JERSEY (*Science*, 1921, **53**, 581).—Pure carbonyl chloride has a vapour tension of about 552 mm. at 0°; technical phosgene, which contains impurities probably consisting of carbon dioxide and hydrogen chloride, gives after repeated fractionation a value for the vapour density of 4.5263 g. per litre (uncorr.).

A. A. E.

Cryoscopy of Carbonyl Chloride Solutions. I. System with Chlorine. A. F. O. GERMANN and VERNON JERSEY (*Science*, 1921, **53**, 582).—The melting-point curve of solutions of carbonyl chloride and chlorine exhibits a eutectic point at 25 mol. % of chlorine, and angular points at 6%, 11%, 50%, 63%, 75%, and 91%, indicating the existence of the following compounds which dissociate at the melting point: $16\text{COCl}_2, \text{Cl}_2$; $8\text{COCl}_2, \text{Cl}_2$; $\text{COCl}_2, \text{Cl}_2$; $3\text{COCl}_2, 5\text{Cl}_2$; $\text{COCl}_2, 3\text{Cl}_2$; and $\text{COCl}_2, 10\text{Cl}_2$. The mechanism of the catalytic preparation of carbonyl chloride from carbon monoxide and chlorine is briefly discussed.

A. A. E.

The Identity of Amorphous and Crystalline Silicon. WILHELM MANCHOT (*Z. anorg. Chem.*, 1922, **124**, 333—334).—The identity of amorphous and crystalline silicon has been proved by an X-ray examination carried out by Debye and Frauenfelder. The preparation and properties of the two forms have been given in previous papers (cf. A., 1922, ii, 144, 286, 764). They can also be distinguished by rubbing them with lead peroxide; nothing happens in the case of the crystalline variety, but the pseudo-amorphous forms ignite, the brown form exploding. The greater reactivity of the latter is due to its very fine state of division.

W. T.

Magnetic Analysis of Silicates and Silicic Acids. PAUL PASCAL (*Compt. rend.*, 1922, **175**, 814—816).—Three types of hydrated silicon dioxide were investigated magnetically, all of which behaved as a mixture of anhydrous oxide and water. The conclusion is drawn that definite silicic acids do not exist (cf. van Bemmelen, A., 1908, ii, 838; 1909, ii, 234; and Le Chatelier, A., 1908, ii, 1033).

H. J. E.

The Reduction of Potassium Chlorate by Ferrous Sulphate. M. HERSCHKOWITSCH (*Z. anorg. Chem.*, 1922, **125**, 147—154).—A dry mixture of potassium chlorate and ferrous sulphate remains unchanged up to 100°; a trace of water causes the evolution of chlorine dioxide and chlorine. In very dilute solutions, the chlorate is completely reduced to the chloride.

W. T.

Crystal Structures of Potassium Chloroplatinite and of Potassium and Ammonium Chloropalladite. ROSCOE G. DICKINSON (*J. Amer. Chem. Soc.*, 1922, **44**, 2404—2411).—Tetragonal crystals of potassium chloroplatinite and potassium and ammonium chloropalladite have been examined by X-ray methods, using photographs of spectra and symmetrical and unsymmetrical Laue photographs. The simplest structure which will account for

the X-ray data has been described. In this structure, each platinum or palladium atom is surrounded by four equidistant and equivalent chlorine atoms lying in one plane. The distance between the platinum atom and a chlorine atom in potassium chloroplatinite is 2.33 ± 0.05 Å.U. It is further shown that the structure of the chloroplatinites is very closely connected with that of the cubic crystals of the chloroplatinates. The tetragonal structure is only slightly larger than the cubic one in its horizontal dimensions, but considerably shorter vertically. A table is given in which the dimensions of the salts under examination are compared with those of the chloroplatinates and chloropalladates. J. F. S.

The Hydrates of Sodium Sulphide. A. SANFOURCHE and (MLLE) A. M. LIEBAUT (*Bull. Soc. chim.*, 1922, [v], **31**, 966—972; cf. Sabatier, A., 1879, 865 and 866; Gottig, A., 1886, 980; Parravano and Fornaini, A., 1907, ii, 951).—A thermal study of the system sodium sulphide-water reveals or confirms the existence of three hydrates, $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, $\text{Na}_2\text{S} \cdot 5.5\text{H}_2\text{O}$, $\text{Na}_2\text{S} \cdot \text{H}_2\text{O}$. The evidence for the existence of the last is less trustworthy than for the former two hydrates, the reason being that experimental difficulties hinder the investigation of the system under those conditions which render the hydrate stable. The monohydrate and nonahydrate both decompose at temperatures below their respective melting points. The hydrates $\text{Na}_2\text{S} \cdot \text{H}_2\text{O}$ and $\text{Na}_2\text{S} \cdot 5.5\text{H}_2\text{O}$ appear to undergo transformation into each other in the solid state. Other hydrates which have been described are not detected in this method of investigation. H. J. E.

Sodium Silicate Crystals: ALFRED HEINRICH ERDEN-BRECHER (*Z. anorg. Chem.*, 1922, **124**, 339—354).—This investigation of the hydrates of sodium silicate was carried out by plotting the cooling curve of the fused salt. This on melting gives a viscous paste; it was therefore mixed with a little paraffin oil, the latter having no effect on the cooling curves of sodium carbonate and sodium sulphate. The following hydrates were obtained. $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$, rhombic, m. p. 47.0° ; $\text{Na}_2\text{SiO}_3 \cdot 6\text{H}_2\text{O}$, monoclinic, m. p. 62.5° ; and $\text{Na}_2\text{SiO}_3 \cdot 4\text{H}_2\text{O}$, hexagonal, m. p. about 85.0° . The hydrate $\text{Na}_2\text{SiO}_3 \cdot 14\text{H}_2\text{O}$ probably exists also.

The concentration of the alkali determines which hydrate crystallises from an alkaline solution. W. T.

Crystal Structure [of Cæsium Chloride and Thallous Chloride]. WHEELER P. DAVEY and FRANCES G. WICK (*Physical Rev.*, 1921, **17**, 403—404).—Cæsium chloride is considered to be a simple cube of cæsium-ions with a chlorine-ion at the centre of each cube of side 4.12 Å. Thallous chloride is similarly constituted, the side of the cube being 3.85 Å. These results are inconsistent with those of Bragg. A. A. E.

The Crystal Structure of Ammonium Chloride. RALPH W. G. WYCKOFF (*Amer. J. Sci.*, 1922, [v], **4**, 469—475; cf. A., 1922, ii, 290).—The structure of the low temperature form of ammonium chloride, as determined from X-ray powder measure-

ments, is at variance with that deduced from a study of the face development and etch figure formation of this substance. Laue photographic data have been obtained by the author, which are in agreement with the powder data in assigning one chemical molecule within the unit cube. The symmetry of the crystal as a whole must be hemimorphic, hemihedral (tetrahedral), or possibly holohedral, but in no case can the arrangement of the atoms of the crystal agree with the enantiomorphic hemihedry, which studies of face development and etch figures assign to it. The latter "chemical" means of deducing crystal structure supplies information with regard to surface of the crystal, and the internal structure of the crystal is only one of a number of factors which bear on the nature of these surface phenomena. W. E. G.

Spontaneous Decomposition of Ammonium Chlorate.

FRED FAIRBROTHER (*J. Amer. Chem. Soc.*, 1922, **44**, 2419—2422).—About 30 g. of ammonium chlorate were kept in contact with 100 c.c. of its saturated solution at ordinary temperature; for about three weeks the salt remained white, whilst a small quantity of a colourless gas was evolved. Later, the gas became tinged with greenish-yellow and a slow but continuous evolution of gas occurred. By the beginning of the fifth week the solution had become quite yellow and the amount of solid had decreased and the rate of decomposition appeared to be increasing. The liquid gradually became darker and considerable quantities of "euchlorine" were evolved. The temperature rose to 30—40° and within a few hours the system exploded. Solutions of ammonium chlorate in the absence of the solid may be kept indefinitely without any decomposition. The solid residue obtained from the decomposition is ammonium nitrate. It is shown that the rate of decomposition of ammonium chlorate is autocatalytically accelerated when the products of decomposition are not quickly removed. The reaction is regarded as taking place as follows. In the initial stage a very slow autoxidation of the molecule is taking place with the production of nitric acid, nitrogen, chlorine, and water. The nitric acid reacts with more chlorate, producing chloric acid and chlorine dioxide. These then oxidise more of the ammonium radicle with the formation of more nitric acid and the liberation of chlorine. This takes place more rapidly than the initial stage and consequently the decomposition tends to increase in speed unless the acid gases are removed quickly. The more stable perchlorate does not appear to be formed. J. F. S.

Crystal Analysis of Metallic Oxides. WHEELER P. DAVEY and E. O. HOFFMAN (*Physical Rev.*, 1920, **15**, 333).—Calcium, magnesium, cadmium, and nickelous oxides form a face-centred cube of the metal, interpenetrating a similar face-centred cube of oxygen, so that the combined lattices form a simple cube of which the side is half that of the face-centred cube; the lengths of the side of this simple cube are 2.37 Å., 2.09 Å., 2.36 Å., and 2.10 Å., respectively. Alumina forms a rhombohedron, of which the

hexagonal axes each have a length of 4.86 Å., and the vertical axis 6.62 Å.

A. A. E.

The Ammines of the Strontium Haloids. GUSTAV F. HÜTTIG (*Z. anorg. Chem.*, 1922, **124**, 322—332).—Oetamine strontium chloride was degraded isothermally, constancy of pressure indicating the existence of compounds. The formation of the following ammines were thus proved: $[\text{Sr}(\text{NH}_3)_8]\text{Cl}_2$ (3.5°), $[\text{Sr}(\text{NH}_3)_8]\text{Cl}_2$ (45.5°), $[\text{Sr}(\text{NH}_3)_8]\text{Br}_2$ (30°), $[\text{Sr}(\text{NH}_3)_2]\text{Br}_2$ (68°), $[\text{Sr}(\text{NH}_3)]\text{Br}_2$ (146°), $[\text{Sr}(\text{NH}_3)_8]\text{I}_2$ (31°), $[\text{Sr}(\text{NH}_3)_6]\text{I}_2$ (74.5°), $[\text{Sr}(\text{NH}_3)_2]\text{I}_2$ (134°), $[\text{Sr}(\text{NH}_3)]\text{I}_2$ (204°). In brackets are given for each complex the temperature at which its dissociation pressure is equal to 100 mm.

W. T.

Separation of the Isotopes of Zinc. ALFRED C. EGERTON (*Nature*, 1922, **110**, 773).—It has been found possible to separate zinc by fractional distillation into a distillate and a residue, the densities of which bear to that of the initial metal the ratios 0.99971:1 and 1.00026:1, respectively, the differences being greater than the probable experimental error. The change in the atomic weight implied by this separation is about 0.035, which is considerably less than might be expected if the metal was composed of equal quantities of an isotope of atomic weight 64, on the one hand, and of isotopes of atomic weight 66, 68, and 70, on the other.

A. A. E.

Preparation of Zinc Nitride. W. J. BENTLY and PAUL L. STERN (*Science*, 1921, **53**, 143).—Ammonia, free from oxygen and moisture, is passed over zinc dust (previously washed with a solution of ammonia and ammonium chloride, alcohol, and ether, and dried in a vacuum) for thirty minutes at 650° and the product cooled to at least 200° before exposure to the air. The highest yield obtained was 36.8% of nitride.

A. A. E.

The Extraction of Glucina (Beryllia) from Beryl. HUBERT THOMAS STANLEY BRITTON (*J. Soc. Chem. Ind.*, 1922, **41**, 349—352t).—Various methods for the separation of glucina and alumina have been reinvestigated with the object of developing, if possible, a method which could be worked for the isolation of glucina from beryl. Although this object has not been completely attained, it was found that more than 90% of the alumina can be easily separated from the glucina by crystallising out the former in the form of potassium alum under suitable conditions. The ore is ground to a flour and fused with potassium hydroxide. The ground product is treated with sulphuric acid and the precipitated silica separated. The filtrate containing the sulphates of glucinum, aluminium, and potassium with excess of sulphuric acid is adjusted to about 5*N*-acidity by addition of potassium hydroxide, as it was found that whereas the solubility of glucinum and aluminium sulphates and of alum are somewhat reduced in 5*N*-sulphuric acid, that of potassium sulphate is considerably increased, and an increase in the liquid phase of the proportion of potassium to the other sulphates causes an increased separation of alum. The

acid liquid is therefore saturated with potassium sulphate at the boiling temperature, and set aside to crystallise at 0° . The solid phase obtained under these conditions always consisted entirely of alum, and represented 92.9% of the alumina present in one of the experiments quoted where the molecular proportions of glucina to alumina were 3 : 1 as in beryl, and where 4 mols. of potassium sulphate were present in the solution for crystallisation. At 25° , 87.6% of the alumina was separated. The glucina was separated from the mother-liquor by adding sodium hydroxide sufficient to redissolve the precipitate, diluting and boiling, when glucinum hydroxide was precipitated. The paper contains full data and curves representing the solubility of potassium sulphate in sulphuric acid of various strengths.

G. F. M.

Constitution of Aqueous Solutions of Thallium Salts.

C. DRUCKER (*Z. Elektrochem.*, 1922, **28**, 463—467).—From measurements of the depression of freezing point and concentration potentials of solutions of thallous nitrate, it is shown that this salt gives rise on ionisation to appreciable quantities of Tl_2^{++} -ions. Below $C=0.06$ molar, the solutions follow the simple Ostwald dilution law, and the association of Tl^+ to Tl_2^{++} may be neglected. At higher concentrations, all the ionic equilibria obey the law of mass action, and for $2Tl^+ \rightleftharpoons Tl_2^{++}$, $K=2.1$. For $TlNO_3 \rightleftharpoons Tl^+ + NO_3^-$, $K=0.27$ for all of the concentrations investigated. The mobility of the complex thallium-ion is 110.

These data for the bivalent thallium-ion are in accord with the previous work on thallium sulphate solutions (cf. A., 1921, ii, 161). The interpretation of the conductivities of thallous salts is satisfactorily explained on the classical dissociation theory. The Ghosh theory of complete ionisation of electrolytes leads to erroneous results when applied to solutions of thallous nitrate.

W. E. G.

The Structure and Chemical Activity of Copper Films, and the Colour Changes accompanying their Oxidation.

C. N. HINSELWOOD (*Proc. Roy. Soc.*, 1922, [A], **102**, 318—328).—The diffraction colours produced on a copper surface by oxidation become more intense as the surface increases in chemical activity. After repeated oxidation and reduction, the permanent colour sequence is purple, blue, green, light green (almost yellow), purple, blue, black, and this order of colours may be traversed time after time. The film of copper which is formed in this manner is composed, according to Beilby, of small discrete units giving an "open formation" or granular structure. These granules are shown by the author to possess an order of magnitude less than 1μ . The extent to which these granules are converted into oxide determines the colour of the diffracted light, the colour phenomenon being independent of the thickness of the film. Thus when the granules are one-third copper oxide and two-thirds copper, the colour of the scattered light is bright blue. No diffraction effects occur during the reduction of the oxide. The reduction phenomena are in agreement with the view that fresh nuclei of copper grow at the

expense of the oxide nuclei. After repeated treatment, the copper film becomes incapable of further sub-division, and a limiting velocity of oxidation is attained.

W. E. G.

Phenomena of Diffusion in Metals in the Solid State and Cementation of Non-ferrous Metals. III. Influence of the Vapour Pressure of the Migratory Elements in the Formation of the Superficial Cementated Layer. G. SIROVICH and A. CARTOCETI (*Gazzetta*, 1922, 52, ii, 233—245).—The cementation of copper by means of ferro-manganese or chromo-manganese (cf. A., 1922, ii, 68, 571) consists first of the formation at the surface of the bar of a layer of alloy containing the migratory element in definite concentration and secondly of the flow of this element into the interior of the bar. The authors explain the first stage of the process on the assumption that, at the experimental temperature employed, the cementated material exhibits a certain vapour or dissociation pressure in the various elements constituting it, so that the medium in which the material to be cementated may, after some time, be regarded as saturated as regards the vapours of these elements. This idea is developed, and the results of further experiments are brought into conformity with it.

T. H. P.

Phenomena of Diffusion in Metals in the Solid State and Cementation of Non-ferrous Metals. IV. Cementation of Copper by means of Ferro-aluminium. G. SIROVICH and A. CARTOCETI (*Gazzetta*, 1922, 52, ii, 245—249; cf. preceding abstract).—Cementation of copper by means of aluminium, like that by means of manganese, may result in the penetration of the metal to considerable depths and by relatively high proportions of the migrating metal.

T. H. P.

Relation between Colour and Texture of Alloys. MASUMI CHIKASHIGE (*Z. anorg. Chem.*, 1922, 124, 335—338).—Copper reflects red to orange-yellow light, the addition of tin gives a white alloy, and the whiteness reaches a maximum when the composition corresponds with Cu_3Sn . The colour then gradually assumes the colour of tin, which only reflects light from red to the beginning of blue.

W. T.

Catalysis in the Reduction of Oxides and the Catalytic Combination of Hydrogen and Oxygen. R. N. PEASE and H. S. TAYLOR (*Science*, 1921, 53, 577).—Oxygen and water vapour, when present in hydrogen used for the reduction of copper oxide, markedly inhibit the reaction, whilst the addition of reduced copper to the oxide appears to accelerate the reaction. The induction period in the reaction is attributed (a) to initial drying of the oxide, (b) to slow initial formation of copper, which then acts as a catalyst. The mechanism of the catalytic combustion of hydrogen and oxygen in presence of copper is briefly discussed.

A. A. E.

Separation of Isotopes by Distillation and Analogous Processes. ROBERT S. MULLIKEN (*J. Amer. Chem. Soc.*, 1922, **44**, 2387—2390).—A continuation of previous work on the separation of the isotopes of mercury. It is shown that the separation coefficient of mercury is 0.0063, and not 0.0057 as previously stated (A., 1922, ii, 295). The progress of the separation has been followed by means of density determinations. The effect of various factors, such as pressure, rate of distillation, and form of the apparatus, on the efficiency of separation of isotopes by the method of non-equilibrium distillation has been studied, and it is shown that an efficiency of 50% is readily attained. A film of dirt on the mercury increases the efficiency at the higher rates of distillation. It is pointed out that irreversible distillation may be applied as a new factor in the separation of non-isotopic liquid mixtures. The failure of attempts to secure a separation of the isotopes of mercury by electrolytic solution or by reaction with sulphur is ascribed to the great difficulty of obtaining non-equilibrium conditions at the boundary between two condensed phases. J. F. S.

Potassium Ammonioaluminate and Ammoniomanganite. FRANCIS W. BERGSTROM (*Science*, 1921, **53**, 578).—*Potassium ammonioaluminate*, $\text{Al}(\text{NH}_2)_2\cdot\text{NHK}$, has been prepared by the action of potassamide in liquid ammonia solution on amalgamated aluminium, and *potassium ammoniomanganite*, $\text{Mn}(\text{NHK})_2\cdot 2\text{NH}_3$, by the action of an excess of potassamide on manganese thiocyanate. A. A. E.

The Growth of the Grains in Unworked Iron and the Appearance of a Striated Structure after Heating it at more than 1100°. KARL DAEVES (*Z. anorg. Chem.*, 1922, **125**, 167—172).—Iron which contains but a small amount of carbon assumes a new structure on being heated at 1125°; this is due to the separation of ferrite and pearlite in certain directions which are orientated crystallographically. Rapid cooling results in the incomplete separation of pearlite. This structure is closely associated with the development of coarse grains, and the iron is deteriorated; it can be overcome by heating at 900°. W. T.

Complex Phosphato- and Arsenato-metal Acids. L. DEDE (*Z. anorg. Chem.*, 1922, **125**, 28—46).—The addition of phosphoric acid solution to a ferric chloride solution results in a considerable increase in the specific conductivity of the solution; the latter also increases rapidly with the further addition of the acid solution and reaches a constant value when equivalent amounts of salt and acid are mixed. This is assumed to be due to the formation of the complex trichlorophosphatoferric acid, $[\text{Cl}_3\text{Fe}(\text{PO}_4)]\text{H}_3$. This complex acid could not be isolated; the same applies to its salts. Further addition of phosphoric acid solution, whilst having no appreciable effect on the conductivity, resulted in the replacement of the three chlorine atoms of the complex by another phosphato-group, i.e., *diphosphatoferric acid*; this was isolated and analysed; it corresponds with $[\text{Fe}(\text{PO}_4)_2]\text{H}_3 + 2\frac{1}{2}\text{H}_2\text{O}$. The complex is very stable, and the author points out its application to

analysis. Arsenic acid gave analogous compounds. Aluminium and glucinum salts also show a considerable increase in specific conductivity on being mixed with a solution of phosphoric acid. These are being further investigated. W. T.

Behaviour of the Stannic Acids towards Solutions of Alkaline Hydroxides. GEORGE ERNEST COLLINS and JOHN KERFOOT WOOD (T., 1922, **121**, 2760—2765).

Crystal Structure of Titanium, Zirconium, Cerium, Thorium, and Osmium. ALBERT W. HULL (*Physical Rev.*, 1921, **18**, 88—89).—Titanium crystallises in the hexagonal system, holohedral class, with axial ratio 1.59 ± 0.01 . The side of the unit triangular prism is 2.97 \AA . and its height 4.72 \AA . The lattice is made up of two sets of these prisms, the atoms of one set being in the centre of the prisms of the other set. Zirconium has a similar structure, with axial ratio also 1.59. The side of the unit triangle is 3.23 \AA . and its height 5.14 \AA . Cerium has a similar structure with axial ratio 1.62. The side of the elementary triangle is 3.65 \AA . and height 5.96 \AA . A face-centred cubic form, with side of cube 5.12 \AA ., is also present, but may possibly be due to the presence of impurity. Thorium has a face-centred cubic lattice with side of cube 5.04 \AA . Osmium crystallises in a face-centred cubic lattice with axial ratio 1.59. The side of the unit triangle is 2.714 \AA . and its height 4.32 \AA . A. A. E.

The Isotopes of Antimony. F. W. ASTON (*Nature*, 1922, **110**, 732).—The mass-spectrum of antimony, obtained by the use of antimony trimethyl, gives two lines at 121 and 123, respectively, the former being the more intense by 10—20%. The masses of these isotopes of antimony are most probably less than whole numbers by one to two parts per thousand. The results are in excellent agreement with the atomic weight (121.77) obtained by Willard and McAlpine (A., 1921, ii, 405) but not with the accepted figure (120.2). A. A. E.

The Alleged Variable Composition of Triple Chlorides containing Silver and Gold. HORACE L. WELLS (*Amer. J. Sci.*, 1922, [v], **4**, 476—482; cf. A., 1922, ii, 449, 514).—From Bayer's analyses of caesium silver gold chloride (A., 1920, ii, 688) the conclusion is drawn that the triple salt, $\text{Cs}_2\text{AgAuCl}_6$, is a definite, invariable compound, and that Bayer analysed mixtures of this salt with $\text{Cs}_5\text{Au}_3\text{Cl}_{14}$, and CsAuCl_4 . The rubidium salt, $\text{Rb}_6\text{Ag}_2\text{Au}_3\text{Cl}_{17}$, is also invariable. It is probable also that Suschnig (A., 1922, ii, 514) analysed mixtures in his investigation of the triple bromides of rubidium, silver, and gold. W. E. G.

Hydrolysis of Platinum Salts. II. Potassium Platinibromide. EBEN HENRY ARCHIBALD and WILLIAM A. GALE (T., 1922, **121**, 2849—2857).

Analytical Chemistry.

Bimetallic Electrode Systems in Electrometric Analysis.

I. Systems comprising Two Dissimilar Metals. H. H. WILLARD and FLORENCE FENWICK (*J. Amer. Chem. Soc.*, 1922, **44**, 2504—2515).—The constant half-cell of the usual electrometric titration apparatus may be replaced by a metal or certain alloys of metals of the platinum group, other than pure platinum or pure palladium, and by tungsten. The end-point obtained with such a bimetallic system differs in character from that given by an unimetallic electrode, but is situated in exactly the same position. Such a bimetallic electrode system has the advantage of being essentially simpler than the usual system and the end-point is much more distinct than with the ordinary electrode. J. F. S.

Bimetallic Electrode Systems in Electrometric Analysis.

II. Theory of Bimetallic Systems: Systems comprising Two Similar Metals. H. H. WILLARD and FLORENCE FENWICK (*J. Amer. Chem. Soc.*, 1922, **44**, 2516—2529).—In aqueous solutions of multivalent elements in which the concentration of either state of oxidation approaches the limiting value, the potential, unattackable electrode|solution, is determined by the magnitude of the solution pressure of gas absorbed by the electrode, and the end-point obtained in oxidimetric titrations with systems comprising two unattackable electrodes is given only by virtue of a difference in the solvent power of the two metals for gas. When the concentration of oxygen-ion, or hydrogen-ion, becomes vanishingly small, the osmotic pressure is too low for a saturation of the electrodes with the corresponding gas. The two elements receive the charge in accordance with the distribution law, and a difference in potential develops which is at its maximum with minimum concentration of the corresponding ion and falls rapidly as this ion-concentration rises to a value in excess of that required for the saturation of both electrodes. The bimetallic systems described (cf. preceding abstract) provide a type of electrode system essentially different from those previously used. A comparison of the relative values of the usual unimetallic and bimetallic systems may be based on the difference in the mechanism of the end-point in the two cases. The change in voltage with the former, which is a true oxidation-potential, is continuous throughout, and rises to a maximum at the end-point. With the latter practically all change is confined to within less than 0.5 c.c. of the completion of the titration. Although the actual magnitude of the break is normally less than with unimetallic combinations, it is, relative to the preceding rise, much greater, hence the sharpness of the end-point is correspondingly increased, insuring greater speed and accuracy. With the use of polarised bimetallic systems the break may be increased so much as to leave no possible

comparison favourable to the unimetallic system. It thus becomes possible to titrate solutions which offer too small potential differences between two possible states of oxidation for a good end-point with the usual apparatus. The polarising circuit may be made an integral part of the usual apparatus which requires no attention and presents no difficulties. The disadvantages of the new system lie in the greater localisation of the total potential change which makes it more difficult to anticipate the end-point. Enough warning is given, however, to make the danger of over-titration negligible after very little practice.

J. F. S.

Estimation of Chlorine in Benzaldehyde. J. VOIGT (*Z. angew. Chem.*, 1922, **35**, 654—655).—An apparatus is described by means of which traces of chlorine in volatile organic compounds, particularly in synthetic benzaldehyde, can be accurately estimated. From 10—20 g. of benzaldehyde are weighed into a wickless lamp arranged in an air-bath which can be heated by bunsen burners. The exit of the lamp is connected with a pipette-shaped combustion tube through which oxygen is passed. Hydrogen is passed over the warmed benzaldehyde, and, mixing with the vapours, it carries them forward through a jet situated in the wide part of the combustion tube. The issuing gas is ignited in the oxygen by heating the tube externally, and it continues to burn quietly until all the benzaldehyde has been volatilised. The products of combustion pass over 2—3 g. of granulated anhydrous sodium carbonate packed in the narrow stem of the combustion tube and heated by a row of burners. The water is collected in a calcium chloride tower. About 7 g. of benzaldehyde can be burnt in an hour, and at the end of the combustion the soda is washed out of the tube by means of dilute nitric acid and titrated with standard silver nitrate. As little as 0.001% of chlorine can be estimated accurately by this method, and it is therefore necessary to apply a correction for the chlorine content of the hydrogen employed, as, although undetectable by ordinary methods, the amount which is always present may make an appreciable difference in the present case. Hydrogen in cylinders contains on the average 0.003 g. of chlorine per m³.

G. F. M.

Detection of Chlorides and Bromides in the Presence of Thiocyanates. G. SPACU (*Bul. Soc. Științe Cluj*, 1922, i, 302—305; from *Chem. Zentr.*, 1922, iv, 735).—Neutral solutions containing chlorides and bromides in the presence of thiocyanates are treated with a little pyridine and excess of 10% copper sulphate solution. The thiocyanate ion is quantitatively precipitated as copper pyridine thiocyanate, $[\text{CuPy}_2](\text{CNS})_2$, and the filtrate may be tested in the ordinary way for chlorides and bromides.

G. W. R.

A Gasometric Method of Estimating the Halogen in Organic Compounds. ALEXANDER KILLEN MACBETH (*Chem. News*, 1922, **125**, 305—306).—Some organic halogen compounds in which the halogen possesses an induced electropositive nature

(cf. Henderson and Macbeth, T., 1922, **121**, 892) are reduced quantitatively by hydrazine, the volume of nitrogen evolved depending on the amount of halogen or halogen compound dealt with. A list of substances to which the method has been successfully applied is given. With some halogen-substituted malonic esters the reaction is not quantitative and in the case of certain di-substituted compounds only one halogen atom reacts, the other being unattacked in the cold. H. J. E.

Estimation of Fluorides. N. K. SMIT (*Chem. Trade J.*, 1922, **71**, 325).—A simplification of Greeff's method (A., 1913, ii, 975). To 5 or 10 c.c. of the neutral fluoride solution are added 5 c.c. of 10% ammonium thiocyanate solution and 25 c.c. of alcohol, and the mixture titrated directly with alcoholic ferric chloride, standardised against potassium fluoride. The reaction between ferric chloride and fluorides can also be applied to the detection of the latter. A. A. E.

The Estimation of Oxygen in Steel. GEORGES CHAUDRON and LOUIS BLANC (*Compt. rend.*, 1922, **175**, 885—887).—In estimating oxygen in steel by heating the metal in a current of hydrogen and measuring the quantity of water formed, the addition of other metals to enable the estimation to be carried out at a lower temperature was not found to affect the result obtained. When dealing with molten mixtures of iron and oxide of manganese, or of iron and silicon dioxide, the method is inaccurate owing to incomplete reduction of the oxides and to the relatively small amount of water obtained which is of the same order as the corrections necessitated by the method. H. J. E.

Estimation of Sulphur in Iron and Steel. FERDINAND NIKOLAI (*Chem. Ztg.*, 1922, **46**, 1025—1026).—The iron or steel turnings or powder are treated with hydrobromic acid (d 1.48=47.4%) in an apparatus consisting of a small flask ground on to a tube, the first 12 cm. of which act as a reflux air condenser, and is then bent round and carried vertically downwards into a cylinder containing 2.5% sodium hydroxide solution. The mixture of iron and hydrobromic acid is gradually raised to its boiling point and the hydrogen sulphide liberated is absorbed in the sodium hydroxide solution, which, after adding 10 c.c. of potassium iodide solution and some starch, is titrated with $N/150$ -iodine solution. The whole estimation requires twenty to twenty-five minutes, and very concordant results are obtained, which agree well with those obtained using Fresenius's method. The results obtained by the above method are higher than those obtained using either dilute or concentrated hydrochloric acid because the aqueous solution of hydrobromic acid which distils unchanged contains 47.4% HBr, whereas the corresponding hydrochloric acid solution only contains 20% HCl. H. C. R.

The Rapid Estimation of Sulphur Dioxide. R. MARCILLE (*Ann. Falsif.*, 1922, **15**, 398—401).—For the rapid and approximate

estimation of sulphur dioxide in wines, 10 c.c. of the wine are heated with 10 c.c. of a solution of 60 g. of sodium hydroxide per litre, in a wide-necked conical flask until the volume of the contents is reduced to one-half. The solution is cooled, diluted with 100—150 c.c. of water and enough dilute sulphuric acid added to neutralise the sodium hydroxide. Starch solution is added and the solution is titrated with iodine solution containing 4 g. or 8 g. per litre (1 c.c.=1 mg. or 2 mg. of sulphur dioxide). If the alcohol and aldehydes are not driven off by heating, the results may be 200 mg. per litre too low. The presence of more than 5 g. of dextrose per litre in the wine affects the results obtained and the sulphur dioxide must then be separated by distilling 10 c.c. of the wine acidified with 5 or 6 drops of syrupy phosphoric acid, the distillate being led into 10 c.c. of the sodium hydroxide solution, which is afterwards treated as in the direct method described above. The results obtained by this method agree well with those given by Haas's method, and the degree of accuracy is sufficient for all practical purposes.

H. C. R.

New Process for the Volumetric Estimation of Ammonia and Carbamide Nitrogen by the Hypobromite Method.

J. TILLMANS and A. KRÜGER (*Z. angew. Chem.*, 1922, **35**, 686—687).—A simple glass apparatus is described for the estimation of ammonia or carbamide by the hypobromite method. It consists essentially of an upper cylindrical portion provided with a ground-glass stopper and a draw-off cock drawn out to a fine opening. The upper vessel fits with a ground-glass joint into a lower vessel and communication between them is established through a vertical tube extending nearly to the top of the upper chamber, which is charged with brine to a level of 3—4 cm. below the top of the vertical communication tube. When the draw-off cock is opened and the apparatus is otherwise closed, brine runs out until equilibrium is attained between the inside and outside pressures. The lower vessel being previously charged with hypobromite solution, the reaction is then started by rotating a boat containing the carbamide or ammonium salt on its axis so that its contents fall into the solution, and the nitrogen evolved causes the displacement of an equal volume of brine from the upper vessel through the draw-off cock. The boat is fixed to a horizontal axis which is ground to pass through, and fit into a tubulure in the side of the lower vessel, and the boat can be reversed by turning the projecting portion of the axis through 180°. The apparatus can be utilised for urine investigations by placing the urine in the lower vessel, and running in the hypobromite by means of a tap funnel through the vertical communication tube.

G. F. M.

The Estimation of Aliphatic Nitrates in the Presence of certain Nitro-aromatic Compounds. WILBERT J. HUFF and RICHARD D. LEITCH (*J. Amer. Chem. Soc.*, 1922, **44**, 2643—2645).—Aliphatic nitrates may be estimated in the presence of certain aromatic nitro-compounds by reduction with ferrous sulphate in

excess, the unoxidised ferrous salt being titrated with standard permanganate solution. A Kjeldahl flask is fitted with a two-holed rubber cork carrying a pear-shaped dropping funnel and a tube bent twice at right angles and having its external orifice closed by a mercury seal. The air is expelled from the flask by boiling in it 25 c.c. of distilled water, and when the flame is removed the nitrate ester mixed with the aromatic compound and dissolved in glacial acetic acid is slowly run into the flask. Then a known volume of a standard solution of ferrous sulphate in dilute sulphuric acid is slowly added and this is followed by concentrated hydrochloric acid in volume equal to that of the liquid already in the flask. The reaction mixture is then evaporated to 10–15 c.c. and nearly neutralised with sodium carbonate, and when cool is diluted to 600 c.c. and after the addition of 2–3 g. of manganous sulphate is titrated with permanganate solution. Satisfactory results were obtained for mannitol hexanitrate, but those for glyceryl trinitrate were slightly low, probably owing to the partial vaporisation of the nitrate before it was completely hydrolysed. W. G.

New Reagent for the Detection of Nitrites in Water. GEORGES RODILLON (*J. Pharm. Chim.*, 1922, [vii], 26, 376–379).—To the water to be examined, contained in a test-tube, 3–4 c.c. of a reagent, composed of a 6% solution of resorcinol in pure sulphuric acid, are added so as to form two layers. In presence of nitrites, a rose-coloured ring is formed at the junction of the two layers. An approximate estimation of nitrous acid can also be arrived at if desired by comparing the density of colour and the appearances of the ring and the aqueous and sulphuric acid layers with those obtained with standard sodium nitrite solutions. Thus the coloration of the ring with solutions containing in 1 litre 1 g. of sodium nitrate is brownish-black, fading away above and below to red; 0.1 g., brownish-red, similarly fading to red at the edges; 0.01 g., carmine, and 0.001 g., a very pale rose. The sulphuric acid layer ranges in colour with these concentrations from an intense amethyst-violet to the unchanged yellow of the original reagent.

G. F. M.

Volumetric Estimation of Phosphate in Solution. FRANK W. BURY (*J. Soc. Chem. Ind.*, 1922, 41, 352T).—In the volumetric estimation of phosphate in solution by Rosin's method (A., 1911, ii, 768), the solution is kept neutral by means of zinc oxide. The neutralisation is very tedious, and copper carbonate was tried, but showed no advantage. The best results were obtained by neutralising with borax, the procedure being as follows. A measured quantity of phosphate solution is added to a measured excess of $N/10$ -silver nitrate, and $N/10$ -borax solution is run in until the liquid is neutral to litmus. The solution is then filtered, and the excess of silver nitrate estimated either by Volhard's method, or by adding a measured excess of $N/10$ -potassium chloride and titrating back the excess with $N/10$ -silver nitrate, using potassium chromate as indicator. G. F. M.

The Titration of Boric Acid in Presence of Phosphoric Acid. I. M. KOLTHOFF (*Chem. Weekblad*, 1922, **19**, 545—546; cf. A., 1922, ii, 867).—An answer to the criticisms of Deerns (A., 1922, ii, 867) on the citrate method put forward by the author.

S. I. L.

Estimation of the Radium Content of Low-grade Radium-Barium Salts. VICTOR F. HESS and ELIZABETH E. DAMON (*Physical Rev.*, 1922, **20**, 59—64; cf. *Trans. Amer. Electrochem. Soc.*, 1922, **41**).—The γ -ray method for the estimation of radium is inapplicable to salts containing much less than 10^{-4} g. of radium per g. if the customary apparatus is used, and the emanation method involves errors due to dilution and other causes, if the sample contains more than 10^{-7} g. of radium per g. For the examination of salts of intermediate radium content, the γ -ray method has been modified by the adoption of a shallow container with two curved sides, each concentric with the cylindrical string electrometer, and only a small fraction of the radius of curvature apart. Readings are taken with the container in position, full of the salt to be measured, first alone, and then with a small radium tube of known strength placed first immediately in front and then immediately behind the container. The ratio of the first reading to the mean of the other two gives that of the radium content of the salt under examination to the sum of the same and the standard to within 1%.

A. A. E.

Bismuth Sodium Thiosulphate ; its Preparation and Use in the Estimation of Potassium. V. CUISINIER (*Bull. Soc. chim.*, 1922, [iv], **31**, 1064—1068).—Observations on the thiosulphates of bismuth and alkali metals have been made by Carnot (A., 1876, ii, 426), Hauser (A., 1903, ii, 487), Sanchez (A., 1912, ii, 562), and by Vanino and Mussnug (A., 1920, ii, 44), but the substances have not been fully described and their use in the estimation of potassium salts has given inconsistent results. A salt of the approximate composition $\text{Na}_3\text{Bi}(\text{S}_2\text{O}_3)_3$ can be prepared, crystallising in yellow, prismatic plates rapidly turning brown on exposure to air. On attempting to carry out estimations of potassium by precipitation as potassium bismuth thiosulphate and subsequent treatment of the precipitate with iodine, it was found that the results obtained were too high. Further, the amount of precipitate obtained appears to be influenced by the concentration of the reacting solutions; the iodine value is not proportional to the potassium content of the solution investigated, and the volume of the alcohol used as precipitant also affects the result obtained. [Cf. *J.S.C.I.*, 1922, 981A.]

H. J. E.

A Photochemical Test for Silver in Thin Sections of Ores. G. SILBERSTEIN and E. WIESS (*Z. anorg. Chem.*, 1922, **124**, 355—356).—On placing the section in a saturated solution of an iodide for five minutes, the silver is covered with a thin film of silver iodide, which, under the microscope, showed the characteristic reaction to light. The authors propose investigating the practical

limits of this test, and also the light reaction of silver sulphide, with the object of applying it to test for sulphur in metals by shaking them with a solution of a silver salt.

W. T.

Contradictions and Errors in Analytical Chemistry. III. The Separation of Zinc from Magnesium, Calcium, and Aluminium by Precipitation of the Phosphates. IV. The Conversion of Alkali Sulphates into Chlorides. FRIEDRICH L. HAHN [with (III) J. DORNAUF and (IV) R. OTTO] (*Ber.*, 1922, 55, [B], 3434—3436; cf. *A.*, 1922, ii, 873).—III. The separation of magnesium, calcium, and aluminium from zinc can be effected according to Voigt (*A.*, 1910, ii, 74) by precipitation with phosphate in ammonical solution containing ammonium salts whereby only the zinc remains dissolved. This method of separation has great advantages when only small quantities of foreign metals are present, but the subsequent operation of precipitating the zinc as the zinc ammonium phosphate cannot be effected quantitatively by simply boiling the solution until the excess of ammonia is expelled. Accurate results are obtained if the filtrate containing the zinc is treated with hydrochloric acid until just acid to methyl-red and subsequently with an excess of phosphate. If the solution is rich in ammonium salts, it is preferable to expel the bulk of the ammonia before addition of the acid.

IV. Potassium cannot be separated from sodium as the perchlorate or chloroplatinate if the metals are present as sulphates. The usual procedure of precipitating the latter with barium chloride, removal of excess of barium with ammonium carbonate, and subsequent volatilisation of the excess of ammonium salts, is inaccurate, since barium sulphate always carries down alkali sulphate. This difficulty can be overcome by precipitating the barium sulphate in extreme dilution. For this purpose, moderately dilute solutions of sulphate and barium chloride are added simultaneously and at approximately equivalent rates to a small quantity of boiling hydrochloric acid. Pure barium sulphate is thereby precipitated in well-formed, coarse crystals which are readily filtered and washed. The presence of varying amounts of alkali chloride and even of nitrate in the sulphate solution is without influence. If ferric iron is present, ammoniacal barium chloride solution must be used and the solution be acidified after the precipitation. H. W.

The Carrying-down of Zinc by Copper Sulphide. I. M. KOLTHOFF and J. C. VAN DIJK (*Pharm. Weekblad*, 1922, 59, 1351—1360).—The fact that zinc sulphide is almost always precipitated to some extent with copper sulphide from solutions of the two metals is not due to adsorption, since zinc sulphide is only with difficulty soluble in acids of low concentration. The precipitation of zinc from acid solutions by hydrogen sulphide depends on time and temperature, as well as on the concentration of zinc-, hydrogen-, and sulphide-ions, and is accelerated by presence of copper sulphide.

In the quantitative separation of copper and zinc by hydrogen

sulphide, the time must be as short as possible. If sulphuric or hydrochloric acid is used, the acidity must be at least 0.5*N*; with the former, room temperature is best; with the latter, the gas should be led in at the boiling point.

S. I. L.

Some Applications of Sodium Peroxide in Analytical Chemistry. W. M. STERNBERG (*Science*, 1920, 52, 162).—The decomposition of lead and zinc ores by fusion in an iron crucible with at least six to eight parts of sodium peroxide is rapid and complete. In the case of lead ores, the aqueous solution of the fused mass, after treatment with 1.4 parts of oxalic acid to reduce the lead dioxide, is acidified with sulphuric acid, boiled, cooled, and the lead sulphate collected and washed with 5% sulphuric acid. It is then dissolved in a solution of ammonium chloride or of ammonium chloride and sodium acetate, and titrated with ammonium molybdate. In the case of zinc ores, the fused mass is dissolved in ammoniacal ammonium chloride solution, the solution boiled, filtered, and washed with hot ammonium chloride solution, acidified with hydrochloric acid, boiled, and titrated with potassium ferrocyanide after the addition of hydrogen sulphide. It is necessary that the solutions should be standardised against a standard ore treated by the same method.

A. A. E.

Gravimetric Analysis. XXVI. Estimation of Lead. L. W. WINKLER (*Z. angew. Chem.*, 1922, 35, 662—663).—For the gravimetric estimation of lead in neutral solution, 100 c.c. of lead nitrate or lead chloride solution containing from 0.60 to 0.01 g. of lead is acidified with 1 c.c. of normal nitric acid solution and boiled. Ten c.c. of 10% ammonium sulphate solution are slowly run in, and the whole is allowed to remain, then filtered. The precipitate is washed with 50 c.c. of a cold saturated solution of lead sulphate, and the edge of the filter washed with 1—2 c.c. of dilute alcohol. The precipitate is dried for two hours at 130°. Modifications of the procedure necessitated by the presence of nitric or hydrochloric acid, and salts of potassium or other metals, are discussed and details are given of the method of estimation of lead in crude lead, minium, lead chromate, and lead salts of organic acids.

J. S. G. T.

A New Sensitive Reaction for Copper, Thiocyanate, and Pyridine. G. SPACU (*Bull. Soc. Stiințe Cluj*, 1922, 1, 284—291; from *Chem. Zentr.*, 1922, iv, 737).—The reaction consists in the formation of a light green precipitate when a neutral solution of a copper salt is treated with a neutral thiocyanate and a few drops of pyridine. The precipitate has the composition $[\text{CuPy}_2](\text{CNS})_2$ and is almost completely insoluble in water. The reagent must be neutral and excess of pyridine must be avoided. The pyridine should be added before the thiocyanate. One part in 300,000—800,000 of copper can be detected according to the conditions of experiment. For pyridine, the sensitiveness is one part in 2000 and for thiocyanate one in 50,000.

G. W. R.

The Hindering of the Precipitation of Copper Sulphide by the Presence of Sodium Chloride. WILHELM BILTZ (*Ber.*, 1922, 55, [B], 3393).—In a recent communication, Dede and Bonin (*A.*, 1922, ii, 766) have shown that lead and cadmium sulphides are only incompletely precipitated in hydrochloric acid solution in the presence of relatively large quantities of the chlorides of the alkali or alkaline-earth metals. Similar observations have been recorded in the case of copper (cf. Biltz and Marcus, *A.*, 1909, ii, 1011). Precipitation of copper sulphide is, however, quantitative in a 5% solution of sodium chloride. Magnesium chloride or carnallite does not appear to have an inhibiting action. H. W.

A New Microchemical Reaction for the Estimation of Copper. G. SPACU (*Bull. Soc. Ştiinţe Cluj*, 1922, 1, 296—301; from *Chem. Zentr.*, 1922, iv, 737—738).—After precipitation of copper as copper pyridine thiocyanate, $\text{CuPy}_2(\text{CNS})_2$ (see this vol., ii, 40), the precipitate is separated in an appropriate apparatus (Rothe's shaking funnel) by successive extraction with chloroform. The precipitate is then weighed, after removal of the chloroform in a vacuum desiccator. Alternatively, the precipitate may be ignited, and the copper estimated as cupric sulphide or cupric oxide. G. W. R.

Volumetric Estimation of Copper, and its application to the Estimation of Reducing Sugars. ED. LASAUSSE (*J. Pharm. Chim.*, 1922, [vii], 26, 401—406).—The precipitated cuprous oxide formed by the reducing action of the sugar on a cupro-tartrate solution is collected on a Gooch crucible and dissolved by means of 2—3 c.c. of nitric acid. The filter is finally washed with water, the total volume of filtrate and washings being kept below 25—30 c.c. The nitrous acid present is then eliminated by adding 2% permanganate solution drop by drop to the boiling liquid until the pink coloration just persists, and the latter is reduced by the addition of a few drops of alcohol. After boiling for a minute longer, the precipitated oxides of manganese are filtered off, the filtrate is made up to 100 c.c., and the copper is estimated iodometrically in the usual way after the addition of an excess of sodium acetate to displace free mineral acid. In order to obtain the best results in the estimation of reducing sugars, the procedure of Quisumbing and Thomas should be followed (*A.*, 1922, ii, 92) as a granular cuprous oxide is thereby obtained, which can readily be collected and washed. The amount of dextrose is given by the formula $0.474x + 0.000115x^2$, and of invert-sugar by $0.504x + 0.000087x^2$, where x is the weight of copper reduced. G. F. M.

Iodometric Estimation of Copper in Bronze and Brass. G. BATTÀ and G. LATHIERS (*Bull. Soc. chim. Belg.*, 1922, 31, 297—302).—The application of the iodometric method of copper estimation to bronze and brass gives results which are of sufficient accuracy for many purposes. It is rapid and useful when electrolytic methods cannot be employed. H. J. E.

Rapid Electrolytic Estimation of Mercury. A. DE MEEÛS (*Bull. Soc. chim. Belg.*, 1922, **31**, 302—323; cf. Böttger, A., 1921, ii, 351).—A study of the factors which are said to cause inaccuracies in the electrolytic estimation of mercury. Good results were obtained with a platinum cathode, but gold was found to be more suitable for the purpose as the mercury deposit is more adherent and so permits of the use of alcohol and ether for washing; in the case of other metals this should be done with water only as the more rapid method occasions loss. Experiments carried out with mercuric salts in presence of substances which form complexes give similar results with gold and platinum cathodes, but the method is more satisfactory when simple acid electrolytes are used as solvents. The method is applicable to mercurous salts, which are oxidised before electrolysis. H. J. E.

Constancy of the Titer of Permanganate Solutions, and Different Methods of Standardisation. O. HACKL (*Chem. Ztg.*, 1922, **46**, 1065).—*N*/10-solutions of potassium permanganate made from the freshly prepared pure salt remained permanent, if stored in a dark place for one year, whereas solutions made from a ten-year old preparation altered considerably in the course of a few months. Tests showed that the most satisfactory compound for use in standardisation of permanganate solutions is sodium oxalate. The composition of oxalic acid crystals and ferrous ammonium sulphate was found to vary within narrow limits, but these are sufficient to lead to discordant results in the titration. A. R. P.

The Electrometric Estimation of Iron and Vanadium when present together. ERICH MÜLLER and HANS JUST (*Z. anorg. Chem.*, 1922, **125**, 155—166).—Ferrous salts and vanadium salts can be accurately estimated electrometrically with permanganate. Ferrous salts are more vigorous reducing agents than the salts of quadrivalent vanadium, and the authors find that they can be estimated when together in the same way. To the mixture, a decinormal solution of potassium permanganate is gradually added until there is a sudden change in the *E.M.F.* This indicates the end-point for the ferrous salt; the titration is then continued until a second sudden change occurs which represents the end-point for the vanadium salt. The latter titration is best carried out at about 70° as the reaction is very slow at the ordinary temperature. W. T.

Electrometric Standardising of Titanous Solutions. W. S. HENDRIXSON and L. M. VERBECK (*J. Amer. Chem. Soc.*, 1922, **44**, 2382—2386).—A slightly acid solution of titanous sulphate may be used to standardise solutions of potassium permanganate or potassium dichromate. The method consists in adding the titanous solution to the permanganate or dichromate solution and measuring the *E.M.F.* of the solution toward a platinum electrode against a calomel electrode. The *E.M.F.* changes very rapidly at the end-point which is therefore made very precise; in the case of

dichromate, the change in *E.M.F.* on adding a slight excess of titanous ion to a slight excess of dichromate is about 0.6 volt, whilst in the case of permanganate the change in *E.M.F.* is about 0.9 volt. This difference makes it possible to estimate two substances of quite different oxidising power in the same solution. The authors have investigated the estimation of titanous and ferrous ions by means of permanganate or dichromate, of ferric-iron and dichromate or permanganate by means of a titanous solution, and have found that the method is trustworthy. J. F. S.

New Method for the Gravimetric Estimation of Germanium. JOHN HUGHES MÜLLER (*J. Amer. Chem. Soc.*, 1922, **44**, 2493—2498).—A new method of estimating germanium is described which is based on the precipitation of this metal as magnesium orthogermanate and weighing the dried and ignited precipitate. Magnesium orthogermanate is a snow-white, infusible substance, which is prepared by the action of magnesium sulphate, ammonium sulphate, and ammonium hydroxide on a solution of germanic acid. No precipitate is formed until the ammonium hydroxide has been added, and the reagents are added in the order named. Magnesium orthogermanate is amorphous and is very soluble in dilute solutions of acids, but after ignition it is only slowly dissolved by concentrated acids. It dissolves in water to the extent of 0.000016 g. per c.c. at 26°. In a mixture of two volumes of ammonia (0.880) and three volumes of water the solubility is 0.00002 g. per c.c., whilst in an ammoniacal solution of 10% ammonium sulphate the solubility is 0.00013 g. per c.c. at 26°. The estimation of germanium is effected by adding an excess of 2*N*-magnesium sulphate to the cold solution of germanic acid; this is followed by at least an equal volume of 2*N*-ammonium sulphate, and then ammonium hydroxide (0.880) is added in amounts varying from 15 c.c. to 20 c.c. for each 100 c.c. of solution and the mixture stirred vigorously, raised to the boiling point for a few minutes, and kept for ten to twelve hours before filtering. The precipitate is filtered, washed with a mixture of 90 c.c. of water and 10 c.c. of ammonia, dried, and ignited with free access of air. The results of the analyses are excellent. J. F. S.

Analysis of Mixtures of Hydrogen with Paraffin Hydrocarbons. J. G. KING (*Fuel*, 1922, **1**, 103—106).—The estimation of hydrogen in admixture with paraffin hydrocarbons is effected by fractional combustion over copper oxide at 280°, in an apparatus which is a modification of that of Jäger (*J. Gasbeleuchtung*, 1898, **41**, 764). Carbon monoxide and hydrogen are thereby consumed, whereas the paraffins remain unchanged. CHEMICAL ABSTRACTS.

Identification of Methyl Alcohol in Liquids containing Ethyl Alcohol. I. M. KOLTHOFF (*Pharm. Weekblad*, 1922, **59**, 1268—1274).—The method of Denigès (*A.*, 1910, ii, 461), namely, oxidation with permanganate in presence of acid, removal of excess with oxalic acid, and testing for formaldehyde with Schiff's reagent, will detect 0.05% of methyl alcohol in ethyl alcohol. The reagent

is best prepared as suggested by Elvove (A., 1917, ii, 341), and if kept in stoppered bottles is stable for long periods. The use of phosphoric acid in place of sulphuric acid, as recommended by Chapin (A., 1921, ii, 598), is found advantageous.

The method can be applied to the examination of tinctures and medicinal preparations containing alcohol, without preliminary distillation. The reagent will also detect formaldehyde in milk.

S. I. L.

Colour Reaction for Phenols based on the Use of Selenious Acid. VICTOR E. LEVINE (*Science*, 1920, 52, 207).—A reaction of great sensitivity and wide applicability consists in the fact that phenols in contact with a solution of selenium dioxide (0.5%) or sodium selenite (0.75%) in concentrated sulphuric acid give rise to characteristic green or blue colorations. On heating, or on the addition of water, the colour changes to brown or red. It is considered that the phenol causes the liberation of selenium, which then dissolves with a green colour in concentrated sulphuric acid to form selenosulphur trioxide. A list is given of phenolic substances to which the test has been applied. A. A. E.

The Action of Proteins on the Phenol Reagent of Folin and Denis. VICTOR E. LEVINE (*Science*, 1920, 52, 612—613).—The phosphotungstic-phosphomolybdic reagent of Folin and Denis (A., 1912, ii, 1011) is not specific for the phenolic group. The colour reaction is given by proteins, and in fact by a large number of inorganic and organic substances. The reagent appears to be affected by substances possessing more or less reducing properties. A. A. E.

Test for Sugar in Urine. VICTOR E. LEVINE (*Science*, 1920, 52, 391).—One to 2 c.c. of urine are heated for several minutes with 5 c.c. of a 2% solution of sodium tellurite in 10% sodium carbonate. Reduction to tellurium takes place in the presence of carbohydrates possessing a free carbonyl group. With small amounts of sugar, the tellurium forms a colloidal solution; which has a characteristic brown colour in transmitted light and is greyish-black in reflected light; larger amounts yield a greyish-black precipitate. A. A. E.

The Partition Coefficients, and the Estimation by Extraction of Organic Acids. JOH. PINNOW (*Z. Unters. Nahr. Genussm.*, 1922, 44, 204—209).—Acetic and formic acids form double molecules in ethereal solution, and the irregularities observed in the partition coefficient of the latter acid may be ascribed to this cause. Assuming that no double molecules occur in the aqueous solutions, the dissociation coefficients of the double molecules have the following values at 15°: acetic acid, 1.776; formic acid, 4.77. The partition coefficients (water/ether) of the simple molecules at 15° are: acetic acid, 2.21; formic acid, 2.38. At 26.3°: formic acid, 2.79. Sugar has no effect on the extraction of succinic acid from its aqueous solution. H. C. R.

General and Physical Chemistry.

The Secondary Spectrum of Hydrogen. A. C. MENZIES (*Nature*, 1922, **110**, 876).—Silberstein's solution of the three-substance problem, applied by him to the case of neutral helium, has been modified so as to apply to hydrogen, and the value of N has been corrected so as to take account of the fact that with two electrons instead of one, the correction to the mass of the electron for the finite mass of the nucleus is no longer the same. Frequencies have been calculated from the formula $\nu = N_{\infty} (1/n_1^2 + 1/n_2^2 - 1/m_1^2 - 1/m_2^2)$ where $N_{\infty} = N_H(1 + m/M)$. Forty-seven lines in the secondary spectrum of hydrogen were found to agree with the calculated values within an absolute error of one unit of frequency. The frequencies are regarded as a kind of "summation tone," being the sums of a Balmer or a Paschen frequency and a frequency in the ultra-red. In several cases, a physical similarity of behaviour was common to "series" of the lines grouped according to values of m and n .
A. A. E.

Spectrum of Active Nitrogen as Affected by Admixture of the Inert Gases, with a Note on the Origin of the Cyanogen Spectrum. LORD RAYLEIGH (*Proc. Roy. Soc.*, 1923, [A], **102**, 453—459).—The afterglow accompanying the reversion of active nitrogen to ordinary nitrogen was shown by Fowler and Strutt (A., 1911, ii, 678) to be composed of a selection of the first positive bands of nitrogen. The addition of inert gases to the nitrogen produces considerable changes in the intensities of these bands. The maxima of the three groups of bands, green, yellow, and red, are shifted towards the red. The addition of helium, neon, or argon makes the red group as a whole; more intense at the expense of the others. The movement of the bands is proportional to the concentration of the inert gases present. Evidence is adduced for the belief that the red aurora line, λ 6320, is due to the presence of nitrogen and helium in the upper atmosphere. It is not yet determined whether the effects on the after-glow spectrum are produced in the electric discharge or in the process of the after-glow. The influence of carbon in developing the cyanogen bands is discussed.
W. E. G.

The Carbon Arc Spectrum in the Extreme Ultra-violet. F. SIMEON (*Proc. Roy. Soc.*, 1923, [A], **102**, 484—496).—Measurements are made of the ultra-violet lines of the carbon arc spectrum by means of a vacuum grating spectrograph. Colour sensitised Schumann plates were used both for the extreme ultra-violet as well as for the ordinary violet region. A table is given of the wavelengths and intensities of the lines observed, and comparison made with the values of other workers. Some of the lines photographed in the Lyman region have not been mentioned by any previous
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worker, and some of the lines in the higher orders of spectrum have been shown to consist of close groups of lines. The line 599.0 attributed by Lyman to helium is due to carbon present as an impurity in the helium. The lines in the Lyman region at 1194, 945, 858, 687, 651, 640, 599, and 595 have not been previously observed in the arc spectrum of carbon, but these lines correspond with prominent lines in the "hot spark" spectra of Millikan. Groups at 1657, 1329, 1260, 1194, 1036, and 651 have been resolved into a number of lines.

W. E. G.

The Spectrum of Neutral Helium. LUDWIK SILBERSTEIN (*Nature*, 1923, **111**, 46—47).—In reply to Raman's criticisms (*A.*, 1922, ii, 803), it is shown mathematically that the probability that the forty-five coincidences previously described are fortuitous is less than 1.7×10^{-13} ; it is further claimed that the use of the value 109723 for the Rydberg constant in the formula applied to the case of the neutral helium atom (with two electrons) is justifiable. It is now found that the whole diffuse series of singlets, $1P-mD$, is represented by the formula $\nu = 4N(18.2n/20.4) \equiv N(9.n/10.2)$, two final and one initial quantum numbers being fixed. The possibility of reducing $4N$ to N , based on the fact that all numbers are even, is mentioned but not discussed; physically interpreted, it would mean that the helium nucleus attracts each of its electrons with only one-half of its total charge, as if its lines of force formed two bundles, each entirely engaged with one of the two trabants.

A. A. E.

Relative Visibility of Spectra when an Electric Discharge is Passed Through the Vapours of Alkali Amalgams. F. H. NEWMAN (*Phil. Mag.*, 1923, [vi], **45**, 181—189).—The relative intensities of the spectra of the alkali metals and mercury have been examined by placing alkali amalgams in an electric discharge tube. For sodium and mercury the spectrum of the former was prominent at all temperatures, but below 100° the mercury spectrum was the brighter. At 200°, the mercury lines are almost entirely masked. At this temperature, a very brilliant yellow radiation is emitted, which forms a very convenient source of the sodium *D*-lines. The ionising potentials of sodium (5.13 volts) and mercury (10.2 volts) and the partial pressures of their vapours are the two main factors operative in determining the intensity of the spectra. At low vapour pressures, the atoms of both sodium and mercury will be so far apart that the electrons attain the necessary energy to ionise the mercury atoms before inelastic collision occurs. Under these conditions, approximately equal numbers of mercury and sodium atoms will be ionised. As the temperature rises, the density of the vapour increases, and the electrons attain less frequently the speeds corresponding with 10.2 volts, so that although the number of mercury atoms will be far more numerous than those of sodium, the actual number of the former ionised will be very small. Thus at 200° the mercury lines are suppressed. Except in the case of potassium, where the

lines are faint at all temperatures, the other alkali amalgams show similar phenomena. W. E. G.

The Excitation of the Mercury Spectrum. The Influence of Helium. GEORGES DÉJARDIN (*Compt. rend.*, 1922, **175**, 952—955).—An examination of the radiations emitted by mercury vapour traversed by electrons of different velocities showed that when the speed of the electrons is slightly greater than the critical ionisation velocity a large number of the arc spectrum lines are obtained, these being due to collisions between electrons and mercury atoms. When the conditions are such that the electron charge is neutralised, a luminous region appears near the electrodes the spectrum of which also exhibits the characteristics of that of the mercury arc. The author concludes that the emission spectrum appears to depend on the ionisation of the atom and notes the conditions under which certain of the lines become visible. In the presence of helium and with a potential greater than 20.4 volts, considerable modifications of the mercury spectra take place. Details of the variations in intensity and the appearance of new lines are given, the action of helium being apparently selective on certain lines as in the case of cadmium (cf. Collie and Watson, A., 1918, ii, 383). H. J. E.

Spectroanalytical Investigation of a New Element in the Terbium Group and the Arc Spectrum of Terbium. JOSEF MARIA EDER (*Sitzungsber. Akad. Wiss. Wien, Math.-naturwiss. Klass.*, 1922, [iia], **131**, 199—298; cf. *ibid.*, 1920, **129**, 422).—The determination of the spectra of a number of terbium, dysprosium, and gadolinium fractions has led to the discovery of a new element giving a well-defined and characteristic line spectrum. This element, which was present in a fraction between terbium and dysprosium, is named *Welsium*. The lines of the new element are weakened in the spectra of the fractions rich in terbium, and are practically absent in the spectra of the dysprosium fractions. In agreement with the observations of Eberhard, no evidence has been found for a new element in the fractions between terbium and gadolinium.

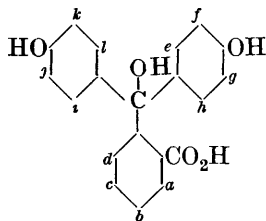
Many thousands of lines of the terbium spectrum have been measured between λ 7257 and 2400 Å., and compared with the measurements of Urbain, Eberhard, and Auer. W. E. G.

The Line Spectrum of Vanadium in Fused Salts. A. DE GRAMONT (*Compt. rend.*, 1922, **175**, 1129—1133; cf. A., 1921, ii, 73).—A solution of vanadium pentoxide in fused sodium carbonate was used in order to ascertain the limiting quantity of vanadium capable of spectroscopic detection. The results are shown in two tables which give, for visual and photographic observation, respectively, the smallest quantity corresponding with each line in the spectrum. Non-conducting materials which contain vanadium give good spark spectra which are in accordance with the author's observations. H. J. E.

Absorption of Light by Chlorine. H. VON HALBAN and K. SIEDENTOPF (*Z. physikal. Chem.*, 1922, **103**, 71—90).—The absorption of light by chlorine between $254\ \mu\mu$ and $643\ \mu\mu$ has been determined for nineteen wave-lengths, using lines of mercury, zinc, and cadmium, and between $383\ \mu\mu$ and $451\ \mu$, using a Nitra-lamp for twelve wave-lengths. The method of observation was the previously described photoelectric two-cell arrangement (A., 1922, ii, 332). The results show that within the pressure range investigated (760 mm. and downwards) Beer's law is true. The absorption curve shows a maximum in the ultra-violet at about $334\ \mu\mu$ and a minimum in the yellow. From yellow to red, the absorption again increases, and reaches a maximum which probably lies between $614\ \mu\mu$ and $643\ \mu\mu$. No difference could be observed between the absorption of dry and moist chlorine. J. F. S.

The Ultra-violet Absorption Spectra of Toluene and the Xylenes. F. W. KLINGSTEDT (*Compt. rend.*, 1922, **175**, 1065—1067).—The ultra-violet absorption of hexane solutions of toluene and of the xylenes was measured, and details of the position and form of the bands are given, together with a diagrammatic representation. Toluene exhibits sixteen bands, as compared with eight for benzene in the same region; the intensity of absorption is a little greater than that of benzene. The bands are divided into four groups, in each of which intensity decreases with wave-length. Three large bands are observed with *o*-xylene and five with *m*-xylene, whilst in the case of *p*-xylene the absorption coefficient is about four times as great, and the spectrum contains twelve bands arranged in three groups. H. J. E.

Colour and Chemical Constitution. XV. A Systematic Study of Fluorescein and Resorcin-benzoin. JAMES MOIR (*Trans. Roy. Soc. S. Africa*, 1922, **10**, 159—164; cf. A., 1922, ii, 333).—The quantitative study of the colour of compounds of the phenolphthalein type has been continued. The results previously recorded for the bromophenolphthaleins (A., 1921, ii, 365) are restated in another form. The different positions open to substitution in the phenolphthalein molecule are lettered as shown. The colour modification due to the introduction of bromine into any particular position can be expressed by a factor, the "dicyclic



colour factor," by which the characteristic wave-length of phenolphthalein must be multiplied to give that of the derivative. These factors, for the respective positions, are: *a* and *d*, 1.018; *b*, 1.002; *c*, *f*, and *g*, 1.0145; *e* and *h*, 1.0270; *i* and *l*, 1.0235; *j* and *k*, 1.0125. If two or more positions are substituted, all the corresponding factors must be used in calculating the colour of

the derivative. The colour factors for chlorine and iodine are, respectively, about 1/1500 smaller and greater than those for bromine.

Similar factors have been worked out for various substituents

in fluorescein, $\lambda=493.5$. For bromine, the factors for the different positions are: *a* and *d*, 1.0162; *b*, 1.0000; *c*, 1.0091; *f* and *k*, 1.0122; *g* and *j*, 1.0157. The factors for nitro-derivatives are very similar to those for bromo-derivatives, the methyl factors are smaller and the methoxy-factors smaller still, the largest being 1.006. The hydroxy-factors are smallest of all, and in sodium hydroxide solution the hydroxy-derivatives have their absorption bands in the same position as fluorescein itself. Gallein and hydroxyquinolphthalein are exceptions to this rule.

Resorcin-benzein, which is fluorescein without the carboxyl group, is practically identical with fluorescein in alkaline solution; the absorption band is at λ 492. A few derivatives which have been examined show that the colour factors for the *f*, *g*, *j*, and *k* positions are the same as those of phenolphthalein. In the phenyl ring, the effect diminishes in the order *d*, *c*, *b*, but is still positive for *b*, although in fluorescein it appears to be nil for this position.

E. H. R.

Ultra-violet Absorption Spectra of Alkaloids of the iso-Quinoline Group. Papaverine and its Hydrochloride. PIERRE STEINER (*Compt. rend.*, 1922, **175**, 1146—1149).—A comparison of the absorption spectra of papaverine with those of *iso*-quinoline and veratrole, the substances of which the alkaloid is constituted, shows that it is similar to that of *iso*quinoline but simpler. The simplification appears to be due to the veratrole group, which also determines a displacement towards the red and an increase in absorption. The spectrum of the alkaloid is similar in ethereal and in alcoholic solutions; in the latter, a shifting of four bands towards the red is observed. The combination with hydrochloric acid causes a fusion of three absorption bands exhibited by the alkaloid together with a general displacement towards red and increase in absorption. The spectrographic method applied to the detection of papaverine permits of the recognition of 0.03 mg. in 2 c.c. of solution.

H. J. E.

Kinetics of Photochemical Reactions. RUDOLF WEGSCHEIDER (*Z. physikal. Chem.*, 1922, **103**, 273—307).—A theoretical paper in which the laws of photochemical kinetics are developed on the basis of the assumptions made for ordinary chemical reactions. Van't Hoff's law of the proportionality between the amount of chemical change and the amount of light absorbed holds when the conversion of only one molecular species into the reactive condition by the light determines the velocity of the reaction; that is, the spontaneous return of the active molecules into the inactive form may be neglected and all other partial reactions of the total change take place instantaneously. It is to be expected that the law will not hold for the total reaction if the photosensitive molecular species is in excess of the other molecular species participating in the reaction; this is particularly the case in changes which have proceeded nearly to completion. Einstein's equivalent law determines, for energy storing reactions, the velocity constant of van't Hoff's formula, or gives at least the upper limit

for the total reaction. An upper limit of the velocity, only, can be obtained by thermodynamical methods for energy storing reactions. Velocity equations have been integrated on the assumption of van't Hoff's law and a homogeneous parallel beam of light, for a system which is continuously agitated and in which the light is absorbed either by a molecular species which is being destroyed by the reaction or by a sensitizer, which may have a constant concentration or may be produced by the reaction. A number of other possibilities and conditions in the reactions are also theoretically considered. It is also shown that when in a given reaction two photosensitive molecular species are present it is not likely that the velocity of reaction will be proportional to the product of the two quantities of absorbed light, but rather is a proportionality between the velocity and the second or higher power of the light intensity to be expected if a slower subsequent reaction requires the participation of several activated molecules.

J. F. S.

Photochemical Decomposition of Hydrogen Peroxide.

CHR. WINTHER (*Danske Vid. Selsk. Mat.-phys. Medd.*, 1920, **2**, 3—18; from *Chem. Zentr.*, 1922, iii, 981).—Hydrogen peroxide in the presence of potassium ferrocyanide in dilute solution is decomposed on illumination with ultra-violet light. The reaction proceeds at first slowly, then more rapidly, and finally slows down. This decomposition of hydrogen peroxide is attributed to the formation of a catalyst by the influence of light on potassium ferrocyanide solution. The production of the catalyst increases with the time of illumination and reaches a maximum which depends on the amount of energy of the ultra-violet radiation and also, to some extent, on the concentration of hydrogen peroxide.

G. W. R.

Spacial Progression of Photochemical Reactions in Jellies.

A. BENRATH and K. SCHAFFGANZ (*Z. physikal. Chem.*, 1922, **103**, 139—154).—The photochemical actions between ferric chloride and tartaric acid, silver bromide, and chlorine water have been examined when the reacting substances were uniformly distributed through various jellies such as silicic acid, starch, egg-albumin, gelatin, and various animal membranes. It is shown that the progression of photochemical reactions in jellies proceeds according to Lambert's law if the jelly absorbs the active rays, but if the jelly does not absorb these rays then the progression of the reaction is proportional to the time. From the experiments on the decomposition of chlorine water it is shown that the photosensitive component is the hypochlorite-ion. Organic jellies are shown to possess a considerable transparency for ultra-violet light, whilst animal membranes allow only a very little of the ultra-violet light to pass through them.

J. F. S.

Photocatalysis. III. The Photosynthesis of Naturally Occurring Nitrogen Compounds from Carbon Dioxide and Ammonia. EDWARD CHARLES CYRIL BALY, ISIDOR MORRIS HEILBRON, and HAROLD JACOB STERN (*T.*, 1923, **123**, 185—197).

Spectrophotoelectrical Sensitivity of Argentite (Ag_2S). W. W. COBLENTZ (*Bull. Bur. Standards*, 1922, **18**, 265—280; *Sci. Paper*, No. 446).—A study of the effect of crystal structure on the photoelectrical sensitivity of silver sulphide. A comparison is made between the results for acanthite (A., 1920, ii, 212), and those now obtained for argentite. Appreciable changes in the electrical resistance of argentite and acanthite occur when these substances are exposed to wave-lengths of light extending from $0.3\text{--}2\ \mu$, maxima being obtained at $1.35\ \mu$ and $0.41\ \mu$. Argentite reacts slightly to radiation of wave-lengths 0.5 to $1.1\ \mu$, whereas acanthite shows a strong photoelectrical sensitivity in this region. The maximum at $1.35\ \mu$ is symmetrical in the former, and unsymmetrical in the latter case. The maximum shifts to short wave-lengths at low temperatures. The photoelectrical reaction of argentite differs from that of acanthite in being free from an induced photonegative polarisation. On increasing the intensity of the radiation, in both cases, a more rapid change is produced in the long wave-lengths than in the short wave-lengths, and the maximum photoelectrical sensitivity is shifted toward the long wave-lengths.

Mechanical working of the crystals of acanthite and argentite lowers the photoelectrical sensitivity. The worked specimens of these minerals give practically identical infra-red maxima at low temperatures, the effect of temperature being less than in the naturally occurring crystals. Thus, apart from the effect of crystal structure, silver sulphide has a characteristic photoelectrical response spectrum. Crystal structure has, however, a marked effect upon photoelectrical sensitivity. W. E. G.

The Excitation of Characteristic X-Rays from Light Elements. J. C. McLENNAN and (Miss) M. L. CLARK (*Proc. Roy. Soc.*, 1923, [A], **102**, 389—410).—Following the method of Hughes (A., 1922, ii, 184), the critical absorption wave-lengths of the *K*- and *L*-series were determined for the elements boron, glucinum, and lithium, and the critical absorption wave-lengths of the *L*-series for carbon. The following values were obtained: carbon, *L*-series, $\lambda=166.7\ \text{\AA}$.; boron, *K*-series, $\lambda=83.6\ \text{\AA}$., *L*-series, $\lambda=292.2\ \text{\AA}$.; glucinum, *K*-series, $\lambda=118.2\ \text{\AA}$., *L*-series, $\lambda=428.1\ \text{\AA}$.; lithium, *K*-series, $\lambda=290.8\ \text{\AA}$., *L*-series, $\lambda=1019.0\ \text{\AA}$. The result for the *K*-series for boron is in good agreement with that obtained by Hughes, but considerable difference occurs between the respective values for the *L*-series. The critical absorption *K*-wave-lengths for lithium represent the first two members of a series with a frequency formula given by $\nu=N(1-1/m^2)$ beginning approximately at $387.7\ \text{\AA}$., and extending to $290.8\ \text{\AA}$. The model of the atom put forward by Bohr makes no provision for this series. The wave-lengths for the *K*-series for glucinum would extend from about $\lambda=157.6\ \text{\AA}$. to $\lambda=118.2\ \text{\AA}$., and the configurations $4_{(3)}\text{--}4_{(2)}$ would appear to provide a spectral series with limits approximating to the above wave-lengths.

For the elements from potassium to glucinum, the square roots

of the critical potentials for the *K*-series are very closely proportional to the respective atomic numbers, but lithium, helium, and hydrogen show a departure from the linear relation. The results however, support the view that the Lyman ultra-violet series for hydrogen is the *K* X-ray series of this element, and also that the convergence wave-length of the *K*-series for helium is approximately $\lambda=485.5 \text{ \AA}$. The Moseley law which is known to apply for the *L*-series of the heavier elements ceases to apply for elements lighter than argon, but a linear relationship obtained between the atomic numbers of the lighter elements and the exciting voltages of their *L*-series merges into the ordinary Moseley law when the element argon is reached.

W. E. G.

Corpuscular Spectra and the Photoelectric Effect. MAURICE DE BROGLIE and LOUIS DE BROGLIE (*Compt. rend.*, 1922, **175**, 1139—1141).—Whiddington has stated (*Phil. Mag.*, 1922, [vi], **43**, 1126) that corpuscular rays were not observed when $h(\nu-\nu_c)$ is less than $h\nu_c$, ν being the frequency of the exciting radiation and ν_c that of the critical discontinuity *c*. The authors point out that under these conditions the rays are much less easy to obtain. Further, Whiddington's generalisation that the *K*-rays of tungsten do not excite corpuscular rays in the case of elements of atomic number greater than 50 does not appear to hold in the case of barium (Atomic No.=56), where very feeble rays were observed. This was also the case with iodine (Atomic No.=53), but no visible rays were obtained with samarium (Atomic No.=62). The variation in intensity of the corpuscular rays excited by a radiation of frequency ν is calculated; the total energy of the corpuscles composing the ray is $A\nu_c a \frac{\nu-\nu_c}{\nu^4}$ and if ν_c is replaced by its value

as a function of the atomic number, the expression may be regarded as such a function. Brillouin's theory (*Compt. rend.*, 1920, **170**, 274), introducing the idea of thermal agitation on electronic impact, is briefly discussed, and it is stated that its developments are not inconsistent with the experimental results obtained with respect to the photoelectric effect of X-rays.

H. J. E.

Dielectric Constants at the Critical Temperature. W. HERZ (*Z. physikal. Chem.*, 1922, **103**, 269—272).—The author has calculated the dielectric constant of thirty-three liquids at the critical temperature. These substances at ordinary temperature have dielectric constants varying between 81.1 and 1.491. The dielectric constant at the critical temperature ought theoretically to be constant for all substances. The author finds that although the value is not constant it shows a decided tendency toward a constant value; the calculated values vary between 2.40 and 1.17.

J. F. S.

The ϵ and ζ Potential at the Interface Barium Sulphate-Water. A. GYEMANT (*Z. physikal. Chem.*, 1922, **103**, 260—268).—The dependence of the ζ potential of barium sulphate on

the concentration of the barium-ions has been determined by means of *E.M.F.* measurements. The experiments lead to the conclusion that in order to explain the ζ potential, the barium-ions and all other ions present must be taken into account. The observed dependence of the ζ potential on the concentration of barium-ions cannot be deduced from the dependence of the ϵ potential on the barium-ion concentration, when the changes of ϵ are evaluated by the method of Chapman (*Phil. Mag.*, 1913, [vi], **25**, 475), and of Herzfeld (*Physikal. Z.*, 1920, **21**, 28), in which the adsorption is neglected.

J. F. S.

Curves of Electrocapillarity in Non-aqueous Solutions.

H. WILD (*Z. physikal. Chem.*, 1922, **103**, 1—38).—Electrocapillarity curves have been constructed for saturated solutions of potassium chloride, potassium nitrate, mercurous nitrate, and also for nitric acid in each of the two liquid layers of the liquid pairs water and amyl alcohol, phenol, furfuraldehyde, ethyl acetate, ethyl ether, aniline, chloroform, propyl alcohol, and *isobutyl* alcohol, respectively, the whole system in each case being in partition equilibrium. The results show that two such solutions in equilibrium have the same Nernst potential $\pi_1 = \pi_2$ towards a given metal. This equality is true within the limits with which the absolute potential can be deduced from the electrocapillarity curves, that is, 5—10 m.-volts. With the same accuracy, it is deduced that the tension at the interface between the two phases at equilibrium π_3 is zero or smaller than 5—10 m.-volts. This behaviour is true for all the cases examined, and can be held to be a general rule for all solvents, but the generalisation of the rule to all ions would be unsafe, for it is quite possible that the capillary active ions may behave differently in different cases, particularly in those cases where well-marked ion adsorption potentials are shown. In these cases an additional potential difference must be noticed, namely, that due to the partition of the ions.

J. F. S.

Forces at the Boundary between Phases. EMIL BAUER (*Z. physikal. Chem.*, 1922, **103**, 39—42).—A theoretical paper in which, on the basis of the experiments of Wild (cf. preceding abstract), the author discusses the origin of the potential difference at the boundary between two liquid phases. In an earlier paper (A., 1916, ii, 231), the author expressed the view that the potential difference was due to ion adsorption, whilst Beutner (A., 1918, ii, 214; 1919, ii, 263) maintains that a partition of the ions between the phases is the cause. The author now shows that his view is supported by the electrocapillarity measurements of Wild.

J. F. S.

Theory of Electrocapillarity. I. Electrocapillary Phenomena in Non-aqueous Solvents. A. FRUMKIN (*Z. physikal. Chem.*, 1922, **103**, 43—54).—Curves of electrocapillarity have been determined for 0.1*N*- and *N*-ammonium nitrate, *N*-sodium bromide, and *N*-sodium iodide in methyl alcohol, 0.2*N*-ammonium

nitrate, *N*-lithium chloride, and *N*-sodium iodide in ethyl alcohol, *N*-lithium chloride in mixtures of ethyl alcohol and water, 0.9*N*-lithium nitrate, 0.5*N*-lithium chloride, and *N*-ammonium thiocyanate in acetone, *N*-ammonium thiocyanate and 1.6*N*-sodium iodide in pyridine. The results show that the activity of the anion in these solutions manifests itself in exactly the same way as in aqueous solutions. The maximum in these solutions, when compared with aqueous solutions of corresponding composition, is found to be displaced to the left, that is, it corresponds with a smaller cathodic polarisation.

J. F. S.

Theory of Electrocapillarity. II. A. FRUMKIN (*Z. physikal. Chem.*, 1922, **103**, 55—70; cf. preceding abstract).—It is shown that the whole of the electrocapillary phenomena are governed by the equation $d\gamma = e d\phi - \sum \Gamma_i d\mu_i$, where γ is the thermodynamic potential in the solution containing μ_i ions, ϕ is the potential difference of solution/metal, and Γ_i the number of ions which must be added to the solution so that μ_i remains constant when the surface of the metal is increased by a unit. The values of $d\gamma/d\phi$ and E , the quantity of electricity combined with Γ_i ions, have been determined experimentally for 2*N*-sulphuric acid saturated with mercurous sulphate, E (calc.) 39×10^{-6} coul./cm.², E (obs.) 39×10^{-6} coul./cm.²; *N*-sodium chloride saturated with mercurous chloride, E (calc.) 50×10^{-6} coul./cm.², E (obs.) 47×10^{-6} coul./cm.²; *N*-potassium hydroxide saturated with mercuric oxide, E (calc.) 21×10^{-6} coul./cm.², E (obs.) 17×10^{-6} coul./cm.²; *N*-potassium nitrate and 0.01*N*-potassium iodide saturated with mercurous iodide, E (calc.) 86×10^{-6} coul./cm.², E (obs.) 90×10^{-6} coul./cm.², with the results stated. It is shown that the Lippmann-Helmholtz differential equation for solutions is true both for those with normal electrocapillarity curves and for those with abnormal curves. The potential of a dropping electrode always coincides with the value given by the corresponding electrocapillarity curve. A potential difference exists between mercury on the one hand and water, methyl alcohol, ethyl alcohol, and acetone on the other when the surface layer contains either ions or adsorbed molecules of a dissolved substance. In investigations of the present type, it is necessary to differentiate between thermodynamic and electrocapillary solution tensions.

J. F. S.

Decomposition Tensions of Fused Mixtures of Sodium Hydroxide with Zinc Oxide or Cadmium Oxide. L. ROLLA and R. SALANI (*Gazzetta*, 1922, **52**, 286—313).—Experiments similar to those of Sacher (*A.*, 1902, ii, 120) have been made on mixtures of molten sodium hydroxide with zinc oxide or cadmium oxide. Fused sodium hydroxide shows two points of cathodic decomposition, the lower one, 1.20 volts, corresponding with the discharge potential of the hydrogen-ions; the higher point, corresponding with the discharge potential of the sodium-ions, has the value 2.08 volts at 460°, 2.13 volts at 412°, and 2.24 volts at 364°. With the mixtures containing zinc or cadmium oxide, the decom-

position occurring is that of zinc or cadmium hydroxide, the decomposition tensions for the zinc- and cadmium-ions being, respectively, 1.80 and 0.89 volts.

T. H. P.

The Electrolytic Dissociation of Dibasic Acids. Determination of the Second Dissociation Constant of Acids from Electrometric Measurements. ERIK LARSSON (*Z. anorg. Chem.*, 1922, **125**, 281—294).—The author applies the theory of Bjerrum (A., 1919, ii, 9) to the ionic equilibria in a solution which contains the neutral salt and the free dibasic acid. He shows how the second dissociation constant can be calculated from the hydrogen-ion activity measured electrometrically. The results obtained agree well with some earlier results obtained by the conductivity method.

W. T.

Formic Acid. II. Electrolytic Dissociation of Formic Acid. FR. AUERBACH and H. ZEGLIN (*Z. physikal. Chem.*, 1922, **103**, 178—199).—The electrical conductivity of formic acid and of sodium formate has been determined over a wide range of concentration at 18°. It is shown in agreement with earlier investigators that small quantities of formic acid and sodium formate are decomposed at the platinised electrodes. The decomposition has been investigated and in the case of the formate shown to consist in an oxidation to sodium hydrogen carbonate and to be due to the oxygen occluded in the platinised electrodes. This disturbing factor may be removed by suitable treatment of the electrodes with hydrogen before the measurements. The limiting value of the molecular conductivity of sodium formate at 18° is extrapolated to 91, and from this value the limiting value for formic acid is calculated to be 362.5. The dissociation constant for formic acid is shown to be inconstant and to vary with increasing dilution from 2.05×10^{-4} to 1.91×10^{-4} , and this difference is shown not to be due to experimental error. Formic acid belongs, therefore, to the acids of medium strength which do not follow the law of mass action closely. Values have been calculated for the electrical conductivity of formic acid which agree with the experimental values exactly, over the whole range of concentration, on the basis of Ghosh's hypothesis.

J. F. S.

The Anomaly of Strong Electrolytes. HENRY J. S. SAND (*Phil. Mag.*, 1923, [vi], **44**, 129—144).—A critical examination of the theories of Ghosh (A., 1918, ii, 215, 348, 392, 790), and of Milner (A., 1918, ii, 148). Employing the Boltzmann theorem and the Born theory of the potential energy of a pair of attracting ions, estimations are made of the degree of association of a completely ionised electrolyte immersed in a medium of uniform dielectric constant. It is shown that the probability of the two ions of a binary electrolyte (*N*/10-solutions) being in contact in a given small volume is only 8.1 times as great as the probability of their occurrence in any two volumes of the same size so situated that the attraction between the ions is negligible. The hypothesis of complete ionisation in the case of salts like sodium chloride is

thus completely established. It is shown that a preponderating proportion of the ions will be subject to the inverse square law of electrical action.

The relation $PV=2RT-\frac{1}{3}RT\bar{h}f(h)$ obtained by Milner from the Clausius' virial theorem can have only approximate validity. The Ghosh theory of the "crystalline" arrangement of the ions in aqueous solutions is criticised, and it is concluded that the space lattices in this theory are merely theoretical "distributions of reference." The deductions from Ghosh's and Milner's osmotic pressure formulæ are compared with the experimental results. The agreement between the mean experimental values of $(2-i)$ for univalent binary chlorides in aqueous solutions and the same value derived from Ghosh's formula is good; the agreement at the higher concentrations is better than that attained by Milner's theory.

W. E. G.

Relationship between the Specific Heat of Liquids. W. HERZ (*Z. anorg. Chem.*, 1922, **125**, 295—300).—A theoretical paper. It is shown that the specific heats of liquids at two-thirds their critical temperature divided by the values at one-half the critical temperature gives a fairly constant value. This constant for the twenty organic liquids quoted is about 0.8. Liquids in a homologous series show an increase of about 9 for the introduction of a CH_2 group, but with aniline-dimethylaniline there is an exception, the difference being very small; in this series, the specific heat decreases with increasing molecular weight. In homologous series, the molecular heat of evaporation increases about 10 for each CH_2 group, but there are many exceptions. The introduction of a chlorine atom in place of a hydrogen atom increases the molecular heat of evaporation by about 9.5 units, the introduction of a second chlorine atom has a less effect. A double bond lowers it by about two units.

W. T.

[Determination of Boiling Points.] Boiling Points of Ammonia, Sulphur Dioxide, and Nitrous Oxide. F. W. BERGSTROM (*J. Physical Chem.*, 1922, **26**, 876—894).—A comparison has been made of the efficiency of single-walled and vacuum-jacketed boiling vessels. It is found that the boiling point of ammonia, determined in a single-walled vessel, is about 0.2° high, even with internal electrical heating. Determination in a Cottrell tube reduces this error. Boiling points may be determined accurately in a vacuum-jacketed vessel at temperatures as low as -90° , but in such cases a correction should be applied for the depth of immersion of the bulb, and there should be no uncooled stem. The Cottrell apparatus can be used successfully at temperatures at least as low as -33.4° . Better equilibrium between vapour and liquid is obtained and uncertain temperature corrections are eliminated by using this apparatus, and a smaller quantity of liquid is generally required. The following boiling points have been determined at 760 mm.: ammonia, $-33.41^\circ \pm 0.1^\circ$, sulphur dioxide, $-10.02^\circ \pm 0.1^\circ$, and nitrous oxide, $-89.5^\circ \pm 0.2^\circ$.

J. F. S.

Application of the Method of Continuous Variations to Ebullioscopic Phenomena for the Determination of Double Salts in Solution. F. BOURION and E. ROUYER (*Compt. rend.*, 1922, **175**, 1406—1408).—The method of continuous variations as applied to ebullioscopic measurements was tested in the case of solutions of cadmium chloride with potassium chloride and ammonium chloride, respectively, and solutions of cadmium iodide with potassium iodide, and found to give quite as satisfactory results as when applied to cryoscopic measurements. W. G.

A Micro-method for the Determination of Molecular Weight in a Melting-point Apparatus. II. Determinations with Extremely Minute Quantities. KARL RAST (*Ber.*, 1922, **55**, [B], 3727—3728).—The author has succeeded in further refining his micro-method for the determination of molecular weight in freezing camphor to such an extent that it is possible to obtain accurate results with scarcely visible amounts of substance. The capillary tube is slightly conical in shape, and rather wider (2—3 mm.) than those recommended previously; it is essential that it should be very thin in the wall and that the bottom should be hemispherical. The solutions are prepared in the capillary itself, the substance under investigation being first introduced and subsequently the camphor. The materials are pressed together by a small glass rod. The capillary is sealed and subsequently drawn out to a long thread, by means of which it is attached to the thermometer. Mixing of the components is effected by melting and re-solidification. The column in the capillary must not be more than 2 mm. in height so that in general 0.2—0.3 mg. of substance and 2—3 mg. of camphor are required. It is essential to guard against undue concentration of the solutions, which, however, may sometimes be greater than normal. H. W.

The Influence of the Velocity of Cooling on the Hardness and Microstructure of Eutectic Mixtures. N. S. KURNAKOV and A. N. ACHNASAROV (*Z. anorg. Chem.*, 1922, **125**, 185—206).—The hardness of eutectic mixtures increases with the rate of cooling and with the degree of fineness of the grains. This tendency to increase in hardness decreases with increasing brittleness, e.g., zinc-antimony. Increasing fineness of grains also results in increasing passivity of the alloy. Homogeneous phases of pure metal and solid solutions show no change in hardness on rapid cooling. The above conclusions were obtained from a study of the systems cadmium-silver, silver-copper, gold-nickel, zinc-antimony. W. T.

General Theory of the Adsorption of Solutions. BROR. GUSTAFVER (*Kolloid Z.*, 1922, **31**, 358—362).—A theoretical paper in which the author criticises the views put forward on the adsorption of solutions by Ostwald and Izaguirre (*A.*, 1922, ii, 480). It is shown that the theory is not in keeping with the author's results on the sorption of vapours by charcoal (*A.*, 1922, ii, 479), neither is

it in keeping with respect to the thickness of the adsorbed layer as determined by the author and others. J. F. S.

Adsorption of Ions by Freshly Precipitated Manganese Dioxide. P. B. GANGULI and N. R. DHAR (*J. Physical Chem.*, 1922, **26**, 836—844).—The authors have investigated the adsorption of kations by manganese dioxide, and also the effect of various anions on the adsorption. Manganese dioxide was prepared in the solution of ions under investigation by the addition of equivalent quantities of potassium permanganate and manganous sulphate and the amount of adsorption determined by analysing the filtered solution after equilibrium had been reached. Some thirty-five salts have been used in the investigation, and the results show that the coagulating powers of the different electrolytes as calculated from the percentage of kation adsorbed from approximately normal solutions of the electrolytes follow the Schulze-Hardy law very imperfectly. The effect of the anions on the adsorption of kations by manganese dioxide is found to be very marked. There is, however, no regularity in the variations shown by the adsorption values of the kations with variation of the anion. In the case of ferric salts, the adsorption of ferric-ions by manganese dioxide is abnormally large; a result which is probably to be attributed to a partial hydrolysis of the ferric salt with the separation of ferric hydroxide. Among the electrolytes of metals occurring in the same group of the periodic system, the values of the percentage adsorption are generally found to be in the order of the atomic weights of the kations. J. F. S.

Physical Chemistry of Dyeing. Acid and Basic Dyes. T. R. BRIGGS and ARTHUR W. BULL (*J. Physical Chem.*, 1922, **26**, 845—875).—The process of dyeing wool with acidic and basic dyes has been investigated from the point of view of the adsorption hypothesis as formulated by Pelet-Jolivet and Bancroft (*Applied Colloid Chemistry*, 1921, 115). The effect of dyes on the adsorption of acids by wool and of acids on the adsorption of dyes has been determined quantitatively for typical acid dyes. It is shown that the taking up of dyes is a case of adsorption and that the amount of dye adsorbed varies continuously with a change in the hydrogen-ion concentration of the dye-bath. No evidence of chemical action between dyes and wool has been obtained. J. F. S.

The Determination of the Dissociation Pressures of Hydrated Salts by a Dynamical Method. II. JAMES RIDDICK PARTINGTON and DONALD BENNETT HUNTINGFORD (*T.*, 1923, **123**, 160—170).

A New Explanation of Diffusion. ALEXANDR BATĚK (*Chem. Listy*, **16**, [9], 295—299).—Fick's theory for the diffusion of liquids (*Ann. Phys. Chem.*, 1855, [ii], **94**, 59) is discussed, and its experimental basis questioned. Certain discrepancies between

the results calculated on this theory and those obtained experimentally by Voit (*Ann. Phys. Chem.*, 1867, [ii], 130) are pointed out. The technique of optical methods for the determination of rates of diffusion is examined, and possible sources of error are suggested. Weber's confirmation (*Ann. Phys. Chem.*, 1870, [iii], 7, 469, 536) of the applicability of Fourier's law to the diffusion of liquids is shown to be doubtful, and the necessity for a reconsideration of the whole question emphasised. The mechanism of the diffusion of liquids is then discussed from first principles, and the use of the conception of limiting states of solutions in helping to elucidate the problems of diffusion of liquids is substantiated.

R. T.

Diffusion in Solid Solutions. H. WEISS and P. HENRY (*Compt. rend.*, 1922, 175, 1402—1405).—A study of the interpenetration, by diffusion, of gold and silver at the temperatures 935°, 885°, and 835° shows that the form of the law of diffusion in fluids is valid. The values of the constant K at the temperatures used, when interpolated to 870°, give a value 0.0000375, which is in very close agreement with the value obtained by Fraenkel and Houben (*A.*, 1921, ii, 491).

W. G.

Process of Diffusion in Gelatin. Liesegang's Phenomenon. CARL ADOLF SCHLEUSSNER (*Kolloid Z.*, 1922, 31, 347—352).—With the object of employing the diffusion into gelatin as a means of testing the suitability of various specimens of this substance for use in the manufacture of photographic plates, the author has examined the conditions under which the Liesegang rings are produced. It is shown that for a regular and uniform diffusion the gelatin must be in a uniform condition. The necessary condition can only be obtained after the gelatin has been held in solution for at least twenty-four hours. It is shown that from the character of the ring formation conclusions may be drawn as to the purity of the gelatin. The intermediate rings which may be observed with a lens between the main rings are shown to be silver salts of phosphoric and halogen acids and are due to impurities in the gelatin. A bibliography of the work on the formation of Liesegang rings and allied phenomena is included in the paper. J. F. S.

The Relation between the Crystal Structure and the Constitution of Carbon Compounds. I. Compounds of the Type CX_4 . ISABEL ELLIE KNAGGS (*T.*, 1923, 123, 71—79).

Double Compounds and Mixed Crystals. Racemates and Pseudo-racemates. PHILIPPE LANDRIEU (*Bull. Soc. chim.*, 1922, [iv], 31, 1217—1241).—Lectures delivered at the Collège de France. G. F. M.

Hydrogen-ion Concentration and the Properties of Emulsoid Colloids. ROBERT HERMAN BOGUE (*J. Physical Chem.*, 1922, 26, 801—811).—A theoretical paper in which it is shown that the various physical properties of the emulsoid colloids, including

the viscosity, jelly strength, melting point, and joining strength, are at a minimum at a hydrogen-ion concentration corresponding with the isoelectric point. As the acidity or alkalinity of the solution is increased from this point, the whole of these properties increase in value. It is shown that salt precipitations for gelatin contents should be made at the isoelectric point if the maximum precipitation is to be obtained. The necessity for a careful control of the hydrogen-ion concentration in investigations on the proteins is emphasised, and the desirability of a similar control in the gelatin and glue plant during manufacture is also pointed out. The limitation of the benefit obtainable from such control, however, makes the practicability of such methods, when applied to the improvement of the quality of the material, very questionable. The estimation of the hydrogen-ion concentration is urged as a test in the evaluation of gelatin and glue, but it is not recommended that all tests of viscosity, jelly strength, and joining strength be made at a specified hydrogen-ion concentration. J. F. S.

Present Position of the Theory of Peptisation. W. MOELLER (*Z. Leder Gerb. Chem.*, 1922, **1**, 360—376; cf. A., 1915, i, 439).—A theoretical paper in which the author discusses the theory of peptisation, particularly in connexion with its application to tanning and the leather industry. It is shown that the mechanism of tanning consists in the destruction of the sol-condition of the peptised solution by the substance of the hide. The hide substance removes the sol by adsorbing the peptising agent, and the separated coagulated oil surrounds the micellæ of hide to form micro-crystals. The author defines tan as a system which of itself is quite insoluble, but by peptisation may be converted into a colloidal solution. Leather is defined as an animal hide the elementary particles of which are crystalline micellæ protected by a sheath of tan particles from hydrolytic influences. J. F. S.

Protective Colloids. XII. Gelatin as a Protective Colloid.
III. Colloidal Platinum. A. GUTBIER and A. ZWEIGLE (*Kolloid Z.*, 1922, **31**, 346—347; cf. A., 1922, ii, 485).—Solid platinum colloids may be prepared by reducing chloroplatinic acid in aqueous chloroform solution by means of hydrazine hydrate in the presence of solutions of gelatin. When five parts of a 1% solution of chloroplatinic acid in water saturated with chloroform is mixed with five parts of 0.14% gelatin solution and slowly reduced by the addition of 0.1% solution of hydrazine hydrate, a colloidal solution which is black by transmitted light and dark brown by reflected light is produced. This sol on keeping deposits a small quantity of a black powder, and on dialysis yields a very stable sol. The black precipitate is reversible to the extent of about 70%. The sol is stable towards heat and quite insensitive to electrolytes which are capable of producing an hydroxyl-ion. Solutions of neutral salts coagulate the sol only after keeping for several days, whilst acids, even in dilute solution, produce a rapid coagulation. On evaporation at 27° in a vacuum over sulphuric acid, a solid

colloid is obtained which is completely reversible in cold water and contains 18.76% of platinum. When the quantities of the reagents employed are one part of 0.14% gelatin, five parts of 0.1% solution of chloroplatinic acid, and four parts of chloroform water, the solid sol obtained by the same process is also completely reversible to form stable secondary sols in dilute solution, and the solid itself contains 55.67% of platinum. J. F. S.

Validity of the Law of Mass Action for Ionic Equilibria.

J. N. BRÖNSTED and KAI PEDERSEN (*Z. physikal. Chem.*, 1922, **103**, 307—315).—The reaction between ferric chloride and potassium iodide has been investigated in aqueous solution at 25°, and from the results it is shown that the law of mass action is valid for ionic equilibria when these are set up in concentrated salt solutions as solvents. A convenient method for determining solubility in the absence of air is described and used to determine the dissociation constant of the tri-iodide-ion. The value for the equilibrium constant of the dissociation $I_3' \rightleftharpoons I_2 + I'$ at 25° is 0.00611, at 15.0°, 0.00502, and at 18.5°, 0.00540. J. F. S.

Formic Acid. III. Partition of Formic Acid between Ether and Water and its Application to Analytical Purposes.

FR. AUERBACH and H. ZEGLIN (*Z. physikal. Chem.*, 1922, **103**, 200—237).—The partition coefficient of formic acid has been determined at 18° for ether and water, 0.5*N*-sulphuric acid, and 0.5*N*-sulphuric acid containing 100 g. of sodium chloride per litre, respectively. In the case of ether and water, the coefficient was determined for concentrations up to 1 mol. per litre, and in spite of corrections for the electrolytic dissociation of the formic acid in water the partition coefficient of the undissociated acid was found to be inconstant, but to vary in a linear manner with the concentration in the aqueous phase; the value $f = C_a/C_w$ varies from 0.395 for $C_w = 0.0446$ to 0.454 for $C_w = 1.343$. In the case of ether and 0.5*N*-sulphuric acid, in which the electrolytic dissociation in the aqueous phase is practically zero, the partition is displaced in favour of the ether layer, but here also the coefficient is dependent on the concentration of the aqueous layer. Sulphuric acid containing sodium chloride gave similar results to the acid and ether alone. The progression of the partition coefficient is explained by the polymerisation of the formic acid in ethereal solution. From the law of mass action the extent of the polymerisation is calculated on the assumption of double molecules by means of the formula $x = [(HCO_2H)_2]/[HCO_2H]^2$; the following values of x are obtained: for ether saturated with water, $x = 0.139$; for ether saturated with 0.5*N*-sulphuric acid, $x = 0.147$, and for ether saturated with 0.5*N*-sulphuric acid containing 100 g. of sodium chloride per litre, $x = 0.158$. The small differences in the polymerisation constant are due to the varying water content of the aqueous phase. The true partition coefficients have been calculated from the above-mentioned quantities and the experimental results. The partition coefficient of undissociated unimolecular formic acid

at 18° has the following values : between ether and water, $f_0=0.393$; between ether and 0.5*N*-sulphuric acid, $f_0=0.398$, and between ether and 0.5*N*-sulphuric acid containing 100 g. of sodium chloride per litre, $f_0=0.400$. For the purpose of applying the partition coefficient to analytical purposes, the volume changes of the phases when ether is shaken with water or *N*/2-sulphuric acid solution were either determined or taken from the unpublished work of Mylius. By means of the volume correction factor and the partition coefficient, the concentration of formic acid in a 0.5*N*-aqueous sulphuric acid solution may be calculated from the concentration in the ethereal layer after shaking the sulphuric acid solution with ether. Equations for this calculation have been derived, and tables of numerical factors are given in the paper. Formic acid in 0.5*N*-sulphuric acid solutions may be estimated by this method for amounts of formic acid between 2.4 g. and 0.011 g. with an average error of 0.38%. If the sulphuric acid also contains 100 g. of sodium chloride per litre, the average error of the estimations is 0.26%.

J. F. S.

Velocity Law of Unimolecular Reactions. J. A. CHRISTIANSEN (*Z. physikal. Chem.*, 1922, **103**, 91—98).—A theoretical paper in which on the assumption that only molecules in a definite quantic condition react, the author has developed a velocity formula for reactions of the type $AB \rightarrow A+B$. The equation deduced has the form $k=(p_m/p_n)e^{-(\epsilon_m-\epsilon_n)/RT} \cdot \nu'/(1-e^{-h\nu'/RT})$, where k is the velocity constant, p_m and p_n are the a priori probabilities, respectively, that the molecules are in the m -quantic or normal condition when the m -quantic condition is that necessary for reaction; the other symbols have their usual significance; those with the dash, such as ν' , refer to the products of the reaction. The author shows that when $h\nu'/RT$ is small the equation reduces to the form $k=(p_m/p_n) \times e^{-(\epsilon_m-\epsilon_n)/RT} \cdot RT/h$, which is practically the same as the expression deduced by Herzfeld (*A.*, 1922, ii, 136) from Stern's expression for unimolecular reactions. When $h\nu'/RT$ has a comparatively large value, the expression reduces to $k=(p_m/p_n) \cdot e^{-(\epsilon_m-\epsilon_n)/RT} \times \nu'$ which is the same as the expression obtained by Dushman (*A.*, 1921, ii, 315).

J. F. S.

Thermal Decomposition of Carbonyl Chloride. J. A. CHRISTIANSEN (*Z. physikal. Chem.*, 1922, **103**, 99—138).—The thermal decomposition of carbonyl chloride, both alone and mixed with chlorine, has been investigated at a number of temperatures between 655° and 782° absolute. The results indicate that over the range of temperature 705—745° Abs. the reaction takes place according to the equation $h=k\sqrt{C_{Cl_2}}(C_{COCl_2}-\xi)$, where h is the velocity, k a constant, and $\xi=C_{CO} \cdot C_{Cl_2}/K$, K is the equilibrium constant of the reaction $COCl_2 \rightleftharpoons CO+Cl_2$. The equation only holds when the concentration of the carbonyl chloride, carbon monoxide, and chlorine are of the same order (10^{-3} — 10^{-4} mol./litre). At the commencement of the reaction, that is, until the above condition obtains, the divergences from the equation are always positive,

in the sense that the observed velocity is always greater than the value calculated according to the above equation. The velocity is not markedly affected by a change in the relative glass surface in the ratio 50/38. The velocity is unaffected by the presence of air when the concentrations of carbon monoxide and chlorine are considerable from the commencement of the reaction. When it is assumed that the expression for the velocity does not change with temperature, the value of the constant k can be found by means of the expression $\log k = -11420/T + 15.154$ for the temperature range 685—782°. An experiment at 655° was found to be less exact, but it agreed with the above expression within the limits of the experimental error.

J. F. S.

The Velocity of Reaction in Mixed Solvents. IV. The Influence of the Base on the Velocity of Saponification of Esters. ALBERT ERIC CASHMORE, HAMILTON MCCOMBIE, and HAROLD ARCHIBALD SCARBOROUGH (T., 1923, 123, 197—207).

Chemical Kinetics of Heterogeneous Systems. IV. The Mechanism of Chemical Reaction, when Noble Metals Dissolve in Potassium Cyanide Solution. EIICHI YAMAZAKI (*J. Chem. Soc. Japan*, 1922, 43, 686—690).—According to Bodländer (*Z. anorg. Chem.*, 1896, 19, 583), gold and other noble metals dissolve in potassium cyanide solution owing to the catalytic action of hydrogen peroxide produced as an intermediate; but this explanation and Bodländer's formulæ cannot explain the author's experiences. The reaction velocity is approximately proportional to the square root of the concentration of oxygen, but not to the concentration itself. The production of hydrogen peroxide is a secondary reaction, which may, of course, accelerate the dissolution of the metals and produce the peroxides, when Ba^{++} or Ca^{++} are present in the solution. When the dissolution of the metal is normal, the reaction proceeds as follows: $Ag = Ag^+ + \ominus$; $O + 2\ominus \rightarrow O''$; $H_2O + O'' \rightarrow 2OH'$; or $2Ag + H_2O + \frac{1}{2}O_2 = 2Ag^+ + 2OH'$, etc.

K. K.

Some Properties of the Active Nickel used as Catalyst in Organic Chemistry. ANDRÉ BROCHET (*Compt. rend.*, 1922, 175, 1073—1075; cf. this vol., ii, 18).—The pyrophoric property of nickel prepared for use as a catalyst is entirely due to occluded hydrogen, and if the metal is freed from that gas under conditions which maintain in the nickel the property of being readily transformed into oxide, its catalytic activity remains unimpaired. There is no relation between the pyrophoric condition and the catalytic efficiency, although the extent of the former is a convenient indication of the progress of the preparation of the catalyst. Catalytic nickel if washed and dried loses its pyrophoric property; in cases in which the catalytic activity is affected by this operation, it may be restored by heating for a short time in hydrogen. The author appends a brief discussion, from the point of view of employment as a catalyst, of the extent and condition of the metallic surface and the property of occluding hydrogen.

H. J. E.

Catalytic Hydrogenation with Nickel. Factors Determining Catalytic Activity. R. THOMAS (*J. Soc. Chem. Ind.*, 1923, 42, 21—26r).—A description is given of some of the methods which may be employed for the preparation of catalytically active nickel, and the relative activities of variously prepared nickel catalysts in the hydrogenation of oils have been determined. The most active catalyst was that obtained by the reduction by means of hydrogen at 350—500° of nickel hydroxide precipitated on kieselguhr. A nickel catalyst prepared by reduction with charcoal at 600°, or by electrical disintegration, or by the decomposition of nickel carbonyl was less than one-fourth as active, whilst nickel precipitated from its salts by means of aluminium showed only about one-sixth of the activity. The author concludes with a theoretical discussion as to what are ultimate factors which influence catalytic activity, and what form of energy transference occurs between the catalyst and reacting substances. It is suggested that the catalyst activates a certain number of molecules of the reactants by thermionic emission, and that the bulk of the molecules are then successively activated by electron emission from molecules already in an activated condition through the instrumentality of the catalyst. G. F. M.

Heterogeneous Catalysis and the Orientation of Adsorbed Molecules. H. R. KRUYT and C. F. VAN DUIN (*Proc. K. Akad. Wetensch. Amsterdam*, 1923, 25, 324—326).—In continuation of previous work (A., 1921, ii, 392), the authors find that the reaction between aqueous solutions of dibromosuccinic acid (meso- or racemic form) and potassium iodide is considerably accelerated in the presence of charcoal. The greater acceleration occurred in the case of the meso-form, a result in accord with stereochemical considerations. The result confirms the conclusion that positive contact catalysis is to be anticipated only when the reacting group of molecules is directed away from the adsorbent and towards the surrounding medium. J. S. G. T.

A Type of Ideal Electric Atoms. J. L. (*Nature*, 1922, 110, 873).—The mathematical solutions arrived at by Hargreaves (this vol., ii, 19) give a possible structure for an ideal atomic nucleus of the Rutherford type. A. A. E.

Speculation Concerning the Positive Electron. HORACE H. POOLE (*Nature*, 1923, 111, 15—16).—Lodge's speculation (A., 1922, ii, 836) is examined from the point of view of the relative abundance of the lighter and heavier elements, the case of hydrogen being considered in particular. An immense discrepancy is apparent. Doubtless, some negative protons would combine with previously formed positive complexes, but since about half the complex nuclei first formed would be negative, so that some of the positive protons would be lost by combination with them, these effects would be expected to balance approximately. If, however, it is assumed that when two unequal nuclei combine, the

sign of the combination is determined by that of the larger constituent, it is conceivable that if the first set of nuclei formed happened to be positive, they might so direct the course of subsequent events as to lead to the existing distribution of the elements. A. A. E.

A Laboratory Apparatus for Rapidly Drying Sensitive Organic Substances. J. BOUILLOT (*J. Pharm. Chim.*, 1923, [vii], 27, 23—28).—A tube of glass, 15 cm. long and 30 mm. wide, sealed at one end and fitted with a heat-resistant cork at the other, carries the substance to be dried in a boat. The tube has two slightly narrower tubes attached vertically to its upper surface by narrow necks containing plugs of cotton wool, and in the openings of these tubes are fitted corks carrying narrow glass tubing terminated inside, by being drawn out, in narrow hooks, so as to avoid violent currents of air impinging on the boat below. The whole apparatus can be immersed in an air-bath at the required temperature, and currents of dried air can be aspirated over the contents of the boat at any required pressure. H. K.

A Simple Check Valve. J. F. BREWSTER (*J. Ind. Eng. Chem.*, 1923, 15, 32).—A solid rubber stopper is cut about three-quarters through at the small end so that a thin flap of rubber is left to serve as the valve leaf. The stopper is then bored, leaving the flap intact, to receive a short length of glass tubing which is pushed through to within a few mm. of the valve seating. A piece of glass tubing of such diameter as to allow free play of the valve flap, but at the same time to fit the stoppers tightly, is closed at one end by the valve stopper and at the other by a one-hole stopper. The contrivance will allow the passage of air or liquid from the direction of the valve stopper to the one-hole stopper, but not in the reverse direction, and is useful for preventing, amongst other things, a "suck back" of water from a water vacuum pump into the apparatus during a vacuum distillation, etc. G. F. M.

Inorganic Chemistry.

A Convenient Method for the Preparation of Aqueous Hydrobromic Acid of Constant Boiling Point. J. G. F. DRUCE (*Chem. News*, 1923, **126**, 1).—The method described by Pickles (A., 1919, ii, 411) gives rather a dilute acid, and the distillation is difficult to carry out without “bumping” taking place. The following modification obviates the latter difficulty and gives a distillate containing more than 48% of hydrogen bromide: 10 c.c. of strong sulphuric acid are added to a solution of 15 g. of potassium bromide and 0.2 g. of stannous chloride in 25 c.c. of water. After remaining over-night, the clear liquid is decanted from the crystals of potassium hydrogen sulphate which have

separated, and distilled, the fraction coming over between 120° and 125° being collected. The yield is more than 90% of the theoretical, and the product contains only a trace of chlorine.

A. R. P.

The Structure of the Sulphur Dioxide Molecule. A. O. RANKINE and C. J. SMITH (*Proc. Physical Soc.*, 1922, **35**, 33—38).—The authors' method of determination of the molecular dimensions of gaseous molecules from viscosity measurements (A., 1921, ii, 192) has been employed to decide between the relative merits of two formulæ for sulphur dioxide. That proposed by Langmuir, $\text{O}=\text{S}=\text{O}$, should possess the dimensions of a neon-argon-neon complex with the components arranged in a line, or arranged so that the lines joining the neon to the argon atoms make an angle of 135°. The calculated mean collision area of this model is considerably in excess of that deduced from viscosity measurements, 0.94×10^{-15} cm.². On the other hand, the calculated value for $\text{S} \begin{smallmatrix} \text{O} \\ \diagup \diagdown \\ \text{O} \end{smallmatrix}$ is 0.99×10^{-15} cm.², which is in much closer agreement with experiment.

W. E. G.

Formation of Sulphur Dioxide from the Sulphates of the Alkaline Earths and Iron or Iron Sulphide. F. MARTIN and O. FUCHS (*Z. anorg. Chem.*, 1922, **125**, 307—348).—The authors found that the alkaline sulphates on being heated with metallic iron are completely reduced to the sulphides; this reduction begins at temperatures lower than that required in the case of coal. The reduction is complete in half an hour at 750° for calcium sulphate, at 850° for strontium sulphate, and at about 950° for barium sulphate. In the presence of insufficient iron and at about 150° higher, a rapid evolution of sulphur dioxide takes place. The best conditions for this are, for calcium sulphate the mixture $16\text{CaSO}_4 + 15\text{Fe}$, giving 80% of the theoretical yield of sulphur dioxide; for strontium sulphate the mixture $9\text{SrSO}_4 + 8\text{Fe}$, giving an 88.9% yield. These reactions lead to the formation of well defined ferrites, $3\text{CaO} \cdot 2\text{Fe}_2\text{O}_3 = \text{Ca}_3\text{Fe}_4\text{O}_9$; $2\text{SrO} \cdot \text{Fe}_2\text{O}_3 = \text{Sr}_2\text{Fe}_2\text{O}_5$, and $\text{BaO} \cdot \text{Fe}_2\text{O}_3 = \text{BaFe}_2\text{O}_4$. Too little iron leads to the formation of alkaline-earth sulphide, too much iron gives also iron sulphide. Sulphur dioxide is also evolved by heating the alkaline-earth sulphates with iron sulphide; this can be carried out commercially by using pyrites to which has been added a little iron oxide.

W. T.

Catalytic Hydrogenation of Sulphurous Anhydride. (MLLE) MARGARET G. TOMKINSON (*Compt. rend.*, 1923, **176**, 35—36).—When a mixture of dry sulphur dioxide and dry hydrogen is passed over finely divided nickel or over nickel sulphide at 400—450°, a mixture of water vapour, hydrogen sulphide, and sulphur is obtained, and if the gases are passed sufficiently slowly the whole of the sulphur dioxide is decomposed. Cobalt sulphide, and, to a lesser degree, ferrous sulphide, may also be used as catalysts for the hydrogenation.

W. G.

Preparation of Sulphuryl Chloride. LÉONCE BERT (*Bull. Soc. chim.*, 1922, [iv], **31**, 1264—1270).—Ruff's method (A., 1902, ii, 13), consisting in boiling chlorosulphonic acid with about 1% of mercury or mercuric sulphate, is the most practical process for the laboratory preparation of sulphuryl chloride, the operation being conducted under a reflux condenser kept at about 70°, in order to return unchanged chlorosulphonic acid to the flask. For the successful conduct of the process, attention must be directed to the following important, but hitherto unpublished, points. To prevent risk of fracture, the tube of the reflux condenser should be of iron connected with the neck of the flask with a stopper of asbestos paper and silicate cement, which resists the action of chlorosulphonic acid admirably. The top of the iron tube is connected by means of asbestos thread and silicate to a short glass tube leading to a condenser and receiver for the sulphuryl chloride. The reaction does not proceed so rapidly as Ruff asserted (*loc. cit.*), and slows down considerably in the latter stages. In one hour a 40% yield, in three hours 60%, and six hours 75·8% yield was obtained, and for this reason, when considerable quantities of sulphuryl chloride are required, it is preferable to collect for one hour only and then change the flask for another containing a fresh charge of chlorosulphonic acid. The latter is conveniently obtained by saturating 70% fuming sulphuric acid with hydrogen chloride, and distilling.

G. F. M.

Phosphorus. ALFRED STOCK (*Z. anorg. Chem.*, 1922, **125**, 228—234).—A theoretical paper in which the paper of Marckwald and Helmholtz (A., 1922, ii, 845) is criticised. The author points out that the melting point of phosphorus depends to a very large extent on the rate of heating.

W. T.

Boron Hydrides. MAURICE L. HUGGINS (*J. Physical Chem.*, 1922, **26**, 833—835).—The author criticises the view held by Stock that boron in the boron hydrides is quadrivalent, and puts forward structures for the hydrides B_2H_6 , B_4H_{10} , B_6H_{12} , $B_{10}H_{14}$, in which boron is regarded as trivalent. These structures are strikingly like those adopted for ethylene, butadiene, benzene, and naphthalene, respectively. The hydrogen atoms are held by means of four-electron bonds, such as often exist, at least temporarily, in unsaturated organic compounds. Each such four-electron bond is surrounded by four atoms.

J. F. S.

Preparation of Boron Chloride. C. MAZZETTI and F. DE CARLI (*Atti R. Accad. Lincei*, 1922, [v], **31**, ii, 119—120).—Almost quantitative yields of boron chloride were obtained by passing dry chlorine through a porcelain tube containing ferro-boron heated at about 500°.

T. H. P.

Silicon Hydrides. XI. The Action of Oxygen on SiH_4 and Si_2H_6 . ALFRED STOCK and CARL SOMIESKI (*Ber.*, 1922, **55**, [B], 3961—3969).—The oxidation of the simplest hydrides of silicon has been studied in the hope that the reaction would provide

a more convenient method of obtaining compounds of the types $\text{SiH}_3\cdot\text{OH}$, SiH_2O , than is afforded by the hydrolysis of the halides. As oxidising agents, oxygen, air, and mixtures of nitrogen and oxygen containing less of the latter than air have been used. The violence of the reaction is moderated by very slowly adding the oxidising agent to an excess of the gaseous hydride under greatly diminished pressure and at a temperature varying between -70° and -140° . Measured volumes of the reagents are employed and the nature of the volatile products is elucidated by the authors' vacuum process. The necessary apparatus is fully figured and described in the original text. Reaction invariably occurs immediately and, in spite of the precautions described above, is frequently explosive. The products consist of unchanged hydride (including SiH_4 during the oxidation of Si_2H_6), nitrogen (and argon) when air or artificial mixtures of nitrogen and oxygen are used (the oxygen is invariably consumed completely), a considerable quantity of free hydrogen, water, and, in certain cases, small quantities of volatile silicon compounds formed during the oxidation. In addition, a colourless, non-volatile residue which generally contains brown particles is produced. This consists partly of compact crusts formed near the point of entry of the oxidising agent, partly of a fog in the interior of the reaction vessel, and partly of a uniform, vitreous deposit on the whole wall of the vessel. The colourless components are fairly readily dissolved by very dilute alkali and appear to consist of substances such as polymeric prosiloxan $(\text{SiH}_2\text{O})_x$, silicoformic anhydride, $[(\text{SiHO})_2\text{O}]_x$, etc.; the brown components contain silicon and possibly highly condensed silicon hydrides poor in hydrogen; they appear to be formed chiefly when the action is accompanied by considerable local heating and a deficiency of oxygen.

In spite of variation in the temperature and in the degree of dilution of the oxygen, the reaction occurs fairly uniformly. The oxidation proceeds beyond the stage $\text{SiH}_3\cdot\text{OH}$, since the presence of $(\text{SiH}_3)_2\text{O}$ in more than traces could not be established and the stability of the gas is such that it could not have escaped detection. The main derivatives of silicon produced during the oxidation are the polymeric forms of SiH_2O , $\text{OH}\cdot\text{SiHO}$, $\text{SiO}(\text{OH})_2$, etc. The water is regarded as produced from hydroxylated silicon compounds which become decomposed as the temperature is allowed to become atmospheric, thus $\text{SiH}_2(\text{OH})_2 \rightarrow \text{SiH}_2\text{O} + \text{H}_2\text{O}$. The liberation of free hydrogen is surprising. In those cases in which elementary silicon is deposited, a part of it is doubtless due to the thermal decomposition of monosilane. Its production is not due to a secondary hydrolysis of silane, or its primary oxidation products by water formed during the reaction. It appears to be a primary product of the oxidation: $\text{SiH}_4 + \text{O} = \text{SiH}_2\text{O} + \text{H}_2$; a reaction of this type is unusual and apparently due to the preponderating affinity of silicon for oxygen.

The production of hydrogen accounts for the peculiarities observed during the combustion of silicon hydrides, which differs markedly in its violence from similar cases of spontaneous ignition such as

the quiet inflammation of phosphorus hydride. The process consists of the following successive steps: inception of oxidation, liberation of hydrogen, formation of a mixture of oxygen and hydrogen, and ignition of the latter when the temperature has been raised sufficiently by the heat of the reaction. H. W.

Theory of the Structure and Polymorphism of Silica.

ROBERT B. SOSMAN (*J. Franklin Inst.*, 1922, **194**, 741—764).—A theory of the molecular structure of the various forms of silica is advanced. It is suggested that the silica atom-triplet maintains a certain degree of individuality in its amorphous and crystalline states, as well as in its compounds, and the freedom of the oxygen atoms to change their positions with respect to the silicon is restricted. The triplets are assumed to assemble into chains or threads in the liquid and glassy states, and a thread structure persists in the crystalline states. The three principal crystalline modifications (cristobalite, tridymite, quartz) are built up by combining the threaded triplets in three different ways, the connexion between the threads being through the oxygen atoms, and it is maintained by the sharing of electrons. The high-low (α — β) inversions in all the forms are thought to be due to the same underlying mechanism, namely, a change in the state of motion of certain electron orbits, resulting from increased thermal vibration of the atoms, whereby the shape of the silica triplet and the relative positions of the two oxygen atoms are suddenly altered. The theory gives a satisfactory explanation for many silica phenomena, such as the minimum in the temperature-volume curve of silica glass, the relation between the specific heats of the crystalline forms, the fact that natural quartz formed at a high temperature is always homogeneous, whilst low-temperature vein quartz is right- and left-twinned, etc. G. F. M.

The Constitution of the Silicates. G. TAMMANN (*Z. anorg. Chem.*, 1922, **125**, 301—306).—The author finds that the molecular specific heats of the silicates are additive, and concludes that the molecules are independent and at temperatures far removed from their melting point do not vibrate appreciably. This conclusion is supported by the fact that only in the neighbourhood of the melting point do isomorphous complex substances diffuse into one another visibly. In solution, silicates undergo hydrolysis, and this therefore gives no definite information as to the molecules which exist in the solid. The structure of molten silicates cannot be investigated. The complex silicates differ from the carbon compounds in that they are decomposed in solution and in the fused state, and the molecular theory of organic chemistry finds no application in the chemistry of silicates. W. T.

The [Suggested] Formation of Helium and Neon in Discharge Tubes containing Hydrogen. A. PIUTTI and E. BOGGIO-LERA (*Mem. Accad. Lincei*, 1921, [v], **13**, 687—701).—Full details of work a summary of which has already appeared (cf. Piutti, this

vol., ii, 20, and also Piutti and Cardoso, A., 1920, ii, 311; Baly, *Annual Report*, 1914, 45; 1920, 29, 30).
T. H. P.

The Rectilinear Diameter of Neon. E. MATHIAS, C. A. CROMMELIN, and H. KAMERLINGH ONNES (*Compt. rend.*, 1922, **175**, 933—935).—The density of neon was studied between its critical temperature (-228.71°) and its normal boiling point (-245.92°). From the experimental values obtained, the angular coefficient of the diameter was found to be $\alpha = -0.00716146$, a notably high figure. At the critical temperature the critical density is calculated to be $d_c = 0.4835$, whilst the critical coefficient is $(RT_c d_c)/p_c = 3.249$, the smallest value yet obtained experimentally with the exception of that for helium. The general conclusion is drawn that neon follows the law of rectilinear diameter.

H. J. E.

Electrical Preparation of Solid Alkali Amalgams in Quantity. PAUL M. GIESY and JAMES R. WITHROW (*J. Ind. Eng. Chem.*, 1923, **15**, 57—60).—Kerp's method (A., 1898, ii, 516; 1900, ii, 656) for the electrical preparation of amalgams can be much simplified and improved by allowing the mercury at the bottom of the cell as well as that from the flowing jet to receive current. In this way, the current can be increased to a very great extent with a corresponding reduction in manipulation and in the time of the run. If the current be led out at the tip of the jet tube a single jet tube with a stop-cock can be used instead of the changeable jets used by Kerp. It was also found that it is not necessary to work in an atmosphere of hydrogen in order to produce a pure product. Smith and Bennett's method (A., 1909, ii, 663; 1910, ii, 500) can be improved by strongly cooling the electrolyte when used for the preparation of sodium amalgam, and also by forcing the current. If a suitable diaphragm could be found which was unacted on by solutions of alkali hydroxides, or by the amalgams themselves, and, whilst offering a low electrical resistance, was a non-conductor, Shepherd's method (A., 1903, ii, 210) would undoubtedly be the best, but no suitable material could be found. It is pointed out, in conclusion, that all solid alkali metal amalgams are lighter than mercury, and not heavier, as recorded by Kerp.
G. F. M.

Isomorphism of Potassium Fluoborate and Permanganate. FERRUCCIO ZAMBONINI (*Atti R. Accad. Lincei*, 1922, [v], **31**, ii, 67—73).—The author claims priority over Barker (T., 1912, **101**, 2484) for his discovery of the isomorphism between potassium fluoborate and perchlorate (*Z. Kryst. Min.*, 1905, **41**, 60). In order to ascertain whether alkali fluoborates are isomorphous with, or merely exhibit crystallographic relations towards, alkali perchlorates and permanganates, the author has examined the crystals deposited from a solution containing equal weights of potassium fluoborate and permanganate. Mixed crystals of the fluoborate type, containing at most 0.4% of the permanganate, are formed, but on the permanganate side the miscibility is practically zero.

T. H. P.

Crystalline Form of Trihydrated Sodium Chlorite. ETTORE ARTINI (*Atti R. Accad. Lincei*, 1922, [v], **31**, ii, 65—67).—This salt, $\text{NaClO}_2 \cdot 3\text{H}_2\text{O}$ (cf. Levi, A., 1922, ii, 567), crystallises in the triclinic system: $a : b : c = 0.4041 : 1 : 0.6353$, $\alpha = 103^\circ 43.5'$, $\beta = 119^\circ 3'$, and $\gamma = 81^\circ 46.5'$. T. H. P.

Purification of Sodium Hyposulphite : A Modification of Jellinek's Method. WALTER G. CHRISTIANSEN and ARTHUR J. NORTON (*J. Ind. Eng. Chem.*, 1922, **14**, 1126—1128).—An apparatus is described by means of which sodium hyposulphite of 98.3% purity can be rapidly obtained in 42% yield from the commercial article by a modification of Jellinek's procedure. It consists essentially of a source of carbon dioxide, connected, on the one hand, with a bottle cemented with litharge and glycerol into a Büchner filter, the bottom of the bottle being removed and replaced with canvas and hardened filter-paper, and, on the other, with a litre bottle, standing in a 2-litre beaker which serves as a water-bath, and provided with a combined stirring and filtering device. The latter consists of an inverted glass funnel sealed on to a glass tube which acts also as the shaft of the stirrer. The whole apparatus is exhausted and filled with carbon dioxide, the solution of commercial hyposulphite in freshly distilled water is introduced into the Buchner filter, and the clear yellow filtrate is passed by the gas pressure into an intermediate receiver and thence into the litre bottle previously charged with the requisite quantity of sodium chloride. The stirrer is set in motion for about thirty minutes to ensure complete solution of the salt and precipitation of the hydrated hyposulphite. The washing, dehydration, and drying of the precipitate is carried out as in Jellinek's method (A., 1911, ii, 278). The ferrieyanide method was found superior to either the copper or silver methods for the estimation of the purity of the product. G. F. M.

Sodium Chromite. ERICH MÜLLER (*Z. angew. Chem.*, 1922, **35**, 557—558).—Chromium hydroxide was precipitated from a solution of a chromic salt by ammonia, dried over sulphuric acid, shaken with sodium hydroxide of different concentrations, and the concentration of chromium determined from time to time. The presence of hydroxide in solution begins to be noticeable with 5*N*-sodium hydroxide solution. The hydroxide used contained about 6 mol. of water to 1 mol. of chromium trioxide. The amount of hydroxide dissolved was found to be dependent on the time the mixture was agitated, rising to a maximum and after this decreasing to an almost constant value. The minimum solubility set in after from ten to fourteen days. The chromium seems to exist in solution as a complex ion, and not as a colloid. It is considered that a tervalent chromium salt of sodium is formed.

H. M.

Ammoniacal Silver Fluoride. DERVIN and OLMER (*Compt. rend.*, 1922, **175**, 1058—1061; cf. Gore, *Chem. News*, 1870, **21**, 28; Bruni and Levi, A., 1916, ii, 482, 617).—Anhydrous

silver fluoride dissolved in cold concentrated ammonia solution and the solution evaporated first in a vacuum, then at normal pressure over concentrated sulphuric acid, yielded colourless orthorhombic prisms having the composition $\text{AgF} \cdot 2\text{NH}_3 \cdot 2\text{H}_2\text{O}$. Light slowly decomposes this substance, but it may be preserved unchanged in the dark. It is very soluble in water, the solubility increasing on addition of ammonia, and although the solubility in alcohol is increased by the presence of water, addition of alcohol to the aqueous solution does not result in precipitation. Dry ammonia gas is without action on the crystals; if placed in a vacuum over sulphuric acid, they lose water, and when the anhydrous state is reached loss of ammonia takes place. On being heated, ammoniacal silver fluoride detonates, the products including nitrogen, finely divided silver, and ammonium fluoride. The authors suggest that the decomposition may be represented by the equation $3(\text{AgF} \cdot 2\text{NH}_3 \cdot 2\text{H}_2\text{O}) \rightarrow \text{Ag}_3\text{N} + 3\text{NH}_4\text{F} + 2\text{NH}_3 + 6\text{H}_2\text{O}$, with subsequent breaking up of the silver nitride into its elements.

H. J. E.

The Dissociation of Calcium Sulphate at High Temperatures. P. P. BUDNIKOV and J. K. ŠYRKIN (*Chem. Ztg.*, 1923, **47**, 22).—Samples of calcium sulphate were heated to constant weight at temperatures of from 800° to 1375° and the proportion of calcium oxide in the product was determined in each case. After heating at 1000° , only 0.21% of calcium oxide was present, at 1300° , 3.00%, and at 1375° , 98.67%. Above 1300° the salt melts and a vigorous evolution of fumes takes place corresponding with almost complete decomposition.

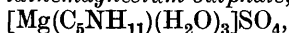
A. R. P.

Valency. XIX. The Ammonia Compounds of Barium Halides. GUSTAV F. HUTTIG and WILHELM MARTIN (*Z. anorg. Chem.*, 1922, **125**, 269—280).—The following ammonia compounds were found to exist, $\text{BaCl}_2 \cdot 8\text{NH}_3$; $\text{BaBr}_2 \cdot 8\text{NH}_3$; $\text{BaBr}_2 \cdot 4\text{NH}_3$; $\text{BaBr}_2 \cdot 2\text{NH}_3$; $\text{BaBr}_2 \cdot \text{NH}_3$; $\text{BaI}_2 \cdot 10\text{NH}_3$; $\text{BaI}_2 \cdot 9\text{NH}_3$; $\text{BaI}_2 \cdot 8\text{NH}_3$; $\text{BaI}_2 \cdot 6\text{NH}_3$; $\text{BaI}_2 \cdot 4\text{NH}_3$, and $\text{BaI}_2 \cdot 2\text{NH}_3$. The method of investigation was the same as before (cf. A., 1920, ii, 293 and 318). The dissociation temperature at which the pressure equals 100 mm. is given in each case, and also the heat of formation as calculated by Nernst's formula.

W. T.

Complex Magnesium Salts. III. G. SPACU and R. RIPAN (*Bulet. Societ. Științe Cluj*, 1922, **1**, 267—283; from *Chem. Zentr.*, 1922, iii, 1046—1047; cf. this vol., i, 96).—*Monoaquopentammine-magnesium chloride*, $[\text{Mg}(\text{NH}_3)_5 \cdot \text{H}_2\text{O}]\text{Cl}_2$, prepared by passing ammonia into a solution of magnesium chloride in absolute alcohol at the ordinary temperature, is a colourless, crystalline powder. The following are also mentioned: *hexamminemagnesium bromide*, a white, crystalline powder; *tetra-aquodiamminemagnesium sulphate*, $[\text{Mg}(\text{NH}_3)_2(\text{H}_2\text{O})_4]\text{SO}_4$, a crystalline powder; *triaquotriammine-magnesium sulphate*, $[\text{Mg}(\text{NH}_3)_3(\text{H}_2\text{O})_3]\text{SO}_4$, colourless crystals; *diuquodiamminemagnesium sulphate*, $[\text{Mg}(\text{NH}_3)_2(\text{H}_2\text{O})_2]\text{SO}_4$, white

powder; *triaquopiperidinemagnesium sulphate*,



a slightly green substance; *penta-aquobenzylaminemagnesium sulphate*, a white, crystalline powder.

G. W. R.

The Solidification of the System $\text{MgCl}_2\text{--KCl--BaCl}_2$. J. VALENTIN (*Compt. rend.*, 1922, **175**, 1061—1063).—A thermal study of the three salts was made and the results are shown in a series of diagrams. Two compounds, $\text{MgCl}_2\cdot\text{KCl}$ and $\text{BaCl}_2\cdot 2\text{KCl}$, are formed, so that the complete triangular diagram is divided into five regions, each corresponding with the deposition of a pure substance and contains three triple points.

H. J. E.

A Simple Method for the Preparation of Highly Phosphorescent Zinc Sulphide. JULIUS SCHMIDT (*Ber.*, 1922, **55**, [B], 3988—3989).—Equal weights of pure zinc sulphate and sodium acetate are dissolved in water and the hot solution is treated with hydrogen sulphide until the precipitation of the zinc is complete. The zinc sulphide is washed by decantation and finally completely on the filter, after which it is dried on the water-bath. The product (200 g.) is moistened uniformly with a solution of magnesium chloride (20 g.), calcium chloride (10 g.), strontium chloride (10 g.), and crystalline barium chloride (10 g.) in water (200 c.c.) to which 0.04 g. of ammonium tungstate dissolved in 10 c.c. of water has been added. The mixture with the zinc sulphide is evaporated to dryness with occasional stirring on the water-bath. The product is slowly heated to redness in a crucible (the operation should require about an hour) and maintained at this temperature during thirty to forty minutes, after which it is allowed to cool in the furnace. The soluble salts are removed by water and the residual zinc sulphide is dried on the water-bath. It exhibits a strong, green fluorescence.

Mixtures of salts other than those described have little influence on the strength but considerable effect on the colour of the phosphorescent light and the readiness with which the phosphorescent effect is excited by illumination, Röntgen rays, or radioactive materials. Most metallic salts induce a green phosphorescence, but that caused by manganese is yellow (cf. Hofmann and Dacca, A., 1904, ii, 690). Phosphorescence appears to be weakened or completely inhibited by metallic salts, which give dark coloured or black sulphides (cf. MacDougall, Stewart, and Wright, T., 1917, **111**, 663).

H. W.

Action of Natural Waters on Lead. JOHN C. THRESH (*Analyst*, 1922, **47**, 459—468, 500—505).—The presence of varying quantities of silicates, carbonates, sulphates, and salts of organic acids, together with the organic acid and free carbon dioxide, causes the differences observed in the action of natural waters on lead. Silicates prevent the oxidation of lead, iron, and aluminium, and moorland water after treatment with sodium silicate ceases to act on lead.

W. P. S.

Complex Salts of Copper and Thallium. G. CANNERI (*Gazzetta*, 1922, 52, ii, 266—270).—The following complex compounds, analogous to the simplest types of those of the alkali elements (cf. Rosenheim and Steinhäuser, A., 1900, ii, 653), are described: $\text{Ti}_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, blue crystals; $\text{Ti}_2\text{Cu}(\text{SO}_3)_2$, yellow powder; $\text{CuSO}_3 \cdot 3\text{Cu}_2\text{SO}_3 \cdot \text{Ti}_2\text{SO}_3$, cinnabar-red crystals, dissolving in aqueous ammonia to a blue solution; $\text{Ti}_4\text{Cu}(\text{S}_2\text{O}_3)_3$, a straw-yellow, microcrystalline powder. No more than one compound corresponding with one and the same series was obtained, in spite of variation of the conditions of formation. T. H. P.

The Vapour Tension of some Copper-Zinc Alloys in the Solid State. LÉON GUILLET and MARCEL BALLAY (*Compt. rend.*, 1922, 175, 1057—1058).—The rate of volatilisation of zinc from copper-zinc alloys depends on the temperature and on the nature of the surrounding atmosphere. When the latter can exhibit oxidising properties, the surface film of oxide mechanically retards loss of zinc from the alloy, whilst in an atmosphere of carbon monoxide, nitrogen, or hydrogen no film is formed and the temperature alone is the controlling factor. In such cases, the vapour pressures observed cannot be represented as a linear function of the atomic percentage of dissolved copper, as the alloys used ($\text{Cu}=55.20\%$, $\text{Zn}=44.75\%$) were not dilute solutions of copper in zinc. Raoult's law, therefore, does not hold. H. J. E.

Solubility of Halides of Univalent Copper in Sodium Thiosulphate. G. CANNERI and R. LUCHINI (*Gazzetta*, 1922, 52, ii, 261—266).—In the compounds originating when cuprous halides are dissolved in ammonium thiosulphate solution, the univalent copper apparently exerts its co-ordinating power, not merely towards the thiosulphuric radicle, but also towards the halogen.

To the compounds formed, which have the general formula, $\text{CuX} \cdot \text{NH}_4\text{X} \cdot 4(\text{NH}_4)_2\text{S}_2\text{O}_3$, where X represents a halogen atom or the thiocyanogen radicle (cf. Rosenheim and Steinhäuser, A., 1900, ii, 653), Werner ("Neuere Anschauungen," 1913, 168) ascribed the formula $\left[\text{R} \begin{smallmatrix} \text{X}_2 \\ (\text{S}_2\text{O}_3)_4 \end{smallmatrix} \right] (\text{NH}_4)_9$, R in this case representing Cu. On the basis of this formula, the integrity of the nucleus within the brackets should not be diminished by replacement of the ammonium residue by an atom of an alkali element of similar chemical character such as sodium. There seems, therefore, to be no reason sufficient to explain the difference in behaviour between the ammonium salts and those of other alkali metals other than the varying solvent power on the cuprous halides.

The authors find that sodium thiosulphate, fused in its own water of crystallisation, dissolves considerable proportions of freshly prepared cuprous halides and cuprous thiocyanate, the following salts being formed: $\text{CuCl} \cdot 5\text{Na}_2\text{S}_2\text{O}_3$; $\text{CuBr} \cdot 5\text{Na}_2\text{S}_2\text{O}_3$; $\text{CuBr} \cdot \text{Cu}_2\text{S}_2\text{O}_3 \cdot 9\text{Na}_2\text{S}_2\text{O}_3$; $\text{CuBr} \cdot 5\text{Na}_2\text{S}_2\text{O}_3 \cdot \text{NaI}$; $2\text{CuCNS} \cdot 5\text{Na}_2\text{S}_2\text{O}_3$.

To these compounds, which form white crystals unaffected by the action of light, and give clear, colourless, aqueous solutions,

the following formulæ, analogous to those attributed by Werner to the complexes formed by ammonium thiosulphate, might be ascribed: $\left[\text{Cu} \begin{smallmatrix} \text{Cl} \\ (\text{S}_2\text{O}_3)_5 \end{smallmatrix} \right] \text{Na}_{10}$; $\left[\text{Cu} \begin{smallmatrix} \text{Br} \\ (\text{S}_2\text{O}_3)_5 \end{smallmatrix} \right] \text{Na}_{10}$; $\left[\text{Cu} \begin{smallmatrix} \text{Br} \\ (\text{S}_2\text{O}_3)_{10} \end{smallmatrix} \right] \text{Na}_{18}$; $\left[\text{Cu} \begin{smallmatrix} \text{I} \\ (\text{S}_2\text{O}_3)_6 \end{smallmatrix} \right] \text{Na}_{11}$; $\left[\text{Cu} \begin{smallmatrix} (\text{CNS})_2 \\ (\text{S}_2\text{O}_3)_5 \end{smallmatrix} \right] \text{Na}_{16}$.

Such hypothetical structural formulæ cannot, however, be supported by experimental data other than the colour of the salts, this indicating that the cuprous ion forms part of a complex radicle constituted of groupings in such condition that they exhibit increased resistance to react with their specific reagents. The dissociating action exerted by water on these complex compounds prevents physical measurements of any value in this connexion being made.

T. H. P.

The Preparation of Metallic Phosphides by the Action of Hydrogen Phosphide on Solutions of Metallic Salts. A. BRUKL (*Z. anorg. Chem.*, 1922, **125**, 252—256; cf. Moser and Brukl, A., 1922, ii, 393).—*Mercurous phosphide*, PHg_3 , is obtained when hydrogen phosphide is allowed to react on a solution of mercurous sulphate in dilute sulphuric acid, as a black, amorphous precipitate; it is rapidly oxidised by the oxygen of the air, and gradually by dilute nitric acid. Phosphine is gradually evolved by the action of cold concentrated hydrochloric acid, but much more rapidly by the action of the hot acid; with concentrated sulphuric acid, sulphur dioxide is evolved. The compound is not explosive. Pure *mercuric phosphide*, P_2Hg_3 , can be obtained by the action of a solution of mercuric chloride in ether on hydrogen phosphide; it is a dark brown solid, becoming grey on exposure to air. In the cold, water, alkalis, and dilute acids are without action, but on warming phosphine is evolved; it is oxidised in the cold by dilute nitric acid.

A solution of lead acetate in alcohol reacts with phosphine to form a black, flocculent precipitate of *lead phosphide*, P_2Pb_3 , an unstable compound decomposed in the cold by water and alkalis.

Cadmium phosphide, P_2Cd_3 , obtained as a black, flocculent precipitate by the action of phosphine on an ammoniacal solution of cadmium sulphate, is unstable, and yields hydrogen phosphide when treated with dilute hydrochloric acid. It is very vigorously oxidised by concentrated nitric acid. Its reactions are similar to those of lead phosphide.

W. T.

Alloys of Iron and Aluminium. N. KURNAKOV, G. URASOV, and A. GRIGORIEV (*Z. anorg. Chem.*, 1922, **125**, 207—227, and *J. Russ. Phys. Chem. Soc.*, 1918, **50**, 270).—The system iron-aluminium was studied by (1) thermal analysis, (2) the micro-structure of the alloys, and (3) the electrical conductivity and hardness. In the interval 32.1—39.5 atom. % iron the endothermic compound, Al_3Fe_2 , crystallises from the fused mass; below 1100°, this decomposes into the α - and β -solutions of aluminium in iron. Between 24.2 and 34 atom. % iron there exists a stable

phase, which the authors call the δ phase, having properties very different from those of the adjoining phases. This crystalline phase corresponds with the maximum change in properties of the system iron-aluminium; it possesses the minimum electrical conductivity and temperature coefficient, the maximum hardness, and it is extremely brittle. The authors regard it as a chemical individual of variable composition (cf. Kurnakov and Shemtshuschny, A., 1913, ii, 190). W. T.

Reducing Action of Ferrous Hydroxide. SUSUMU MIYAMOTO (*Japan J. Chem.*, 1922, 1, 57—80, and *Sci. Papers Inst. Phys. Chem. Research*, 1922, 1, 31—55).—An English translation of the paper previously published in Japanese (cf. A., 1922, ii, 647). The expression $K = e^{A-B/P}(1+0.79C_{\text{KOH}})$ in the earlier paper should be replaced by $K = e^{A-B/T}(1+0.79C_{\text{KOH}})$. K. K.

The Higher Oxide of Cobalt. OWEN RHYS HOWELL (T., 1923, 123, 65—71).

Triple Nitrites of Bivalent Cobalt. V. CUTTICA and M. PAOLETTI (*Gazzetta*, 1922, 52, ii, 279—286; cf. following abstract).—The analytical data given by Erdmann (*J. pr. Chem.*, 1866, 97, 385) for the three triple nitrites, $\text{Co}(\text{NO}_2)_2$, $\text{Ba}[\text{Ca}, \text{Sr}](\text{NO}_2)_2$, 2KNO_2 , being incomplete, the authors have prepared and analysed these compounds, as well as various other triple nitrites of cobalt. The above three complex nitrites form dirty yellow powders stable in the air and may be regarded as salts of one and the same complex quadrivalent ion, $\text{Co}(\text{NO}_2)_6$. The latter is, however, not stable in presence of water, in contact with which the salts yield an insoluble golden-yellow compound, $\text{K}_2\text{Co}(\text{NO}_2)_4$, the stable cobaltonitrous ion being hence $[\text{Co}(\text{NO}_2)_4]^{''''}$. The high value of the active mass of the ion $[\text{NO}_2]'$ present in the conditions of the reaction in which the triple salt originates tends to displace the equilibrium $[\text{Co}(\text{NO}_2)_4]^{''} + 2\text{NO}_2' \rightleftharpoons [\text{Co}(\text{NO}_2)_6]^{''''}$ towards the right, a displacement in the same sense, that is, towards the formation of undissociated molecules of the triple nitrite, being determined also in the equilibrium $[\text{Co}(\text{NO}_2)_6]^{''''} + 2\text{K}'' + \text{Ca}'' (\text{or } \text{Ba}, \text{Ca}) \rightleftharpoons [\text{Co}(\text{NO}_2)_6]_{\text{Ca}}^{\text{K}_2}$. These cobalt compounds are analogous in composition to the corresponding nickel compounds, but exhibit greater stability towards the dissociating action of water, the co-ordination valency representing a far stronger linking in this case. If the potassium is displaced by thallium, a salt of analogous composition is obtained, but when sodium is introduced the composition is changed. Triple cobalt zinc (cadmium, mercury) potassium nitrites have also been obtained, these being stable in dry air and of the formula $[\text{Co}(\text{NO}_2)_6]_{2\text{K}_6}^{\text{Zn}}$.

The salts described and analysed are: cobalt calcium potassium nitrite; cobalt barium thallium nitrite; cobalt barium sodium nitrite, $\text{Co}(\text{NO}_2)_2 \cdot 2\text{Ba}(\text{NO}_2)_2 \cdot \text{NaNO}_2$, a dirty green powder; cobalt zinc potassium nitrite, $2\text{Co}(\text{NO}_2)_2 \cdot \text{Zn}(\text{NO}_2)_2 \cdot 6\text{KNO}_2$, dirty yellow; cobalt

cadmium potassium nitrite, pale chestnut, and *cobalt mercuric potassium nitrite*, rather deeper chestnut precipitate. T. H. P.

Triple Nitrites of Nickel. V. CUTTICA and G. CAROBBI (*Gazzetta*, 1922, 52, ii, 270—279; cf. A., 1922, ii, 448).—Both the double and triple nitrites of nickel undergo profound ionic scission immediately on contact with water, the supposed ion, $[\text{Ni}(\text{NO}_2)_6]'''$, being hence classified with the “imperfect” complex ions. Hence in the passage of these salts into solution, the mobility of the constituent simple ions predominates over the co-ordinating action exerted in such conditions by the nickel. In general, accumulation of electronegative radicles in a complex ion is accompanied by increase in the extent of the ionic dissociation of its salts. With the complex nitrites, the large number of NO_2 radicles displaces the electrolytic equilibrium, $[\text{Ni}(\text{NO}_2)_6]\text{K}_4 \rightleftharpoons 4\text{K}^+ + [\text{Ni}(\text{NO}_2)_6]'''$, almost completely towards the right, and the equilibrium $[\text{Ni}(\text{NO}_2)_6]''' \rightleftharpoons \text{Ni}(\text{NO}_2)_2 + 4\text{NO}_2'$ must also undergo displacement in the same sense. The results of cryoscopic measurements in water of some of the double and triple nitrites of nickel show, indeed, the almost exclusive presence of simple ions, the nickel nitrite molecules alone remaining undissociated. The following triple nitrites have been prepared.

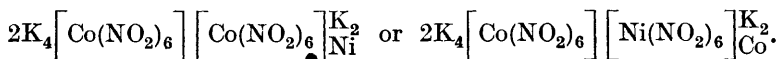
Nickel mercuric potassium nitrite, $[\text{Ni}(\text{NO}_2)_6]\text{K}_2\text{Hg}$, forms dark green, almost black, crystals, and gives a green, aqueous solution. Cryoscopic measurements indicate decomposition into seven ions.

Two *nickel mercuric thallium nitrites* of the respective compositions: $3\text{Ni}(\text{NO}_2)_2 \cdot \text{Hg}(\text{NO}_2)_2 \cdot 6\text{TlNO}_2$, orange-yellow crystals, and $2\text{Ni}(\text{NO}_2)_2 \cdot \text{Hg}(\text{NO}_2)_2 \cdot 8\text{TlNO}_2$, are obtained according to the experimental conditions employed.

Nickel zinc potassium nitrite, $2[\text{Ni}(\text{NO}_2)_6]\text{K}_4 \cdot \text{Zn}(\text{NO}_2)_2$, forms a flesh-red, microcrystalline mass.

A chestnut-brown nickel uranyl thallium nitrite was prepared, but no simple formula could be derived from the results of its analysis.

Nickel cobalt potassium nitrite is a greenish-yellow salt of the formula



Nickel cobalt thallium nitrite is a dark red salt which, when treated with water, leaves undissolved the orange-red complex, $\text{Tl}_2\text{Co}(\text{NO}_2)_4$. Its formula is probably $\left[\text{Co}(\text{NO}_2)_6 \right]_{\text{Ni}}^{\text{Tl}_2} \cdot 4\text{TlNO}_2$.

Unsuccessful attempts were made to prepare a nickel magnesium potassium nitrite. T. H. P.

Some New Series of Phosphotungstates. F. KEHRMANN and R. MELLET (*Helv. Chim. Acta*, 5, 942—944).—When a very concentrated solution of a mixture of sodium tungstate and phosphate is acidified faintly with acetic acid, at the end of a few days a mass of crystals separates containing two salts. One of these

can be freed from the other by washing with cold water, in which the first is sparingly soluble. This salt, which cannot be recrystallised, has the composition corresponding with the formula $14\text{Na}_2\text{O}, 5\text{P}_2\text{O}_5, 19\text{WO}_3, \text{aq}$ or $29\text{Na}_2\text{O}, 10\text{P}_2\text{O}_5, 39\text{WO}_3, \text{aq}$. The second salt is readily soluble in cold water and forms supersaturated solutions which may not crystallise for months. The salt corresponds with the formula $3\text{Na}_2\text{O}, \text{P}_2\text{O}_5, 6\text{WO}_3, \text{aq}$, representing the simplest series of phosphotungstates. A sodium salt described by Scheibler (*Ber.*, 1872, 5, 801) was thought to belong to a $\text{P}_2\text{O}_5, 6\text{WO}_3$ series, but is now shown to belong to the series $3\text{M}_2\text{O}, \text{P}_2\text{O}_5, 7\text{WO}_3, \text{aq}$. It is proposed to continue the study of these three new series of phosphotungstates. E. H. R.

Properties of Tin, Especially the Density. R. HOFFMANN and W. STAHL (*Metall. u. Erz.*, 1923, 20, 5—8).—Tin of 99.8% purity produced from Bolivian ore at the Wilhelmsburg Works was found to have d_4^0 7.312 in a vacuum and d_4^{20} 7.311. [Cf. *J.S.C.I.*, 1923, Feb.] A. R. P.

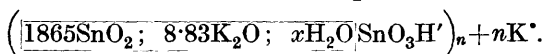
The Equilibrium in the Reduction of Tin Dioxide by Carbon Monoxide. W. FRAENKEL and K. SNIPISCHSKI (*Z. anorg. Chem.*, 1922, 125, 235—252).—The equilibrium $\text{SnO}_2 + 2\text{CO} \rightleftharpoons \text{Sn} + 2\text{CO}_2$ was studied. It was found that the same equilibrium was reached from both sides, and it was independent of the amount and composition of the solid phases. The equilibrium concentration of carbon monoxide increases gradually with increasing temperature up to 900° , and then suddenly increases very rapidly. The temperature coefficient was studied; at 500° , equilibrium sets in after some weeks, whereas at 600° equilibrium is reached in a few days.

An improved method for the preparation of stannous oxide consists in dissolving stannous chloride in the least amount of hot concentrated hydrochloric acid, and gradually adding sodium hydroxide solution until the solution reacts alkaline towards phenolphthalein; the resulting milky liquid is then kept boiling in a bath of saturated sodium chloride solution. In a few hours a blue, lustrous powder is obtained; this is then washed and dried.

W. T.

Composition of Micellæ. I. Stannic Acid Peptised by Alkali. ROBERT WINTGREN (*Z. physikal. Chem.*, 1922, 103, 238—259).—Electrical conductivity and transport measurements have been carried out with stannic acid sols which have been peptised by alkali and also with the filtrates from these obtained by ultrafiltration. From these measurements by Duceaux's method (*A.*, 1905, ii, 432), the portion of the conductivity and of the transport which is due to the micellar portion of the sol has been calculated, and from Zsigmondy's conception of the qualitative composition of the micellæ an attempt has been made to apply Kohlrausch's law of the independent migration of ions to inorganic colloid ions by regarding the micellar ions as ordinary multivalent ions. From the conductivity values the mean quantitative com-

position of the micella equivalent has been approximately determined, that is, the number of molecules of stannic oxide contained in one equivalent of colloidal stannic acid. This quantity has been termed the equivalent aggregation. Further, from the conductivity determinations it is shown, in agreement with Varga's calculations from transport measurements (*Kolloid Chem. Beihefte*, 1919, **11**, 25), that a measurable large quantity of the alkali used for peptisation is enclosed in the micellæ. The amount of enclosed alkali and the equivalent aggregation may be obtained indirectly from the transport measurements, and the quantities so obtained agree within a very little with those obtained from conductivity measurements and with those obtained by Varga. That considerable quantities of alkali are enclosed is shown by the fact that at the cathode, instead of an increase in alkali concentration occurring, a decrease is actually found. From the decrease in alkali concentration the amount enclosed can also be calculated and the quantity so obtained agrees well with the quantity obtained by the other methods. With increasing alkali content the equivalent aggregation decreases, as also does the percentage of enclosed alkali. On account of the small value of the conductivity of the sols with small alkali content, the composition can only be regarded as correct in respect of its order, and not as to its actual value. An example of the composition of a stannic acid sol examined is expressed as follows :



J. F. S.

Magnetic Analysis of the Stannic Acids. PAUL PASCAL (*Compt. rend.*, 1922, **175**, 1063—1065; cf. this vol., ii, 25).—The theoretical values of the molecular magnetic susceptibilities of the acids $\text{Sn}(\text{OH})_4$ and $\text{SnO}(\text{OH})_2$, calculated from those of stannates, methylstannonic acid, and metallic tin were compared with those obtained experimentally from stannic acids prepared by various methods. The results indicate that the acids are not definite compounds, but mixtures of anhydrous stannic oxide with water.

H. J. E.

Zirkite Ore. J. G. THOMPSON (*J. Physical Chem.*, 1922, **26**, 812—832).—The mineral zirkite, an impure zirconium dioxide containing silica, iron, and titanium, has been investigated with the object of making it suitable for use as a refractory. It is shown that 90—95% of the silicon may be removed from the mineral by heating a mixture of the ore and carbon to a temperature above 2220° in an electric furnace. The best results are obtained by heating a mixture of the ore and coke in an arc furnace, the amount of carbon being approximately that required to transform only the silicon into carbide. If carbon in excess of this amount is used the separation of silicon is less complete, due to the formation of stable double carbides of silicon and zirconium. It is suggested that if the above treatment is followed by the removal of iron by treatment with chlorine a product, impure

zirconia, is obtained which is sufficiently refractory for most purposes. Zirconium carbide is shown to be exceedingly refractory, and infusible in a 40–50 kw. arc, but its use as a refractory is restricted, because it is necessary to protect it from oxidation. The various methods of analysis of zirconium compounds are discussed and a method for the estimation of zirconium, silicon, titanium, and iron in zirkite is outlined. J. F. S.

The Missing Element of Atomic Number 72. D. COSTER and G. HEVESY (*Nature*, 1923, **111**, 79).—From theoretical considerations, it is probable that the element of atomic number 72 is not a rare-earth metal, but a homologue of zirconium. Further, the conclusions of Dauvillier (A., 1922, ii, 463) and of Urbain (A., 1911, ii, 115) are considered not to be justified, since it appears that the quantity of the element in the sample examined by the former by an X-ray spectroscopic method must have been so small that its identity with the element claimed to have been detected by the latter in the same sample by optical and magnetic examination is improbable. The only lines, $L\alpha_1$ and $L\beta_2$, detected by Dauvillier were extremely faint, and the wave-lengths given are about 4X.u. (1X.u.= 10^{-11} cm.) smaller than those obtained by a rational interpolation in the wave-length tables of Hjalmar and Coster for the elements in the neighbourhood of atomic number 72. The authors have, however, by investigation of the X-ray spectrum of extractions of zirconium minerals, detected the lines $L\alpha_1=1565\cdot5$, $\alpha_2=1576$, $\beta_1=1371\cdot4$, $\beta_2=1323\cdot7$, $\beta_3=1350\cdot2$, $\gamma_1=1177$ X.u., which must be ascribed to the element of atomic number 72. The $L\alpha$ and $L\beta$ lines exactly agree with the anticipated mutual distance and relative intensity, and the wave-lengths all agree within one X.u. with those obtained by interpolation. A sample of a Norwegian zirconium mineral was estimated to contain at least 1% of the new element, whilst ordinary zirconium probably contains 0.01–0.1%. Experiments are in progress to isolate the new element, for which the name "hafnium" is proposed, and to determine its chemical properties. [Cf. Scott, T., 1923, 123, 311.] A. A. E.

The Anode Oxidation of Gold. FR. JIRSA and OT. BURYÁNEK (*Chem. Listy*, **16**, 299–305; cf. A., 1922, ii, 713).—A strong current was passed through a cell having a gold anode, and dilute sulphuric acid as electrolyte. After twenty-four hours the current was stopped, and the back *E.M.F.* of the anode measured. For the cell $\text{Au}|\text{Au}_2\text{O}_3, \text{NH}_2\text{SO}_4|\text{NH}_2\text{SO}_4, \text{H}_2|\text{Pt}$ this was +1.24 volts at 18°. The same voltage was obtained whether the anode was prepared in the dark, or in the light of a mercury-vapour lamp, and reduction of the strength of acid from normal to $N/1000$ made no difference to this result. The rates of polarisation of gold anodes, using currents of 0.02 and of 0.5 milliampere/cm.² were next measured, and the results shown on a graph. It was noticed that, below 0.02 milliampere, the results obtained were untrustworthy, owing to the slow rate of oxidation producing passivity in the gold. The rate of discharge of polarised gold anodes was

measured, under various conditions, and with the introduction of different resistances, in order to retard the rapidity of discharge. Gold anodes were next depolarised by passing currents of increasing magnitude through the cathode, until the polarisation *E.M.F.* disappears. The magnitudes of the polarisation currents produced by stationary and rotating oxidised gold anodes, using acids of different concentrations, were measured, and curves drawn showing the relation between the galvanometer readings and the voltage.

R. T.

The Occlusion of Hydrogen by Palladium. MITUO YAMADA (*Phil. Mag.*, 1923, [vi], 45, 241—243).—The crystalline structure of palladium, containing large quantities of absorbed hydrogen, has been determined by X-ray analysis. Except for slight contractions of the intervals between the lines on the röntgenogram, there is practically no difference between the figures for pure palladium and for this metal containing occluded hydrogen. The slight contraction corresponds with a uniform expansion of the space lattice. No new lines were observed, and hence a compound is not formed between the hydrogen and the palladium. The results are in accord with the view that the hydrogen is adsorbed in the state of solid solution. The expansion of the lattice determined from the displacement of the lines was 2·8%, which is in good agreement with the expansion, 2·9%, obtained by direct measurement.

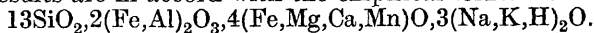
W. E. G.

Mineralogical Chemistry.

Riebeckite from Vallone delle Minière (Valle della Germanasca). E. GRILL (*Atti R. Accad. Lincei*, 1922, [v], 31, ii, 137—142).—Black crystals of riebeckite, up to 7 mm. in length and with submetallic lustre and pronounced prismatic habit, were found on the eastern slope of Vallone delle Minière (Piedmont). They exhibit pleochroism and have *d* 3·44; the angle (100):(110) is 55° 5'—55° 20'. Analysis gives:

SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MnO	CaO	MgO	Na ₂ O	K ₂ O	H ₂ O—	H ₂ O+	Total
51·53	trace	2·71	16·22	17·11	0·22	0·79	1·01	7·81	1·13	0·31	1·20	100·04.

These results are in accord with the empirical formula:



T. H. P.

Analytical Chemistry.

Practical Spectroscopic Analysis. W. F. MEGGERS, C. C. KIESS, and F. J. STIMSON (*Bull. Bur. Standards*, 1922, **18**, 235—255; *Sci. Paper*, No. 444).—A method of quantitative analysis is developed based on a study of the raies ultimes, and sensitive

lines which appear in the spectra of certain alloys. The raies ultimes are the most sensitive spectral lines of an element, and represent vanishing traces of its presence in a mixture or alloy. The most sensitive rays for eighty-three of the elements have been collected in one table by Gramont (A., 1922, ii, 73). In the present method of spectrographic analysis, use is made of standard samples, synthetic alloys, or salts mixed in definite proportions. The spectra of several standard samples are photographed alongside the spectrum of the unknown material, and the quantitative determination becomes a process of simple comparison. The condensed spark with self-induction in the spark circuit has been found to yield the best results. Three examples of the application of the method are illustrated, dealing with the determination of impurities in samples of tin, gold, and platinum. Many of the lines were sensitive for less than 0.001% of impurity. Other applications of spectrographic analysis are discussed.

W. E. G.

A Colorimeter for Bicolorimetric Work. VICTOR C. MYERS (*J. Biol. Chem.*, 1922, **54**, 675—682).—A colorimeter of the Hellige type is described which contains three wedge-shaped vessels for the standards. Only one wedge is necessary for ordinary colorimetric work. For colorimetric estimations of hydrogen-ion concentrations, however, two wedges are employed, one containing a standard on the alkaline side, the other one on the acid side of the unknown. Using these in conjunction, a match can be obtained without the preparation of further standards. If the unknown solution is slightly turbid or coloured, the third wedge may be brought into use.

E. S.

Chromoscope for the Measurement of the Concentration of Hydrogen-ions in Liquids by means of Coloured Indicators. CH. O. GUILLAUMIN (*J. Pharm. Chim.*, 1922, [vii], **26**, 452—454).—The apparatus consists essentially of a wooden box having six holes in two rows into which the tubes containing the solutions fit. Observations are made through lateral openings in a line with the axis of each row of tubes. The openings are shielded from external diffused light by means of a hood. The illumination of the tubes is effected either by diffused daylight or by artificial light, and either directly, or by reflection from an opal plate with a matt surface fixed at an angle of 45° to the plane of the observation tubes. A light filter is provided to correct, where necessary, for the dichroism of certain indicators.

G. F. M.

Electrical Determination of the End-point of a Titration. ERICH MÜLLER (*Z. angew. Chem.*, 1922, **35**, 563—566).—The electrical potential of the reaction may serve as an indicator of the end-point of a titration, in so far as it is a question of the reaction of ions. An electrode has to be selected to correspond with one stage of the reaction, for example, in the titration of an iodide with silver nitrate, an electrode of silver, and an indifferent electrode of platinum. The potential of the reaction $\epsilon = A_1 + 0.058 \log c_{Ag} = A_2 - 0.058 \log c_I$. At the end-point $c_{Ag} = c_I$, and the

potential of this end-point may be determined by saturating water with silver iodide, acidifying with sulphuric acid, and immersing a silver electrode. This end-point electrode is connected through a galvanometer capable of indicating 10^{-5} to 10^{-7} amperes with the indicator silver electrode of a titration; the end-point of the titration is indicated by the needle reaching zero. H. M.

Quantitative Analysis by Measurement of the Degree of Supersaturation. HANS RÖDER (*Chem. Ztg.*, 1922, **46**, 1089).—A number of factors, such as the physical condition of the precipitate formed, the presence of substances which affect the solubility of the precipitate or hinder its formation, etc., must be taken into account in the method proposed by Höppler (A., 1922, ii, 863), and although the method is useful in certain cases much investigation is required before it is capable of wider application. W. P. S.

Contamination of Water Samples with Material Dissolved from Glass Containers. W. D. COLLINS and H. B. RIFFENBURG (*J. Ind. Eng. Chem.*, 1923, **15**, 48—49).—Samples of water in good glass bottles will not dissolve enough glass in a month to cause any detectable change in the ordinary mineral analysis, and even in six months no significant change will be caused. In bad bottles, sufficient mineral matter may be dissolved in a day, and certainly in a week, to change the character of the water. The greatest changes are an increase in silica and sodium, and a change of the alkalinity from bicarbonate to carbonate and hydroxide with an increase in total alkalinity corresponding with the sodium dissolved. Bottles may be tested for resistance to solution by filling with distilled water and examining after a month. Titration with acid and estimation of the total solids and the silica will show the extent of the action. G. F. M.

Alumina as an Absorbent for Water in Organic Combustions. H. L. FISHER, H. L. FAUST, and G. H. WALDEN (*J. Ind. Eng. Chem.*, 1922, **14**, 1138—1139).—The preparation of alumina for use in absorbing water in organic combustions is described. It may be made either from the hydroxide or from the hydrated chloride. In the first case, the hydroxide is first mixed with 20% of purified and ignited asbestos and then ignited over a bunsen flame. In the second case, pumice is saturated with a solution of aluminium chloride, the whole evaporated to dryness with stirring, and ignited at 700—750° until no more hydrogen chloride is given off. The advantages of alumina over other absorption agents are that, being a solid, it offers less resistance to the passage of gases than sulphuric acid, does not form crystalline hydrates like calcium chloride, or contain basic substances which absorb carbon dioxide, and does not clog the apparatus like phosphoric oxide. H. C. R.

Some Sources of Error in the Estimation of Chlorides in Blood and Similar Material. ISIDOR GREENWALD and JOSEPH GROSS (*J. Biol. Chem.*, 1922, **54**, 589—594).—The results obtained

in the estimation of chlorides in whole blood differ according to the particular protein precipitant used. Using as a standard for comparison the results obtained by the oxidation of blood with nitric acid in the presence of silver nitrate, the authors find that tungstic acid is the most suitable precipitant. Picric acid leads to high results owing to the formation of purine-silver picrates, whilst other precipitants cause either low or irregular results.

E. S.

Detection, Elimination, and Estimation of Ammonia in Hydroxylamine Hydrochloride. RAOUL GROS (*J. Pharm. Chim.*, 1922, [vii], 26, 449—452).—For the detection of ammonia, the hydroxylamine in the sample is first destroyed by the addition of a solution of iodine and of potassium hydrogen carbonate or sodium acetate, the excess of iodine being finally eliminated by means of thiosulphate. The liquid thus treated is then tested for ammonia by means of Nessler's solution, or by warming with alkali hydroxide, or by means of sodium hypobromite.

Ammonia may be eliminated from hydroxylamine salts by taking advantage of the volatility of ammonium hydrogen carbonate. The solution of the salt, to which a sufficient quantity of potassium hydrogen carbonate has been added, is warmed in a flask on a water-bath, and air is drawn through by means of a water pump.

The estimation of the ammonia is effected by interposing a flask containing standard sulphuric acid between the flask containing the hydroxylamine solution and the pump. All the ammonia will have been volatilised and absorbed in the acid in about one hour, and the excess of acid is then titrated with alkali. In one instance, ammonia equivalent to 31% of ammonium chloride was found in a reputedly pure specimen of hydroxylamine hydrochloride.

G. F. M.

The Nitrometer Method for the Estimation of Nitrogen in Nitrates and Nitric Acid. H. W. WEBB and M. TAYLOR (*J. Soc. Chem. Ind.*, 1922, 41, 362—364r).—Nitrogen in potassium nitrate can be correctly estimated by means of the nitrometer if 91—92% sulphuric acid is employed, and a correction of 0.2 c.c. per 10 c.c. of acid used is applied for the solubility of nitric oxide in the acid. The correction for the solubility of nitric oxide in sulphuric acid given by Lunge (0.35 c.c. in 10 c.c. acid) is too high. Nitric acid can also be estimated to within $\pm 0.15\%$ if it is weighed out in such a way as to avoid loss of fume by weighing out a large quantity into a known weight of sulphuric acid contained in a deep bottle, and then weighing out the necessary amount of the mixed acid into the nitrometer. The estimations should be conducted in a room free from rapid fluctuations in temperature, and the latter should be read before the volume of gas in each case.

G. F. M.

The Absorption and Analysis of Gaseous Oxides of Nitrogen. A. SANFOURCHE (*Bull. Soc. chim.*, 1922, [iv], 31, 1248—1264).—Determinations of the rate of absorption of nitric oxide, and of

the products of the oxidation of this gas, by sulphuric acid and mixtures of sulphuric and nitric acid, show that the mechanism of absorption is very different in the two cases. Nitrous gases having a composition represented approximately by the formula N_2O_3 were absorbed with much greater rapidity than either pure nitrogen dioxide or peroxide, and the theory that the trioxide reacts as a mixture of the other two is therefore untenable. On the contrary, it is nitrogen trioxide which reacts with the sulphuric acid, and is continuously regenerated from its dissociation products according to the reversible equation $N_2O_3 \rightleftharpoons NO + NO_2$. Absorption by alkalis occurs in the same way, and the contention of Lunge that the peroxide initially reacts giving equimolecular proportions of nitrate and nitrite and that the former is then reduced to nitrite by the dioxide is inadmissible. The use of alkaline liquids as absorbents for nitrous gases in analysis, however, always gives a larger proportion of nitrogen in a higher state of oxidation than when sulphuric acid is used as absorbent. This is due to secondary reactions with the water, or water vapour, and is always more pronounced when the alkali hydroxide is only in slight excess. Nitrous acid is momentarily formed and decomposes into nitric acid and nitric oxide; the latter is either unabsorbed, or else in presence of oxygen again passes through the cycle of changes, the net result of which is to increase the nitrate at the expense of the nitrite. These errors can only be avoided by securing complete absorption on first contact of the gases with the alkaline solution by using a large excess of alkali and stirring the solution vigorously. This is not always possible, and hence absorption by sulphuric acid is considered preferable. G. F. M.

Estimation of Phosphorus. G. E. F. LUNDELL and J. I. HOFFMAN (*J. Ind. Eng. Chem.*, 1923, **15**, 44—47).—The sources of error in the precipitation of phosphorus as ammonium phosphomolybdate and its subsequent estimation by weighing as ammonium pyrophosphate or by titration with alkali, and the precautions necessary to guard against them are described in detail, with special reference to the estimation of small amounts of phosphorus in metallurgical products. The precipitation of the phosphomolybdate should be carried out at 40—60° in a solution containing 5—10% of nitric acid, 5—15% of ammonium nitrate, and a 15—25-fold excess of ammonium molybdate, and the precipitate should be kept with frequent shaking for at least forty minutes for a technical analysis, or over-night where great accuracy is required. The phosphorus must all be present initially as orthophosphate. The precipitate must be washed with 1—2% nitric acid, excessive washing being avoided. Fluorine, quinquivalent vanadium, titanium, zirconium, arsenic, and silicon contaminate the precipitate and delay precipitation, and absolutely correct estimations of phosphorus can only be obtained by dissolving the precipitate, and reprecipitating the phosphorus as a pure compound of definite composition, such as magnesium ammonium phosphate. On dissolving the precipitate in dilute ammonia, as

is usual, a small, insoluble residue of the phosphates of iron, titanium, zirconium, and tin will remain if these elements are present. This may sometimes be dissolved by adding citric acid to the ammoniacal solvent, otherwise the filter-paper and the precipitate must be fused with alkali, and extracted with water, adding the extract to the ammoniacal solution. Magnesium ammonium phosphate is precipitated from this solution by rendering slightly acid with hydrochloric acid, adding 0.2—0.5 g. of citric acid, a 5—10-fold excess of magnesia mixture, and ammonia to slight alkalinity. In presence of the above-mentioned elements, the precipitation must be repeated. If contamination by arsenic is feared, it must be removed at this stage by precipitation with hydrogen sulphide. For routine analysis of small amounts of phosphorus in iron, steel, bronze, etc., titration of the phosphomolybdate precipitated under standard conditions is quite satisfactory. The precipitate is first washed with cold 1—2% nitric acid, followed by 1% neutral potassium nitrate solution. It is then dissolved in excess of standard alkali, and the excess titrated back with standard acid, with phenolphthalein as indicator. The phosphorus equivalent of the alkali must be determined by analysis of a pure phosphate under the standard conditions. A fifteen-minute precipitation is sufficient for alkalimetric estimations except in abnormal conditions, such as when vanadium or much hydrochloric acid is present, when at least thirty minutes should be allowed before filtering. In presence of arsenic, the tendency is towards high values.

G. F. M.

The Iodometric Estimation of Arsenic Acid. I. M. KOLTHOFF (*Z. anal. Chem.*, 1923, **62**, 137—138).—In the determination of arsenic acid by titration of the iodine liberated by addition of potassium iodide to the hydrochloric acid solution, all danger of obtaining high results by atmospheric oxidation may be obviated by warming the solution of arsenic acid with an equal volume of *N*-hydrochloric acid on the water-bath for five minutes, then adding potassium iodide to a concentration of 25%, closing the flask, warming for a further five to ten minutes, cooling, and titrating with thiosulphate. The result may be checked by neutralising the titrated liquor with sodium hydrogen carbonate and titrating with iodine. Slightly high results are obtained in the first process if the iodide is added before warming the acidified solution. (Cf. Rosenthaler, A., 1922, ii, 584; Fleury, A., 1920, ii, 448; Kolthoff, A., 1921, ii, 463.)

A. R. P.

Estimation of Carbon Dioxide in Dilute Concentration. KEIICHI SHIKATA and SHIGERU SARUHASHI (*J. Pharm. Soc. Japan*, 1922, No. **488**, 893—907).—An improvement of the method of estimating carbon dioxide by the decrease of the volume of a potassium hydroxide solution which absorbs it. For the purpose, the authors have constructed an apparatus consisting of a sensitive differential manometer and a graduated capillary (2 c.c. volume and 38 mm. length) attached to a balloon of 198 c.c. capacity. With the

apparatus as little as 0.004% of carbon dioxide can be estimated accurately. K. K.

Gasometric Method for the Estimation of Carbon Dioxide in Carbonates. C. TUBANDT and HARRY WEISZ (*Chem. Ztg.*, 1922, **46**, 1105).—The carbonate is placed in a small reaction vessel which is attached to the lower end of a small vertical condenser, an acid chamber being fitted between the end of the condenser and the reaction vessel. Taps are provided between the acid chamber and the reaction vessel and at the top of the condenser. A tube connects the top of the condenser with a gas-measuring burette. The latter is provided with a water-jacket, and this is connected with the jacket of the condenser and with a bath surrounding the reaction vessel, so that the whole apparatus may be brought to the same temperature. After the acid has been admitted to the reaction vessel and the greater part of the carbon dioxide has been collected in the burette, the water in the vessel surrounding the reaction vessel is boiled for a short time, then cooled rapidly, and after the temperature of the whole apparatus has been brought to that at which it was originally, the volume of the gas is measured. W. P. S.

Estimation of the Titratable Alkali of the Blood. ISIDOR GREENWALD and GERTRUDE LEWMAN (*J. Biol. Chem.*, 1922, **54**, 263—283).—The method is designed for clinical use. Oxalated blood is precipitated with picric acid. Estimations are then made of (1) free picric acid, and (2) total picric acid in the filtrate, the difference representing the alkali previously combined with protein or carbonic acid in the blood. Free picric acid is estimated by direct titration with sodium hydroxide in the presence of a suitable indicator, and total picric acid either gravimetrically as nitron picrate or volumetrically, using titanous chloride. E. S.

Analysis of Sodium Perborate. HERMANN BURKARDT (*Chem. Ztg.*, 1923, **47**, 6).—The available oxygen content of the salt is determined by titration of the solution acidified with sulphuric acid with *N*/4-potassium permanganate. A second quantity of 2.5 g. is dissolved in water and the solution is titrated with *N*/2-hydrochloric acid, using methyl-orange as indicator. After boiling under a reflux condenser for five minutes, the solution is cooled, treated with 10 c.c. of neutral glycerol and a few drops of phenolphthalein, and titrated against *N*/2-sodium hydroxide to a pale pink colour. If, after addition of more glycerol the colour disappears, more alkali and glycerol are added until the pink colour persists. From these three results the percentages of borate and perborate present may be calculated. A. R. P.

Estimation of Calcium in the Blood. GIOVANNI DE TONI (*Arch. Farm. speriment. Sci. aff.*, 1922, **34**, 124—128, 129—130, 145—149).—The author finds that Jansen's method for estimating calcium in the blood (A., 1918, ii, 174) gives results of satisfactory accuracy, provided that the mean of two or three separate estimations is taken; the amount, 10 c.c., of blood required for each

estimation is unduly large, especially in the case of an infant. Marriott and Howland's method (A., 1918, ii, 21) is untrustworthy.

T. H. P.

The Application of Conductometric Methods to Precipitation Analysis. VI. Conductometric Titrations with Lithium Sulphate. I. M. KOLTHOFF (*Z. anal. Chem.*, 1923, 62, 1—7).—Barium salts even in very dilute solution may be accurately titrated conductometrically by means of lithium sulphate solution if about 30% of alcohol is added to the liquid. In the presence of calcium, high results are obtained, probably due to co-precipitation of calcium sulphate. Calcium and strontium salts cannot be titrated in the above manner, but lead salts in greater dilution than 0.01 mol. give excellent results, although more concentrated solutions yield results as much as 4% too low.

A. R. P.

The Application of Conductometric Methods to Precipitation Analysis. VII. Conductometric Titrations with Sodium Chromate. I. M. KOLTHOFF (*Z. anal. Chem.*, 1923, 62, 97—103).—Barium, lead, and silver in neutral solutions may be accurately estimated by conductometric titration with sodium chromate. In acid solutions, only lead gives good results, the other two metals forming dichromates. Strontium salts interfere with the barium estimation. Alone, strontium may be titrated in a similar way to barium, provided 50% of alcohol is added to the solution, but manganese, zinc, copper, and cadmium cannot be satisfactorily titrated in this manner, as they all form more or less basic salts none of which is of constant composition. By addition of an excess of potassium dichromate to a neutral solution of a lead salt of a strong acid and subsequent titration conductometrically of the liberated chromic acid with standard alkali (to dichromate), accurate results are obtained, as the first dissociation constant of chromic acid is so large whilst the second is exceedingly small.

A. R. P.

Colorimetric Method for the Estimation of Small Amounts of Magnesium. F. S. HAMMETT and E. T. ADAMS (*J. Biol. Chem.*, 1922, 54, 565—566).—In the authors' method (A., 1922, ii, 587), separation of the ammonium magnesium phosphate by centrifuging is preferable to filtration through a Gooch crucible owing to the presence of small quantities of phosphorus in the asbestos used in the crucible.

E. S.

The Estimation of Magnesium in Aluminium Alloys. W. H. WITHEY (*Chem. News*, 1923, 126, 17—19).—Two g. of the alloy are dissolved in aqua regia and the solution is evaporated with sulphuric acid until the latter fumes strongly. After cooling and diluting, the silica is filtered off and the filtrate treated with 15 g. of tartaric acid, 5 g. of ammonium chloride, ammonia until distinctly alkaline, 25 c.c. of saturated sodium phosphate solution, and a further quantity of strong ammonia equal to one-third the bulk of the solution. After stirring and remaining over-night, the precipitate is collected, washed, ignited, and weighed as magnesium

pyrophosphate in the usual way. If the alloy contains manganese, the precipitate will be contaminated with this element, the amount of which must be estimated by the bismuthate method and the corresponding weight of manganese pyrophosphate deducted. Copper, nickel, zinc, aluminium, and iron do not interfere.

A. R. P.

A New Method of Estimating Magnesium in Aluminium Alloys. BUNTARÔ OTANI (*J. Chem. Ind. Japan*, 1922, **25**, 1305—1310).—The method depends on the fact that magnesium is precipitated as phosphate by means of sodium phosphate in the presence of tartaric acid (equivalent to 1·5 times the aluminium in the solution), whilst the aluminium remains in the solution as a soluble salt: $\text{Al}(\text{OH})_3 + \text{C}_4\text{H}_6\text{O}_6 \rightarrow \text{C}_4\text{H}_4\text{O}_6\text{Al}\cdot\text{OH} + 2\text{H}_2\text{O}$. For precipitation of the magnesium phosphate the mixture must be left for six hours, but the time must be increased if the magnesium is present in very small amount.

K. K.

Estimation of Zinc as Zinc Ammonium Phosphate and its Application in the Separation of Zinc from other Metals. II. P. ARTMANN (*Z. anal. Chem.*, 1923, **62**, 8—17; cf. A., 1915, ii, 181).—The influence of ammonium nitrate, chloride, tartrate, and acetate and of the corresponding acids on the precipitation of zinc ammonium phosphate has been investigated, and the following conditions are recommended for obtaining the best results. The warm ammoniacal solution (60—70°) containing ammonium-ions in a concentration not exceeding *N*/1 is neutralised with nitric acid and treated with six times the theoretical quantity of ammonium phosphate solution; the minimum amount of the latter, however, should be sufficient to render the solution after precipitation at least *N*/5 in respect to this reagent, *i.e.*, 10 c.c. of 3*N*-ammonium phosphate solution per 150 c.c. If ammonium tartrate is also added, as in the case of separation of zinc from other elements, a further 3 c.c. of the phosphate solution must be used for every 10 c.c. of 2*N*-ammonium tartrate solution added. Prolonged heating after precipitation must be avoided, as it tends to convert the zinc ammonium phosphate into tertiary zinc phosphate; to obtain an easily filterable precipitate the solution should be heated just to boiling with continuous stirring and then left for twenty minutes on the water-bath.

A. R. P.

Estimation of Zinc as Zinc Ammonium Phosphate and its Application to the Separation of Zinc from other Metals. III. **Separation of Zinc from Mercury and Nickel.** P. ARTMANN and WALTER HARTMANN (*Z. anal. Chem.*, 1923, **62**, 17—23).—For the separation of zinc from mercury, the faintly acid solution of the mixed nitrates containing less than 0·1 g. of zinc and 0·4 g. of mercury is treated with 6 g. of ammonium nitrate and made just ammoniacal. Ten c.c. of 3*N*-ammonium phosphate solution are added, and the mixture is heated at 60°, neutralised with 5*N*-nitric acid, heated to boiling, and left for thirty minutes on the water-bath. The precipitate is washed by decantation first with

hot 1% ammonium phosphate solution, then with cold water, dried at 105° , and weighed as zinc ammonium phosphate. If more mercury than zinc is present, the precipitate is dissolved in nitric acid and the zinc reprecipitated as before.

The separation of zinc from nickel is carried out in a similar manner, except that the ammonium nitrate is replaced by 30 c.c. of 2*N*-ammonium tartrate solution and 1–2 g. of sodium acetate are added before neutralisation. Double precipitation is necessary in all cases. A. R. P.

The Electrometric Estimation of Zinc and Lead in the same Solution by Means of Potassium Ferrocyanide. ERICH MÜLLER and KURT GÄBLER (*Z. anal. Chem.*, 1923, 62, 29–34).—Zinc and lead may be titrated consecutively by the addition of a 0.1 mol. solution of potassium ferrocyanide to a neutral solution of the two metals containing 1 c.c. of a 0.1 mol. solution of potassium ferricyanide per 100 c.c., the end-points being determined conductometrically. The first knick in the curve corresponds with the complete precipitation of zinc as $K_2Zn_3[Fe(CN)_6]_2$, and the second to that of lead as $Pb_2Fe(CN)_6$. The titration is carried out at 75° , and a platinum gauze is used as indicator electrode. This is connected through an electrolytic switch filled with saturated potassium nitrate solution to the normal calomel electrode and the potential difference between the indicator and normal electrodes is measured by means of a Poggendorff capillary electrometer. In order to obtain accurate results by this method, the solution must be left for several minutes after each addition of reagent when the zinc end-point is being approached. An alternative procedure consists in dividing the solution into two equal parts and determining the sum of the zinc and lead in one part and the zinc alone, after addition of sufficient sulphuric acid just to precipitate the lead, in the second part. Both titrations are carried out at 75° , the former with an applied potential of +0.19 volt and the latter with +0.50 volt. The presence of excessive quantities of nitrates or acetates interferes with the lead titration. A. R. P.

Gravimetric Analysis. XXVII. Estimation of Lead. II. L. W. WINKLER (*Z. angew. Chem.*, 1922, 35, 715–716).—In the presence of iron, the method described in the previous paper (this vol., ii, 40) is inapplicable. Good results are, however, obtained if the lead and ferric nitrate solution containing 1 c.c. of *N*-nitric acid in 100 c.c. are treated in the cold with 10 c.c. of a cold 10% ammonium sulphate solution. After remaining over-night, the precipitate is filtered on a Gooch crucible, washed first with 10 c.c. of 1% sulphuric acid, then with dilute alcohol, dried at 130° , and weighed as lead sulphate. Potassium salts cause the results to be as much as 50% too high, but most common metals do not interfere. To separate small quantities of lead as sulphate from large quantities of foreign metals, the following procedure is recommended. The solution containing the metals as nitrates together with 1 c.c. of normal nitric acid in 25 c.c. are treated with 25 c.c. of 95% alcohol, then with 5 c.c. of 10% ammonium

sulphate solution. After remaining over-night, the precipitate is filtered, washed, dried, and weighed as before. The method is applicable to the estimation of lead in brass and zinc. [Cf. *J.S.C.I.*, 1923, 122A.]
A. R. P.

The Iodometric Titration of Mercuric Chloride. I. M. KOLTHOFF (*Pharm. Weekblad*, 1923, 60, 18—20).—The method proposed by Kolthoff and Keijzer (A., 1921, ii, 66), namely, reduction by alkaline hydrogen peroxide solution, acidification, solution of the separated mercury by excess of iodine and titration of the excess with thiosulphate, was found very tedious in some cases, from the long time required to dissolve the mercury. Better results are obtained by using barium hydroxide for the peroxide treatment; the mixture must be boiled and well shaken; after cooling, iodine is added to the alkaline liquid, which is acidified, after the mercury is dissolved, for titration of the excess.

S. I. L.

Sensitive Reactions of Copper and certain Phenols (Quinol and α -Naphthol). J. ALOY and A. VALDIGUÉ (*Bull. Soc. chim.*, 1922, 31, 1176—1179).—Dilute aqueous solutions of quinol are coloured blue by the presence of a trace of copper, slowly at the ordinary temperature and more quickly on being heated. The intensity of the coloration is proportional to the concentration of copper, and the test must be carried out in neutral or feebly acid solution. It appears to be specific for copper, as tests with other metals failed to produce the characteristic effects. The author has devised a colorimetric method for estimating copper, based on this reaction. The action is also specific for quinol among phenols, and sufficiently sensitive to detect 0.1 mg. of that substance. Copper salts are also readily detected by α -naphthol, which gives a violet coloration under conditions similar to those in the case of quinol. The colour, however, is quite distinct, and is not given by β -naphthol. The blue substance produced in the case of quinol is not extracted by ether or chloroform. The authors suggest that it may be a compound of quinol or of one of its oxidation products with the copper salt. [Cf. *J.S.C.I.*, 1923, Feb.]

H. J. E.

Precipitation and Titration Method for the Estimation of Copper in Alloys. BR. WINKLER (*Chem. Ztg.*, 1922, 44, 1137).—The alloy is dissolved in a mixture of nitric acid and hydrochloric acid, the solution is diluted, treated with sodium potassium tartrate and an excess of sodium hydroxide, and then boiled with the addition of hydroxylamine hydrochloride. The precipitated cuprous oxide is collected, washed, dissolved in hydrochloric acid, oxidised with nitric acid, the solution is evaporated with the addition of sulphuric acid, and the copper estimated iodometrically.

W. P. S.

Estimation of Aluminium as Phosphate. G. E. F. LUNDELL and H. B. KNOWLES (*J. Ind. Eng. Chem.*, 1922, 14, 1136—1137).—Estimations of aluminium as phosphate are generally in error.

Acceptable results are possible when only a few mg. of aluminium are involved. High values are the rule when more than 5 mg. of aluminium are precipitated by any of the usual procedures. Excessive washing of the precipitate or the use of a weak acid for washing leads to low values, as does the precipitation with only a moderate excess of the precipitant, or precipitation in alkaline solution. Under these conditions, iron behaves like aluminium, whilst titanium invariably yields low values. The precipitation of aluminium in the presence of macerated paper facilitates the washing of the precipitate.

H. C. R.

Estimation of Manganese, Chromium, and Nickel in Steel.

ALOIS EDER and HANS EDER (*Chem. Ztg.*, 1922, **46**, 1085—1086).—A quantity of 0.5 g. of the steel is dissolved in 25 c.c. of dilute sulphuric acid with the addition of 2 c.c. of silver nitrate solution (2.5 g. per litre); 5 c.c. of a mixture of nitric acid and phosphoric acid (equal volumes) are added, and the solution is evaporated to expel nitric acid. After cooling, the solution is diluted, treated with 3 g. of ammonium persulphate, boiled for five minutes, again cooled, 5 c.c. of sodium chloride solution (25 g. per litre) are added, and the permanganate is titrated with standardised arsenious acid solution. The titrated solution is then boiled for twenty-five minutes to decompose the excess of persulphate, cooled, a known volume of standardised ferrous ammonium sulphate solution is added to reduce the chromate, and the excess is titrated with permanganate solution. The mixture is then treated with 50 c.c. of sodium pyrophosphate solution (150 g. per litre); the precipitate formed is dissolved by the addition of ammonia, excess of the latter is neutralised with sulphuric acid, a few drops of ammonia are added to dissolve any precipitate formed, and, after the addition of 5 c.c. of potassium iodide solution (40 g. per litre), the turbid solution is titrated with standardised potassium cyanide solution, the end-point being denoted by the solution becoming clear. This titration, after allowance for the silver added originally, gives the quantity of nickel present.

W. P. S.

A Micro-method for the Estimation of Iron in Colloidal Solutions. I. NEWTON KUGELMASS (*Bull. Soc. Chim. Biol.*, 1922, **4**, 577—583).—To a known volume of the solution, concentrated hydrochloric acid and an oxidising agent (perhydrol) are added. The mixture is boiled and *isoamyl* alcohol added, followed by ammonium thiocyanate, when the ferric thiocyanate passes completely into the *amyl* alcohol layer. This is pipetted off and compared in a colorimeter with a similar *amyl* alcohol solution prepared from a known aqueous solution of ferric-ions. W. O. K.

The Electrometric Estimation of Cobalt with Silver Nitrate.

ERICH MÜLLER and HANS LAUTERBACH (*Z. anal. Chem.*, 1923, **62**, 23—28).—Cobalt may be estimated in a similar manner to nickel (A., 1922, ii, 875) by addition of an excess of standard potassium cyanide solution to a neutral solution of the cobalt salt, followed by titration of the excess by silver nitrate, the end-

point being ascertained conductometrically. The cobalt compound formed in the first stage of the process is $K_3Co(CN)_5$, whereas nickel forms $K_2Ni_1(CN)_4$; a larger amount of cyanide must therefore be added than is required in the nickel estimation. The presence of free ammonia in the cobalt solution leads to slightly low results.

A. R. P.

Estimation and Separation of Titanium, Columbium, Tantalum, and Zirconium. WILLIAM P. HEADDEN (*Proc. Colorado Sci. Soc.*, 1917, **11**, 185—201).—The gravimetric estimation of titanium in the presence of columbic acid appears to be most difficult, if not impossible, but small quantities of titanium may be estimated colorimetrically by means of hydrogen peroxide. To separate titanitic acid from tantalic acid, the two substances are fused with potassium hydrogen sulphate, the mass is dissolved in water and hydrofluoric acid, the solution neutralised with ammonia, ammonium fluoride, ammonium hydrogen carbonate, and hydrogen peroxide are added, and the boiling mixture is poured into hot ammonium carbonate solution. The tantalic acid is precipitated whilst the titanitic acid remains in solution; to ensure complete separation the precipitate should be dissolved and re-precipitated. A method for the approximate separation of tantalic acid from columbic acid depends on the fact that tantalic acid is precipitated when its hydrofluoric acid solution is treated at 70° with an excess of ammonium hydrogen carbonate; under these conditions, columbic acid remains in solution. Titanitic acid may be separated from zirconia by dissolving the freshly precipitated oxides in ammonium fluoride solution and then adding an excess of ammonia; the titanitic acid is precipitated completely and the zirconia remains in solution. When a solution containing zirconia and columbic acid is treated with ammonium fluoride and ammonium hydrogen carbonate, and boiled, the columbic acid is precipitated; this method may also be used for the separation of zirconia from tantalic acid.

W. P. S.

Estimation of Bismuth. KÖSTER (*Chem. Ztg.*, 1923, **47**, 22).—Small quantities of bismuth in lead may be detected by cupelling 25 g. of the metal and moistening the dark spot in the middle of the cupel with dilute hydriodic acid. If bismuth is present, this spot becomes surrounded by a red ring, the extent and intensity of which depend on the quantity of bismuth present. To carry out a quantitative estimation, quantities of 25 g. of pure lead are cupelled with varying amounts of bismuth and the colour produced in the assay is compared with this series of standards. The hydriodic acid is conveniently prepared by passing hydrogen sulphide into water in which iodine is suspended and filtering off the precipitated sulphur. The method is applicable to the detection and estimation of bismuth in ores which are fused with litharge, carbon, and fluxes exactly as in the ordinary gold and silver assay, and the lead button is cupelled as described above.

A. R. P.

Rapid Estimation of Bismuth in Urine. DOMENICO GANASINI (*Boll. Chim. Farm.*, 1922, **61**, 705—708).—The author replies

to Dezani's criticisms (*Biochim. Terap. speriment.*, 1922, 9, 267) on his method for the estimation of bismuth in urine (A., 1922, ii, 590). Dezani's method, based on the yellow coloration obtained on addition of potassium iodide to a very dilute solution of a bismuth salt in presence of hydrochloric acid, gives uncertain results when applied to urine.

T. H. P.

Use of Textile Fibres in Qualitative Chemical Analysis. V. Detection of Gold by means of Stannous Chloride-Pyrogallol Viscose Fibres. HOWARD IRVING COLE (*Philippine J. Sci.*, 1922, 21, 361—364; cf. A., 1918, ii, 129).—Viscose fibres treated with stannous chloride and pyrogallol may be used for the detection of very small quantities of gold; a red or blue coloration is obtained when the fibre is immersed in a drop of solution containing as little as 0.00002 mg. of gold and the solution allowed to evaporate to dryness. More concentrated solutions yield a red or purple coloration at once.

W. P. S.

Direct Estimation of the Caoutchouc Hydrocarbon as the Bromide. M. PONTIO (*Chim. et Ind.*, 1922, 8, 1211—1212).—A solution of 0.2 g. of the raw caoutchouc in 20 c.c. of xylene is treated with 50 c.c. of a solution of bromine in carbon tetrachloride or chloroform (3 vols. to 247 vols.). After one-quarter of an hour, 250 c.c. of acetone are added, the mixture being agitated and filtered immediately, using "tared" filter-papers. The precipitate is washed repeatedly with acetone and finally with alcohol before being dried at 70—80°. After subtracting the weight of residue obtained on incineration, the weight of the product is multiplied by 0.317 for conversion into caoutchouc, the composition of the product approximating to $(C_{10}H_{16})_3Br_{11}$. For this estimation, it is preferable to remove the natural resins previously by extraction of the solid caoutchouc, and also the protein matter by sedimentation or filtration of the solution.

D. F. T.

Use of Iodine in the Estimation of Dextrose, Lævulose, Sucrose, and Maltose. F. A. CAJORI (*J. Biol. Chem.*, 1922, 54, 617—627).—Dextrose may be estimated iodometrically by Bougault's method (A., 1917, ii, 395) in the presence of both lævulose and sucrose. At the ordinary temperature, the oxidation is complete in twenty-five minutes. To avoid risk of enolisation, the concentration of sodium carbonate should not exceed 1—1.5%. When used in conjunction with estimations based on the copper-reducing power, this method may evidently be applied to the estimation of mixtures of the above three sugars. For this purpose, hydrolysis of the sucrose should be effected by heating for two hours at 60° with 1% hydrochloric acid; at higher temperatures, some decomposition of lævulose occurs. In the iodometric estimation of maltose, thirty-five minutes are required for the oxidation. The estimation may also be made indirectly after hydrolysis to dextrose by freshly prepared yeast maltase, provided corrections are made for the reducing power of the maltase preparation. Since maltose is not appreciably hydrolysed under the conditions used

above for sucrose, the method may possibly be extended to include mixtures of all four sugars (cf. also Judd, A., 1920, ii, 395; Baker and Hulton, A., 1921, ii, 417).
E. S.

Methods for the Estimation of Starch in Small Quantities in Plant Tissues [Cantaloupe seeds]. F. E. DENNY (*J. Assoc. Off. Agric. Chem.*, 1922, 6, 175—191).—The most suitable method for the estimation of starch in quantities of 0.1—1.0% is as follows. The ground cantaloupe seeds are extracted with cold light petroleum and oven dried. Starch is extracted with saturated calcium chloride solution at the boiling temperature. Aliquot portions of the extract are treated with $N/10$ -iodine drop by drop until a permanent blue colour appears (satisfying the non-starch iodine-absorbing substances) and then with excess of standard $N/50$ -iodine. After remaining over-night, the precipitate is separated by centrifuging and washed with potassium iodide solution. Absorbed iodine is estimated by boiling the precipitate with excess of thiosulphate solution ($N/200$) and titrating with standard iodine. Comparison is made with figures obtained with pure starch. The average ratio, iodine absorbed: starch, was 0.11, tending to decrease in smaller concentrations. The method of Scales (A., 1919, ii, 435) would appear capable of refinement, to give considerably increased sensitivity.
A. G. P.

Formic Acid. I. Gravimetric Estimation of Formic Acid. FR. AUERBACH and H. ZEGLIN (*Z. physikal. Chem.*, 1922, 103, 161—177).—The gravimetric estimation of formic acid by means of mercuric chloride has been investigated and the original method improved in several particulars. The modified method for this estimation is carried out as follows. The solution of formic acid or formate (50—100 c.c.) is neutralised in an Erlenmeyer flask with either sodium carbonate or hydrochloric acid if it is acid or alkaline in reaction. Then 1 c.c. of N -hydrochloric acid is added followed by 3 g. of crystalline sodium acetate. If the amount of formic acid present is greater than 0.1 g., the amount of sodium acetate must be correspondingly increased, whilst if it is less than 0.005 g. the acetate must be reduced to 1 g. Mercuric chloride is then added in 5% solution in quantity equal to twelve times the amount of formic acid present and an additional excess of 12 mg. for each c.c. of total solution in the flask. If the solution contains salicylic acid or similar acid, then 1 mg. of sodium chloride is added for each c.c. of the total solution in the flask. The flask is covered with a watch glass and heated for two hours on a rapidly boiling water-bath. The precipitated mercurous chloride is filtered in a platinum filter crucible, washed with water at 40—50°, and finally with alcohol. The crucible is dried for forty-five to sixty minutes at 95—100° and weighed. The weight of the precipitate multiplied by the factor 0.09745 gives the weight of formic acid. This method yields excellent results for quantities of formic acid down to 1 mg. Should the formic acid to be estimated be present in ethereal solution it is extracted with an aqueous solution of

sodium acetate and the estimation carried out as above in the aqueous solution. J. F. S.

[**Estimation of Formic Acid**]. FR. AUERBACH and H. ZEGLIN (*Z. physikal. Chem.*, 1922, **103**, 200—237).—See this vol., ii, 61.

Estimation of Formic Acid in the Urine. ETHEL M. BENEDICT and G. A. HARROP (*J. Biol. Chem.*, 1922, **54**, 443—450).—The method of Dakin, Janney, and Wakeman (*A.*, 1913, i, 679) has been modified to avoid the preliminary extraction with ether. The urine (100 c.c.) is diluted with water (500 to 600 c.c.), treated with a 20% copper sulphate solution (100 c.c.), made just alkaline by the addition of a 10% suspension of calcium hydroxide, and diluted to 1 litre. After fifteen to thirty minutes, the mixture is filtered and an aliquot part of the filtrate (600 c.c.) made distinctly acid with 85% phosphoric acid and then steam distilled, the distillate (2 litres) being collected in 0.1N-sodium hydroxide (15 to 20 c.c.). The distillate is evaporated to dryness, dissolved in water (100 c.c.), and an aliquot part (90 c.c.) made just acid by the addition of 0.1N-HCl and treated with 10 c.c. of a mercuric chloride mixture (1 litre contains 200 g. mercuric chloride, 80 g. sodium chloride, and 300 g. sodium acetate). It is then heated for one hour on a water-bath under reflux. The precipitated mercurous chloride, which represents 99% of the theoretical amount, is filtered and weighed. E. S.

Differentiation of Acetic Anhydride from Glacial Acetic Acid. VICTOR E. LEVINE (*Science*, 1920, **52**, 207).—(1) The addition of a few drops of a 0.5% solution of selenium dioxide in concentrated sulphuric acid to acetic anhydride results in the formation of a brick-red, colloidal solution or precipitate of selenium. Glacial acetic acid does not react. (2) Ten drops of acetic anhydride are shaken with 2 c.c. of chloroform in which a small quantity of cholesterol has been dissolved. On the addition of 20 drops of concentrated sulphuric acid, a fleeting purple colour is developed, changing to blue and finally to deep green. With or without glacial acetic acid, a lemon-yellow colour is formed which rapidly becomes deep orange, cherry-red, or burgundy-red. A. A. E.

Estimation of Abietic Acids and of Colophony. FERDINAND SCHULZ and STANISLAV LANDA (*Bull. Soc. chim.*, 1922, [iv], **31**, 1353—1360).—The method is based on the reducing action of abietic acid on mercuric acetate. A solution of about 0.5 g. of the substance in 10 c.c. of a saturated solution of mercurous acetate in glacial acetic acid is warmed for an hour at 50° with the freshly prepared mercuric acetate reagent prepared by dissolving 3 g. of mercuric oxide in 50 c.c. of glacial acetic acid likewise saturated with mercurous acetate. After keeping for a further hour, the precipitate of mercurous acetate is collected, washed, and dissolved in 20% nitric acid, and the mercury in the solution thus obtained is estimated by Votoček's method—oxidation by permanganate, addition of sodium chloride solution, and titration of the excess by mercuric nitrate solution in presence of sodium nitroprusside.

The mean value found for the equivalent of 1 g. of colophony was 1.84 g. of mercuric oxide. Colophony in admixture with shellac, and palm oil or other soap-making materials, can be estimated by this method to an accuracy of about $\pm 10\%$. The estimation of crystallised abietic acid from American colophony gave an equivalent of 1.974 g. of mercuric oxide per g. of acid, corresponding approximately with the ratio $3\text{HgO} : \text{C}_{20}\text{H}_{30}\text{O}_2$. The oleosylvic acid, m. p. $167-169^\circ$, $[\alpha]_D + 56.2^\circ$, from the resin oil was apparently a mixture of reducing and inert acids, as 1 g. reduced only about 0.36 g. of mercuric oxide. G. F. M.

Detection of Acetoacetic Acid in Diabetic Urine. G. FAVREL (*Ann. Chim. Analyt.*, 1922, 4, 337—338).—The urine is acidified with hydrochloric acid and extracted with ether; the ethereal solution is evaporated, the residue dissolved in water, treated with calcium carbonate, and the mixture filtered. If acetoacetic acid (enolic form) is present, the filtrate yields a red coloration with ferric chloride. W. P. S.

Microchemical Detection of Fumaric Acid. L. VAN ITALLIE (*Pharm. Weekblad*, 1922, 58, 1312—1314).—Fumaric acid may be detected by the characteristic appearance of its thallium, lead, and copper salts under the microscope. The first is least satisfactory, requiring definite concentrations of the reagents. The lead salt forms thick, colourless prisms, the copper salt light blue aggregates of needles. S. I. L.

Estimation of Tartaric Acid. ANDRÉ KLING (*Ann. Chim.*, 1922, [ix], 18, 189—216).—Only *d*-tartaric acid occurs naturally and it cannot be precipitated quantitatively as calcium or lead tartrate. But after addition of an equivalent amount of the *l*-acid, quantitative precipitation is practicable in presence of dilute acetic acid. The method of estimation is based on addition to the natural acid of an excess of the *l*-acid or of one of its salts, followed by calcium acetate solution. By this means all the *d*-acid is precipitated as calcium racemate, carrying with it some calcium *l*-tartrate. The precipitate is dissolved in dilute hydrochloric acid and, on addition of sodium acetate, pure calcium racemate is obtained. The precipitate is dissolved in boiling 10% sulphuric acid and titrated with standard permanganate, half the quantity of acid found corresponding with that of the *d*-acid originally present. H. J. E.

Detection of Ethyl Phthalate and Phthaleins. RALPH L. CALVERT (*Amer. J. Pharm.*, 1922, 94, 702—703).—Ethyl phthalate being used as a denaturant for alcohol for use in perfumery in America, its detection is a matter of interest. A satisfactory test is performed as follows: To 3—5 c.c. of the sample 5—10 drops of phenol and 10 drops of sulphuric acid are added, and the mixture is gently heated until most of the alcohol has distilled off, and a red liquid remains. After cooling, 15—25 c.c. of water are added, when, if ethyl phthalate is present, the red colour disappears and a turbid liquid is obtained which becomes red on addition of sodium

hydroxide (phenolphthalein reaction). The reaction is quite delicate, as 1 c.c. of a 0.1% solution gives a distinct coloration.

G. F. M.

The Estimation of Milk in Milk Chocolate. J. GROSSFELD (*Z. Unters. Nahr. Genussm.*, 1922, **44**, 240—244).—The quantity of butter fat in milk chocolate can be arrived at from the Reichert-Meissl value of the total fat extracted with ether. The quantity of milk-protein present can be calculated from the percentage of ash (*a*) and the percentage of calcium oxide (*b*) in the chocolate according to the formula $26.1b - 1.16a$, or alternatively, if *N* is the percentage of total nitrogen in the chocolate, from the formula $21.4b - 1.35N$. Details of the method used for estimating the calcium oxide are given. Comparison of the milk-protein as estimated by the two methods outlined above and of casein as estimated by Baier and Neumann's method (*ibid.*, 1909, **18**, 13) show in general satisfactory agreement.

H. C. R.

Analytical Applications of the Reaction between Sulphites and Aldehydes. JOSÉ ESTALELLA (*Anal. Fis. Quím.*, 1922, **20**, 271—282).—The compounds of aldehydes with sodium hydrogen sulphite are slowly hydrolysed on keeping with liberation of sodium hydroxide. A 1% solution of sodium sulphite in the presence of phenolphthalein is proposed as a reagent for aldehydes. Similarly, formaldehyde in the presence of phenolphthalein may be used as a reagent for sulphites. The positive reaction consists in the development of a pink colour. The reaction is unsuitable as a basis for the quantitative estimation of sulphites. Small quantities of aldehydes may be estimated by means of it, using a colorimetric method.

G. W. R.

Methods of Estimation of Formaldehyde by Oxidation. RAOUL GROS (*J. Pharm. Chim.*, 1922, [vii], **26**, 415—425).—The method of the French Codex is very inaccurate owing to incomplete oxidation of the aldehyde on the one hand, and to the further oxidation of some of the formic acid to carbonic acid on the other. Romijn's method, oxidation with iodine in presence of alkali, is fairly accurate if the prescribed conditions are closely adhered to, but the presence of acetone would interfere. A method uninfluenced by the presence of either acetone or formic acid consists in adding to 5 c.c. of approximately 1% formaldehyde solution, 35 c.c. of potassium mercuric iodide solution (2.71% HgCl_2 , and 7.2% KI), and 20 c.c. of 27% sodium hydroxide solution. The red precipitate gradually changes to a greyish precipitate of mercury, and after ten minutes the liquid is carefully acidified with hydrochloric acid, a known excess of *N*/10-iodine is added to oxidise and dissolve the mercury, and the excess is titrated back with *N*/10-thiosulphate. The accuracy of this and other methods for the estimation of formaldehyde can conveniently be controlled by an analysis of formaldehyde sodium bisulphite, $\text{CH}_2\text{O} \cdot \text{NaHSO}_3 \cdot \text{H}_2\text{O}$, the sulphite being estimated by titration with iodine in presence of potassium hydrogen carbonate, under which conditions the

aldehyde is practically unattacked, and is then estimated by the method under investigation, and the result, of course, should be in accord with that obtained by the sulphite estimation.

G. F. M.

Comparative Tests on the Methods in Use for the Estimation of Formaldehyde in Formalin. F. MACH and R. HERRMANN (*Z. anal. Chem.*, 1923, **62**, 104—137).—The literature of the iodine, hydrogen peroxide, sodium sulphite, and ammonium salt methods of determining formaldehyde and its polymerisation products in commercial formalin is reviewed in detail and a large number of comparative results obtained by each of the methods on different samples are tabulated. The results obtained by the first three methods are in good agreement, whereas those obtained by the fourth method are about 0·5—1·0% lower than these. The presence of ethyl alcohol, acetaldehyde, and acetone leads to very erroneous results in the iodine method, whereas the influence of small quantities of these substances is comparatively slight in the sulphite method and almost negligible in the peroxide method. Larger amounts of acetone or acetaldehyde than 4%, however, give low results when the assay is allowed to remain the normal time and high results if left for some hours before titration. In all the methods the choice of indicator is important, azolitmic acid in the peroxide method and rosolic acid in the sulphite and ammonium salt methods being the most suitable. [*Cf. J.S.C.I.*, 1923, 118A.]

A. R. P.

Detection of Santonin. F. Utz (*Süddeutsch. Apoth.-Ztg.*, 1922, **62**, 77—78).—Santonin is sprinkled into a hot solution prepared by adding one or two drops of dilute ferric chloride solution to 1 c.c. of distilled water and mixing with 1 c.c. of concentrated sulphuric acid, and the liquid shaken with amyl alcohol, which assumes a blood-red colour. The methods described by Thaeter (*A.*, 1898, ii, 59), Jaworowski (*Chem. Ztg.*, 1897, 269), Smith (*Chem. Zentr.*, 1871, 486), Banfi (*Annalen*, **91**, 112), Schermer (*Pharm. Z. Russ.*, 1893, **32**, 120), Mindes (*Pharm. Post*, **44**, 687), and Neuhaus (*Deut. med. Woch.*, 1906, 466), and that of the German pharmacopœia are criticised.

CHEMICAL ABSTRACTS.

Compound of Antipyrine and Xanthidrol. RENÉ FABRE (*J. Pharm. Chim.*, 1922, [vii], **26**, 372—376).—By the interaction at ordinary temperatures of equimolecular proportions of xanthidrol in solution in methyl alcohol and antipyrine in solution in acetic acid, a *xanthylantipyrine* is formed and is slowly precipitated in fine needles, m. p. 178—179°. The formation of this derivative may be utilised to detect antipyrine in presence of pyramidone, quinine, etc., but, owing to its slight solubility, the method cannot be used for its estimation. The presence of antipyrine in urine would cause an error in the estimation of urea by means of xanthidrol unless it is previously removed by defecating the urine with an acetic acid solution of potassium mercuric iodide.

G. F. M.

Modification of Folin, Cannon, and Denis's Colorimetric Method for the Estimation of Adrenaline. SAKUJI KODAMA (*J. Biochem. [Japan]*, 1922, **1**, 280—287).—One c.c. of the uric acid reagent and 10 c.c. of a 20% solution of sodium carbonate are added to the solution under examination, and diluted to 50 c.c. with water. After two minutes the colour is compared in a Duboscq colorimeter with a standard solution containing 4 c.c. of 0.01% solution of water-blue, 4 c.c. of a 0.01% solution of nigrosine, 10 c.c. of a 10% solution of crystalline copper sulphate, 10 c.c. of hydrochloric acid (*d* 1.050), and water to 100 c.c. This solution, which must be standardised against uric acid, when set at 20.6 mm. should match the colour developed by 0.3 mg. of uric acid or 0.1 mg. of adrenaline.
CHEMICAL ABSTRACTS.

Sensitiveness of some Cyanide Reactions. JOHN B. EKELEY and ICIE C. MACY (*Proc. Colorado Sci. Soc.*, 1919, **11**, 269—275).—The Prussian blue test will detect the presence of 1 part of hydrocyanic acid in 170,000 parts of solution; if the test is applied to the distillate obtained after acidifying the solution with tartaric acid, 1 part in 1,700,000 parts may be detected. The sensitiveness of the hanging drop test with silver nitrate is 1 part of hydrocyanic acid in 19,000,000 parts, whilst the Schönbein (guaiaicum paper) test will detect 1 part in 55,000,000 parts. Chlorine, bromine, hydrogen peroxide, and hydrochloric acid do not yield a reaction with the Schönbein test when the dilution is greater than 1 part per million.
W. P. S.

Detection of Urobilin in Blood and in the Cerebrospinal Fluid. GEORGES RODILLON (*Bull. Soc. Chim. Biol.*, 1922, **4**, 474—475).—To 1 vol. of serum from the blood under examination, or of the cerebrospinal fluid, 1 vol. is added of a reagent consisting of a saturated solution of zinc acetate in 95% alcohol strongly acidified with acetic acid. To the filtered liquid thus freed from protein, 1 drop for every 5 c.c. of solution of a 1 in 150 alcoholic iodine solution is added, followed by one-tenth of a volume of chloroform. After agitation, the alcoholic chloroform layer which separates will contain a zinc compound of urobilin if the latter is present, and it is detected by directing a pencil of light concentrated by a converging lens on to the chloroform solution placed in front of a dark background. In presence of the minutest traces of urobilin a green fluorescence will be observed, and a spectroscopic examination will show very clearly a dark band in the blue-green between the *E* and *F* lines, and close to the latter. In presence of larger quantities of urobilin the chloroform layer will show a rose-coloured tint. The test can be carried out with very small quantities of serum, etc., as little as 0.5 c.c. being sufficient.
G. F. M.

General and Physical Chemistry.

Spectrochemical Investigations on Polynuclear Aromatic Compounds in Solution. F. KROLLPFEIFFER (*Annalen*, 1923, 430, 161—229).—Largely a statement in tabular form of the numerical results of the author's measurements of the refractive indices in various solvents of a large number of derivatives of benzene, naphthalene, anthracene, and other polynuclear systems (cf. following abstract). C. K. I.

Spectrochemical Peculiarities and Constitution of Naphthalene, Anthracene, Phenanthrene, and Fluorene. K. VON AUWERS and F. KROLLPFEIFFER (*Annalen*, 1923, 430, 230—268).—In this paper the spectrochemical measurements referred to in the preceding abstract, along with similar numerical data obtained at earlier dates and some new measurements, are collected together and discussed from the point of view of their bearing on the constitution of the various basic ring systems. The authors favour structures for naphthalene and anthracene in which only one ring has full aromatic character, and the usually accepted structures for phenanthrene and fluorene. As regards the effect of substitution in naphthalene on spectrochemical properties, the conclusions are drawn (1) that large increases in the specific refraction run parallel with large dispersion; (2) that the introduction of alkyl, alkoxyl, carbalkoxyl groups, and halogens has but little effect either on the exaltation of the refraction or dispersion; (3) that the effect of halogens is greater than in derivatives of benzene, and (4) β -derivatives have as a rule a stronger exaltation in specific refraction than the corresponding α -derivatives.

C. K. I.

"Aromatic" Carbon. K. VON AUWERS (*Ber.*, 1923, 56, [B], 69—76; cf. von Steiger, A., 1921, ii, 473; 1922, ii, 616; von Auwers, A., 1922, ii, 98).—A further criticism of von Steiger's hypothesis that an essential difference exists between aliphatic and aromatic carbon atoms.

The regularities observed in the thermochemistry of aromatic hydrocarbons do not necessitate the supposition of the tervalency of carbon, but are equally reconcilable with the quadrivalency of the element (cf. Wibaut, A., 1922, ii, 239). They do not necessitate the hypothesis that the C—C and C—H linkings in aromatic hydrocarbons are equivalent from the point of view of energy which, moreover, is not in harmony with the principle of the distribution of energy of combination adopted by von Steiger (*loc. cit.*). It is only proved that the mean energy of formation of the individual linkings can be regarded as equal for purposes of calculation; this is in harmony with the similarity in the constitution of the molecules, but does not necessitate any particular assumption with regard to the nature of carbon in these compounds.

From the spectrochemical point of view, it is shown in detail that the molecular refractions of anthracene and phenanthrene differ from one another to a degree which is completely outside the limits of experimental error, whereas they should be identical if von Steiger's hypothesis is correct. In general, von Steiger regards discrepancies between the observed values and those calculated with the aid of the "normal" equivalents as defects, whereas the whole history of spectrochemistry shows that such discrepancies are of the maximum value in throwing light on the constitution of the compounds under examination. Von Steiger's method of calculating the molecular refractions is quite unsuitable for the homologues of benzene, since the difference increases with increasing number of side chains.

Von Steiger's conception of the peculiar nature of "aromatic" carbon rests on the work of Debye and Scherrer, on the crystalline structure of graphite, the additivity of the heats of combustion of certain purely aromatic hydrocarbons, and the supposed additivity of their molecular refractions. Arguments based on the two latter points have been shown to be invalid, whilst Debye and Scherrer's observations do not depend on the existence of two differing types of carbon atom, but on the formation of different types of molecule owing to the differing mode of union of identical carbon atoms. Further, exception is taken to the sharp differentiation of aliphatic and aromatic carbon, since this is not justifiable on purely chemical grounds and can only be applied to two extreme types of compounds which are not chemically distinctly separated.

H. W.

The Molecular Refraction of Anthracene. F. KROLL-PFEIFFER (*Ber.*, 1922, 55, [B], 77—83).—The molecular refraction of anthracene dissolved in quinoline has been determined, the calculations being made in accordance with the formula $Mr_L = M[r_{LS} \times 100/p - r_{LM}(100-p)/p]$, in which M is the molecular weight of the dissolved substance, r_L its specific refraction according to Lorenz and Lorentz, r_{LS} the specific refraction of the solution, r_{LM} that of the solvent, and p the percentage of solute. The mean value $M_D^{20} = 65.3$; this is considerably higher than that observed by von Steiger (*A.*, 1922, ii, 616) for anthracene dissolved in naphthalene, which is in agreement with the previous observations of Chilesotti. The discrepancy does not appear to be attributable to the particular solvent used, since the molecular refractions of the closely allied 1-methyl- and 9-ethyl-anthracenes are almost identical when the determinations are made with the molten materials or with their solutions in quinoline or naphthalene. Re-determination of the molecular refraction of anthracene dissolved in naphthalene has given values which agree excellently with those observed when quinoline is used as solvent, and are much higher than those found by von Steiger and Chilesotti; the error in the observations of the former appears to lie in the observation of the refractive indices, the latter in that of the density.

The values obtained for the molecular refraction of phenanthrene dissolved in benzene or naphthalene agree with those observed by von Steiger and Chilesotti. H. W.

Calculation of the Hydrogen Dissimilar Spectra from the Inner Movements of the Electrons. II. E. FUES (*Z. Physik*, 1923, **12**, 1—12).—A continuation of a theoretical discussion (this vol., ii, 1), in which it is shown that it is possible to calculate the terms of the Röntgen and optical spectra from the movements of the electrons in a central field of force, and to derive the potential curve of the atomic field. The sodium spectrum is considered in detail, and the terms in its spectrum are deduced from the potential curve. The agreement for the quantum numbers of the 3_1 , 4_1 , 5_1 , 6_1 , 3_2 , 4_2 , 5_2 , 6_2 , 3_3 , 4_3 , 5_3 , 6_3 , and 4_4 members, which is within 3%, is a demonstration of the correctness of the recent views on the origination of series spectra. W. E. G.

Visible and Ultra-red Radiation of Hydrogen. FREDERICK SUMNER BRACKETT (*Astrophys. J.*, 1922, **56**, 154—161).—The radiation from the central section of a long discharge tube has been analysed by means of a rock-salt prism spectrometer, and a sensitive vacuum thermo-junction. Three (probably four) additional members of the Paschen series have been observed, as well as the first two members of a new series corresponding with $\nu = N(1/4^2 - 1/m^2)$, where $m = 5, 6$. These two lines, at $\lambda 4.05 \pm 0.03\mu$ and $2.63 \pm 0.02\mu$ are due, according to Bohr's theory, to an electron falling into the fourth from the fifth and sixth rings of the hydrogen atom. Certain unidentified lines are recorded, and it was observed that, with increase of current, the first Paschen line increased in intensity more rapidly than H_α . A. A. E.

New Bands in the Spectrum of Silicon. ANGEL DEL CAMPO and JOSÉ ESTALELLA (*Anal. Fis. Quím.*, 1922, **20**, 586—588; cf. del Campo, *ibid.*, 1915, **13**, 98).—Seven new bands are described in the spectrum of silicon. They occur between $\lambda 2255.85 \text{ \AA.}$ and $\lambda 2146.0 \text{ \AA.}$, and appear to be composed of lines of variable intensity. A complete list of the components of the silicon spectrum is given. G. W. R.

The Spectrum of Neutral Helium. W. M. HICKS (*Nature*, 1923, **111**, 146).—A criticism of the formula employed by Silberstein (this vol., ii, 46) to express the diffuse series HeD' . A. A. E.

The Visibility of Individual Spectra. F. H. NEWMAN (*Phil. Mag.*, 1923, [vi], **45**, 293—299; cf. this vol., ii, 46).—The relative visibility of the spectra of the vapour from alkali amalgams at 200° is affected by the nature of the electrical discharge through the vacuum tube. The spectrum of the alkali metal is always well developed with the ordinary uncondensed discharge, but is completely masked by the mercury spectrum when the condensed discharge is used. With the latter, the resultant increase in electrical energy is sufficient to impart higher velocities to the colliding electrons

during their mean free path, and to ionise the mercury atoms, although these have higher ionisation potentials than the atoms of the alkali metals. The energy attained is sufficient to remove two or more electrons, as is shown by the production of enhanced lines.

W. E. G.

Revision of the Series in the Spectrum of Strontium.

F. A. SAUNDERS (*Astrophys. J.*, 1922, **56**, 73—83).—Measurements have been made of the spectrograms of light from a great variety of sources, and revised wave-lengths are given for most of the 180 lines from 0.22 to $3.06\ \mu$, including about 70 new lines. Accurate determinations have been made of the limits of all the series, and the various terms have been calculated. About half of the twenty series mentioned are believed to be new, and there is evidence of the existence of new types of singlet series corresponding with the formulæ $(1P)-(mX)$, $(1p)-(mX)$, $(1P)-(mY)$, etc. The terms are all large, so that the series cannot be of the kind suggested by Sommerfeld. In the case of calcium, three singlet lines are found to correspond accurately with $(1P)-(mX)$, $(1p_1)-(mX)$, and $(1p_2)-(mX)$, where (mX) is 8584.8 , thus indicating a series similar to that of strontium.

A. A. E.

Structure of the Spectrum of Scandium.

MIGUEL A. CATALÁN (*Anal. Fis. Quím.*, 1922, **20**, 606—623).—The lines in the spectrum of scandium fall into two classes, namely, those forming doublets and those forming triplets. Sommerfeld's displacement rule holds for scandium, since its enhanced spectrum is analogous to the arc spectrum of calcium. The multiplets (cf. A., 1922, ii, 726) are divided into "multidoublets" and "multitriplets." Complete lists are given of the lines in the spectra of the neutral and ionised atom, respectively.

G. W. R.

The Structure of the Arc Spectra of the Elements of Columns VI and VII in the Periodic Table.

M. A. CATALÁN (*Compt. rend.*, 1923, **176**, 84—85).—It has previously been shown (A., 1922, ii, 726) that the manganese spectrum shows three diffuse triplets, consisting of nine rays instead of six, due to the fact that the diffuse term d is quintuple instead of triple. It is now shown that this is not a property peculiar to manganese, but is common to other elements. The arc spectrum of chromium is very complex and presents several systems of series. Two of these, determined for the first time, are tabulated. They are almost identical, the one being displaced with respect to the other by a constant quantity, $C=4436.4$. The diffuse terms are quintuple and give nine rays as for manganese.

W. G.

The Structure of the Spectrum of Chromium.

A. DE GRAMONT (*Compt. rend.*, 1923, **176**, 216—217).—The author directs attention to the fact that he predicted that in the spectrum of chromium there would be two triplets, one corresponding with the neutral atom and the other with the ionised atom, and that this prediction has now found confirmation by the measurements made by Catalán (preceding abstract).

W. G.

The Structure of the Arc Spectra of Molybdenum, Selenium, and Chlorine. M. A. CATALÁN (*Compt. rend.*, 1923, 176, 247—248).—The arc spectrum of molybdenum is extremely complex. The diffuse term is quintuple and the number of rays is nine. The rays of the triplet of the principal series are the ultimate rays of Gramont. The diffuse triplets of selenium are regarded as exceptional by the number, the intensity, and the position of their satellites. The spark spectrum of chlorine shows triplets. The photograph of the spectrum shows the presence of at least three components in the first ray, although the tables give a number of components equal to $1+3+2$. Thus the diffuse term of the elements of columns VII and VI of the periodic table is quintuple and the number of rays which form the diffuse triplets is nine.

W. G.

Coincidence Method for the Wave-length Measurement of Absorption Bands. H. HARTRIDGE (*Proc. Roy. Soc.*, 1923, [A], 102, 575—587).—A spectroscope suitable for the measurement of wave-lengths of absorption bands is described. It is designed so that two similar spectra are produced, lying side by side and reversed in direction to one another. For the measurement of the mean wave-length of a band, the long wave-length edge of the band in one spectrum is brought into coincidence with the corresponding short wave-length edge in the other. The mode of calibration of the instrument to read directly in wave-lengths is described and the application of the instrument to the quantitative estimation of pigments by wave-length measurements of their absorption bands detailed. The method depends on the principle that if two pigments are present together in solution, and their respective absorption bands have different mean wave-lengths, then the mean wave-lengths of the resultant absorption bands will vary with the relative concentrations of the pigments, provided the band of one pigment is approximately similar to a band of the other, and if at no concentration do the bands appear separate. An illustration of the application of the method is given in the case of the estimation of the percentage saturation of blood with carbon monoxide. The accuracy of measurement attainable was found to be about 0.6 Å. Various sources of error are discussed.

J. S. G. T.

Absorption of Light by Chlorine. H. VON HALBAN and K. SIEDENTOFF (*Z. Elektrochem.*, 1922, 28, 496—499).—A preliminary account is given of measurements of the absorption spectrum of chlorine for a large number of wave-lengths between $254\ \mu\mu$ and $643\ \mu\mu$, making use of the very sensitive method of measurement recently described by the authors (*A.*, 1922, ii, 332). The results show that nowhere is chlorine entirely transparent, but that in all regions absorption occurs, which is generally very difficult to measure. The measurements are reproducible, although the absorption in some cases does not amount to more than 0.2—0.3%.

J. F. S.

The Quantitative Absorption of Light by Simple Inorganic Substances. II. The Chlorides of Arsenic, Antimony, and Bismuth. ALEXANDER KILLEN MACBETH and NORAH IRENE MAXWELL (T., 1923, 123, 370—375).

The Absorption Spectra of Thallium and Indium Vapours. WALTER GROTRIAN (*Z. Physik*, 1923, 12, 218—231).—According to the Bohr atomic theory, emission lines can occur only as absorption lines at any temperature when the initial stage in the absorption corresponds with a molecular or atomic state which is of frequent occurrence in the molecules of the gas. Absorption spectra are thus useful in throwing light on the variation in the quantum condition of gas molecules with temperature. Series schemes of the emission spectra, given for aluminium, gallium, indium, and thallium, show that for these metals, not the s , but the p -terms are the greatest of all the known terms. For thallium, at a temperature of 400° , two absorption lines of the $2p_2$ subordinate series, $\lambda=3775\cdot72$ and $\lambda=2767\cdot87$, first make their appearance, and at 500 — 600° other lines in this series appear. With increasing temperature, these lines broaden, probably owing to molecular (Tl_2) adsorption. At 800° , the $2p_1$ subordinate series is first observed, the order of appearance being $\lambda=5350\cdot46$, and then the doublet $\lambda=3529$ and $\lambda=3519\cdot24$. The indium absorption spectrum behaves similarly with rise in temperature. The differences between the temperatures at which the respective lines of the $2p_2$ and the $2p_1$ series are first observed increase as the series, aluminium to thallium, is ascended; for indium, the temperature difference is 100 — 150° , and for thallium about 400° . An indium adsorption line is observed at $\lambda=2836\cdot90$ which is not included in the series schemes. From these absorption experiments, it is clear that the outermost electron in the aluminium series of elements follows an azimuthal two quantum orbit. W. E. G.

The Ultra-violet Absorption Spectra of Aniline and the Toluidines. F. W. KLINGSTEDT (*Compt. rend.*, 1923, 176, 248—250).—Aniline in solution in hexane shows nine narrow bands between $\lambda=2991$ and 2704 , and a broad band at $\lambda=2340$. The narrow bands are almost equidistant from one another. With respect to benzene, the absorption bands of aniline are displaced towards the red, and the intensity of absorption is about eight times greater. The absorption spectrum of aniline in solution in water, alcohol, or carbon tetrachloride is very different from the normal spectrum. In these solvents, the narrow bands are fused into one broad band. The absorption spectra of *o*- and *p*-toluidines are very different. The ortho has two broad bands, whilst the para has seven narrow bands and a broad band in the extreme ultra-violet. W. G.

The Absorption in the Ultra-violet of a Series of Derivatives of Camphor. A. HALLER and R. LUCAS (*Compt. rend.*, 1923, 176, 45—49).—A study of the absorption spectra in the ultra-violet of the benzylidene-, anisylidene-, piperonylidene-,

m-hydroxybenzylidene-, *m*-methoxybenzylidene-, *p*-tolylidene, and *m*-tolylidene-derivatives of camphor shows that all these compounds present a strong absorption band, the maxima of which vary with each compound. On the other hand, benzylcamphor and anisylcamphor do not give this absorption band. The curves for *m*-hydroxybenzylidenecamphor and for *m*-methoxybenzylidene camphor are practically identical. The maximum of absorption in the compounds named above is displaced further towards the red as the substituent group is of greater weight. W. G.

The Ultra-violet Absorption Spectra of some Alkaloids of the isoQuinoline Group. Narcotine, Hydrastine, and Hydrocotarnine. PIERRE STEINER (*Compt. rend.*, 1923, 176, 244—246).—The results obtained indicate that the ultra-violet absorption spectrum of narcotine is determined by the benzene nucleus of its molecule; the *isoquinoline* nucleus only displaces the absorption towards the red. For papaverine (cf. this vol., ii, 2), on the other hand, it is the *isoquinoline* nucleus, and not the benzene nucleus, which is the determining factor. The spectrum of hydrastine only differs from that of narcotine by a displacement of its maxima and minima towards the shorter wave-lengths and by small differences in the intensity of absorption. Hydrocotarnine, which contains a partly saturated *isoquinoline* nucleus, has a spectrum formed of a single band in the ultra-violet. According to the results tabulated, it should be possible to estimate spectrographically 0.07 mg. of narcotine or hydrastine in 2 c.c. of solvent. W. G.

Absorption Spectra of Pyrrole and its Derivatives. II. The Influence of Methyl Groups on the Absorption Spectra of Pyrrole and its Derivatives. G. KORSCHUN and (MME) C. ROLL (*Bull. Soc. chim.*, 1923, [iv], 33, 55—67).—The absorption spectra of the ethyl esters of the following pyrrolecarboxylic acids were examined: 2:5-dimethyl-, 2:3:5-trimethyl-, 1:2:5-trimethyl-, and 1:2:3:5-tetramethyl-pyrrole-4-carboxylic acids, 2:5-dimethyl- and 2:3:5-trimethyl-1-aminopyrrole-4-carboxylic acids, 2:5-dimethyl- and 1:2:5-trimethyl-pyrrole-3:4-dicarboxylic acids, and 2:5-dimethyl- and 2:3:5-trimethyl-1-carbamidopyrrole-4-monocarboxylic acids, and also that of 1:2:5-trimethyl-pyrrole. The general conclusions drawn are that the introduction of a methyl group into position 1 (attached to nitrogen) causes a displacement of the absorption curve towards the ultra-violet. At the same time, if the derivative has two absorption bands they are united into one band. On the contrary, the introduction of methyl into position 3 causes a displacement of the curve towards the red, and at the same time the first band is lowered and the second raised. The methyl groups in positions 2 and 5 in 1:2:5-trimethylpyrrole displace the curve towards the red. Three methyl groups introduced into pyrrole in positions 1:2:5 only increase very slightly the intensity of the absorption bands. G. F. M.

Colour and Chemical Constitution. XVI. Further Miscellaneous Observations. JAMES MOIR (*Trans. Roy. Soc. S. Africa*, 1922, 10, 233—237).—In this paper are given the absorption wave-lengths of all the "monocyclic" and "dicyclic" dyes which were used in establishing the author's theory of the colour of "cyclic" coloured substances (cf. A., 1921, ii, 6; 1922, ii, 333).

2:4'-Dihydroxybenzhydrol has λ 543 in alkali, λ 486 in hydrochloric acid, and λ 495 in water suspension. The 4:4'-isomeride has λ 539 in dilute alkali but in acid is the same as the 2:4'-compound. 2-Hydroxy-4'-dimethylaminobenzhydrol has λ 561 (broad) in alkali, λ 500 in acid; the 4:4'-compound has λ 572 in alkali and λ 504 in acid. 2:4:4'-Trihydroxybenzhydrol has λ 494 instead of the expected λ 550. 2:4-Dihydroxy-4'-methoxybenzhydrol has λ 380 in alkali and appears to be monocyclic; 2:4-dihydroxy-3':4'-dimethoxybenzhydrol-2'-carboxylic acid is also monocyclic, with λ 390 in alkali, and so is mono- α -naphtholphthalein, from phthalaldehydic acid and α -naphthol, with λ 370. The C-phenyl derivative of the last-named has λ 401 in alkali, but λ 543 in strong sulphuric acid. The hydrol from *p*-hydroxybenzaldehyde and α -naphthol is violet with λ 590, whilst that from β -naphthol is pink, λ 556 in alkali. Phenol- β -naphtholphthalein has λ 570. The following show differences in sodium hydroxide (1) and sodium hydrogen carbonate (2), respectively: 3-hydroxyphenolphthalein λ 556 (1) and λ 562 (2); 3:6-dihydroxyphenolphthalein, λ 549 (1) and λ 563 (2); 4:5-dihydroxyphenolphthalein, λ 558 (1) and λ 568 (2). 5-Methoxyphenolphthalein has λ 565, whilst the 3:6-, 4:5-, and 5:6-dimethoxyphenolphthaleins have λ 568, λ 556, and λ 571, respectively. Other phenolphthalein derivatives examined were: 3-nitro-, λ 570; *a*-nitro-*fgjk*-tetrabromo-, λ 597 (cf. this vol., ii, 48, for nomenclature); 5-nitro-, λ 572; *abcd*-tetrachloro-, λ 581. Phenoldimethyl- α -naphthylaminephthalein is green, λ 625.

The following derivatives of Ghosh's quinolinic acid were examined: phenolquinolinein, λ 533; *o*-cresolquinolinein, λ 544; thymolquinolinein, λ 593; resorcinquinolinein, λ 490; orcinquinolinein, λ 496.

In the triphenylcarbinol series the following are given: *o*-hydroxymalachite-green, λ 627 neutral, λ 572 in alkali, λ 505 in acid; 2'-hydroxy-4-dimethylaminofuchson, λ 490 neutral, λ 533 in alkali, λ 479 in acid; *p*-methoxymalachite-green, λ 605; *p*-methoxybenzaurine, λ 551; *p*-nitromalachite-green, λ 642; *p*-aminomalachite-green, λ 581 in acetic acid. Values are also given for a considerable number of unclassified coloured substances. E. H. R.

Cells with a Fluorescent Liquid. A. GRUMBACH (*Compt. rend.*, 1923, 176, 88—90).—Goldmann (*Ann. Physik*, 1908, 27, 449) has shown that when one of two electrodes plunged into a fluorescent liquid is illuminated an *E.M.F.* is set up and the illuminated electrode is positive. This was shown for saturated alcoholic solutions. It is now shown, working with dilute aqueous solutions, that the same effect may be obtained by keeping the

cell in the dark throughout and introducing into it near to one of the electrodes 1 c.c. of the same solution which has been intensely illuminated by a mercury arc for two hours. In this case, the electrode near to which the liquid is introduced is at first negative. The *E.M.F.* at first increases to a maximum and then decreases and finally changes its sign. With direct illumination of the electrode, it is found that the *E.M.F.* continues to increase for some time after the source of light has been removed. W. G.

Observations on the Phototropy of Inorganic Systems.

JOSÉ RODRÍGUEZ MOURELO (*Anal. Fis. Quím.*, 1922, 20, 601—605; cf. A., 1922, ii, 604).—Further observations on the phototropy of sulphides of barium, strontium, and calcium.

G. W. R.

The Influence of Light on Zinc Sulphide. P. LENARD (*Ann. Physik*, 1923, [iv], 68, 553—573).—The cause of the darkening of zinc sulphide phosphors has been traced to the polymerised sulphide molecules, which are effective in phosphorescence. The darkening occurs, however, in zinc sulphide, which is not phosphorescent, and it appears that the phenomenon has no direct relationship to the phosphorescence. The wave-lengths of the light producing darkening do not correspond with those effective in exciting phosphorescence. Water is necessary, and ozone, hydrogen peroxide, chlorine, etc., destroy the effect. On the other hand, ammonia or reducing agents like formaldehyde reactivate a phosphor which has lost its sensitivity to light. The alkaline earth and magnesium phosphors do not blacken. W. E. G.

Influence of Adsorption of Ions on the Photochemical Sensitiveness of Silver Bromide. K. FAJANS and W. FRANKENBURGER (*Z. Elektrochem.*, 1922, 28, 499—505).—The authors have investigated the dependence of the sensitiveness of silver bromide on the method of precipitation. It is a known fact that silver bromide precipitated in the presence of an excess of silver nitrate is much more sensitive than that precipitated in the presence of an alkali halide. It is shown that under the influence of light the primary process taking place in silver bromide consists in the transference of an electron from a bromine-ion to a silver-ion with the formation of neutral atoms of bromine and silver. The work necessary to effect this change is dependent on the forces exerted on this electron in its initial and final states. In the presence of silver-ions from silver nitrate, these forces are smaller, and consequently the work required to effect the change is smaller, and the sensitiveness of the silver bromide is increased. J. F. S.

The Gamma Rays of the Family of Radium and of Thorium Studied by their Photoelectric Effect. M. DE BROGLIE and J. CABRERA (*Compt. rend.*, 1923, 176, 295—296; *Anal. Fis. Quím.*, 1922, 20, 467—472).—By means of the apparatus previously described (A., 1922, ii, 330), results have been obtained which are in accord with those of Ellis (A., 1921, ii, 422; 1922, ii, 466) and Meitner (A., 1922, ii, 416).

W. G.

Röntgen Spectra and the Periodic System of the Elements.

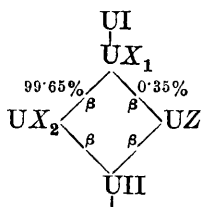
N. BOHR and D. COSTER (*Z. Physik*, 1923, 12, 342—374).—This paper, which forms a continuation of the Bohr theory of atomic structure (A., 1922, ii, 363), and papers by Coster (A., 1922, ii, 491, 677), examines the relationship between the Röntgen spectra, and the periodicity of the chemical properties, and the optical spectra of the elements. It is shown that the movements of the inner electrons are subject to the same laws which operate in the case of the valency electrons.

A table of the number of electrons in the various sub-groups of orbits is given for a large number of elements. This table, which is based on spectroscopic data, illustrates the building up of the electronic orbits with rising atomic number. The appearance of a new type of orbit is accompanied by a marked change in the chemical properties and the optical spectra of the elements. A new classification is proposed for the Röntgen spectra, in which the principal groups are divided into sub-groups, which are designated by Roman numerals, and to each level is given a value for n and k of the form $n(k_1, k_2)$ [for example, $2(2_1 2)L III$]. As in the work of Coster (*loc. cit.*), an arrangement of the Röntgen spectra is put forward which is based on a relationship between the frequency ν of each line, and the difference between two spectral terms T' and T'' . In agreement with the principles of the quantum theory of line spectra, these spectral terms, multiplied by h , give the energy required to transfer the electron from its normal orbit. The values T/R and \sqrt{T}/R (where R is the Rydberg constant) are derived, and tabulated for the K , L , M , N , O , and P spectra, and where the experimental data are missing, the Röntgen spectra are interpolated from known values. Since the spectra are slightly affected by the form in which the element is excited, a little uncertainty is introduced into the values of some of the elements with low atomic numbers; also the fine structure of some of the lines is a source of error. \sqrt{T}/R is plotted against the atomic number for all the Röntgen spectra available, and characteristic breaks are seen to occur in the curves for the L , M , N , and O spectra. The principal changes of slope occur in the neighbourhood of the platinum, the rare earth, and the iron groups. These irregularities are found at those atomic numbers where it is predicted that a new sub-group of electrons makes its appearance. The appearance of electrons in the 4_s orbit at the element cerium, the commencement of the rare earth group, produces a sudden alteration in the slope of the \sqrt{T}/R curve. At this point two of the lines in the M and N series separate into doublets. The binding energy of the 4_s orbit, at atomic number 58 (cerium), is about the same as that of the 6-quantum orbit, and much less than that of the 5 and the 5_s orbits. The energy of the 4_s orbit increases as the atomic number rises, until after the rare earth family of elements it exceeds the energy of the 5-quantum orbits. This behaviour is of undoubted importance for the study of the chemical properties of the rare earth group. The changes in energy of the electronic orbits is more gradual at the end than at the beginning of this

group. The value of $\sqrt{T/R}$ for the O levels (5 quantum) changes very slightly between atomic numbers 58 and 72. This point is of great theoretical interest. The effective values of N and n for the O levels probably remain constant throughout the rare earth group. The constancy of N and n may also explain the similarity of the chemical properties and optical spectra of homologous elements, in spite of considerable changes in the principal quantum number of the outer electronic orbit. The lack of periodicity in the K and L series is accounted for by the suggestion that the effective values of N and n for these orbits differ only slightly from the atomic number and the principal quantum number. Two types of doublets occur in the Röntgen spectra. The curves for one type run parallel throughout the whole of their course, whereas for the other type they rapidly approach one another with decreasing atomic number.

Although there is no evidence of periodicity in the Röntgen spectra in the same sense as it occurs in the optical properties, it is expected that relationships will be obtained which will give a measure of the periodic behaviour of the elements. W. E. G.

Uranium-Z and its Parent Substance. OTTO HAHN (*Z. physikal. Chem.*, 1923, 103, 461—480).—A method is described for the determination of the relation of the activity of uranium-Z to that of uranium-X; the method has been applied to a large number of uranium-X preparations of different ages and a satisfactory constant value for the relationship obtained. The constancy of the value allows the conclusion to be drawn that uranium- X_1 is the parent substance of uranium-Z. Uranium- X_1 therefore undergoes a dual β -ray disintegration, of a kind which has hitherto not been observed with radioactive elements. A new method for detecting uranium-Z is described. From the activity ratio uranium-Z: uranium-X, it is shown that the branching relationship is about 0.35%. In the calculation of this figure, the absorption of the β -radiation of uranium-Z with reference to that of uranium- X_1 and uranium- X_2 is taken into account. The disintegration scheme of the earlier members of the uranium series is therefore most probably represented by the annexed scheme. J. F. S.



Ionisation by Collision of Hydrogen, Nitrogen, and Argon. T. L. R. AYRES (*Phil. Mag.*, 1923, [vi], 45, 353—368).—The ionisation of hydrogen, nitrogen, and argon molecules on collision with electrons has been measured for comparatively small values of the ratio of electric force, X , to the gas pressure p . The range examined is from $X/p=1$ to $X/p=600$, and over part of this range Townsend and Bailey (cf. A., 1922, ii, 836) have recently measured the velocity in the direction of the electric force, and the mean velocity of agitation of the electrons in these gases. Ionisation by the electrons occurred for values of X/p as low as 2 in argon, 5 in hydrogen, and 10 in nitrogen. The effect of positive

ions was observed down to $X/p=10$ for argon, 30 for hydrogen, and 100 for nitrogen. No evidence was obtained for any appreciable variation in the ionisation due to slight contamination of the hydrogen and nitrogen, but small amounts of impurities in the argon caused a marked diminution of the ionisation, and increased the sparking potential. The ionisation with both positive and negative ions is in general agreement with that found by Townsend and Hurst for hydrogen and nitrogen (cf. A., 1906, ii, 262). For argon, however, at low values of X/p , the ionisation is greater than found by earlier investigators. The nature of the metal used as electrodes is without appreciable effect on the ionisation.

W. E. G.

Thermal Ionisation of Gaseous Elements at High Temperatures. ARTHUR A. NOYES and H. A. WILSON (*J. Amer. Chem. Soc.*, 1922, **44**, 2806—2815).—A theoretical paper in which the thermodynamic equation used by Saha (A., 1920, ii, 659) for calculating the thermal ionisation of the neutral atoms of gaseous elements into positive ions and electrons from their ionisation potentials is discussed with reference to the assumptions involved in the calculation. It is shown that the recent measurements of H. A. Wilson (A., 1916, ii, 72), as well as the earlier experiments of Arrhenius (A., 1891, 5, 575), on the electrical conductivity of flames into which salt solutions are sprayed clearly indicate that the conduction arises from an ionisation process of the type under consideration, and that they make possible a computation of the relative magnitudes of the ionisation constants. It is also shown that the relative ionisation constants of the five alkali elements, calculated on the one hand from the conductivity of flames and on the other from the ionisation potentials by the thermodynamic equation, form two series of values which run closely parallel to each other. Thus, although in passing from lithium to caesium the ionisation constant increases 5700 times, the ratio of the constants derived by the two methods for any one element does not differ from the mean value of that ratio for all five elements by more than 40%. The absolute values of the ionisation constants are derived from the flame conductivities with the aid of previous rough determinations of the mobility of the electrons and of the number of them per c.c. in similar flames. Although this could only furnish an estimate of the order of magnitude of the constants, yet they were found to correspond well with the values calculated by the thermodynamic equation, the latter being only 1.1 to 2.3 times as large.

J. F. S.

The Ionisation of Mercury Vapour in Presence of Argon. GEORGES DÉJARDIN (*Compt. rend.*, 1922, **175**, 1203—1206; cf. this vol., ii, 47).—Experiments were made with mercury vapour in presence of argon in order to ascertain whether the effect of the gas is similar to that of helium. The results show that ionisation resulting from impacts on mercury atoms of electrons the speed of which is greater than the critical ionisation speed (corresponding with 10.4 volts) is inappreciable and only becomes evident at a

speed corresponding with 11.3 volts. On increasing the potential, a sudden increase in the current is observed when the spatial charge of the electrons is completely neutralised and simultaneously a glow appears in the neighbourhood of the electrodes. The corresponding potential (the "illumination potential") depends on the shape of the electrodes and on the pressure. Ionisation of the argon by direct impact begins at a potential of about 15 volts. Between 11.3 volts and the illumination potential the intense lines of the mercury arc spectrum are obtained; above this limit the whole mercury arc spectrum and the red spectrum of argon are visible, the latter increasing in intensity above 15 volts. Above 35 volts, lines in the blue spectrum of argon are observed. The author infers from his results that for electrons traversing an atmosphere of argon there exists a first critical velocity of about 11.3 volts and that a resonance radiation emitted by the gas under these conditions ionises mercury vapour. This ionisation is not accompanied by any notable modification of the mercury spectrum analogous to that produced in presence of helium. Argon appears to exert only a feeble selective action on the second spectrum of hydrogen (Merton and Barratt, A., 1922, ii, 461) and on the cadmium spectrum (Collie and Watson, A., 1918, ii, 383). It is possible that the special influence of helium is due to the greater quantum of the radiations which it emits.

H. J. E.

Ionisation Produced by the Hydration of Quinine Sulphate. (MLLE) CHAMIÉ (*Compt. rend.*, 1923, 176, 251—253).—When the hydration is carried out in an ionisation chamber and the curve of increase in weight is compared with the curve of the diminution in current, it is found that the duration of the phenomenon is the same for the two curves and depends on the density of the layer of the salt. Any effect which modifies the one curve modifies the other in the same manner. The weight of water of hydration as well as the maximum intensity of the current of ionisation and the quantity of electricity liberated during the hydration appear to be proportional to the weight of quinine sulphate used.

W. G.

Conduction Process in Ordinary Soda-Lime Glass. CHARLES A. KRAUS and EDWARD H. DARBY (*J. Amer. Chem. Soc.*, 1922, 44, 2783—2797).—The replacement of sodium-ions in soda-lime glasses by ions of other metals has been investigated. It is shown that although the sodium-ions may be replaced by the ions of many other metals from their amalgams as well as from their fused salts, under a potential gradient, replacement occurs more readily from the fused salts than from the amalgams. In most instances, the glass formed on replacement is not stable. In some cases, the glass is completely disintegrated and in others it cracks on cooling. Sodium may be replaced by silver to a depth of about 0.1 mm. without cracking the glass. On replacing sodium by silver under the action of a potential, a sharp boundary is formed between the sodium and the silver ions. From the rate of motion of the boundary, the speed of the ions under a unit potential gradient

has been determined; the following values are recorded: 278° , 4.52×10^{-8} ; 295° , 1.46×10^{-7} ; 323° , 3.26×10^{-7} , and 343° , 5.9×10^{-6} cm./sec. The increased velocity of the ions with increased temperature corresponds with the increased conductivity of the glass with increased temperature. The fraction of the total sodium present in the glass, which takes part in the electrical conduction, has been calculated from the depth of penetration of the boundary and from the amount of electricity passing, as well as from the change in weight of the tube. It is found that 74–82% of the total sodium present in an ordinary soda-lime glass takes part in the conduction. The remaining sodium is either not in a charged state or otherwise the ions are held in fixed positions. The fraction ionised, as defined in this way, increases slightly between 278° and 343° . The following values of the percentage ionisation and the resistance in ohms are recorded: 278° , 74.4%, 72800 ohms; 295° , 76.8%, 35000 ohms; 323° , 79.4%, 14200 and 343° , 81.0%, 6600 ohms.

J. F. S.

Potential Difference between Glass and Electrolytes in Contact with Glass. WALTER S. HUGHES (*J. Amer. Chem. Soc.*, 1922, **44**, 2860–2867).—The potential difference between glass and solutions of electrolytes has been investigated at 25° . It is shown that glass surface potentials are established and maintained by the passage of electricity through glass. The glass surface potential is a linear function of the hydrogen electrode only over a limited range of values. Variations in the glass surface potential may be used as the basis of an electrometric titration method in the presence of oxidising agents which render the hydrogen electrode useless for such purposes. In such cases, the method might yield data which could not be obtained in any other way. The presence of certain substances, other than hydrogen-ions, such as concentrated solutions of salts or gelatin, affects glass surface potentials.

J. F. S.

Significance of the Electrode Potential. JAROSLAV HEYROVSKÝ (*Proc. Roy. Soc.*, 1923, [A], **102**, 628–640).—Evidence is adduced that the process by which a metallic electrode, immersed in an aqueous solution, becomes charged is represented by $M + OH' \rightarrow MOH + \ominus$. By the application of the electronic conception of chemical combination to a reversible thermodynamic cycle, a formula is obtained for the electrode potential in terms of the ionisation potential and basigenity of the metal. The basicity of metallic oxides is discussed by means of Beketoff's principle (*A.*, 1889, 332), and it is concluded that a metallic hydroxide is the more basic the more negative the electrode potential and the greater the equivalent weight of the metal. The mechanisms of galvanic and concentration cells, the phenomena of electrodeposition and overvoltage, and electrode processes in non-aqueous solvents are discussed in the light of the theory developed. "Absolute zero potential" values of contact *E.M.F.* derived from electrocapillary phenomena are shown to be illusory,

and the probable potential at which reversal of the sign of the charges in the double layer occurs is indicated. J. S. G. T.

Determination of Absolute Single Electrode Potentials. ALLEN GARRISON (*J. Amer. Chem. Soc.*, 1923, 45, 37—44).—The methods hitherto employed for determining absolute single electrode potential differences have been enumerated and briefly discussed and a new method of effecting this determination is described. The method is based on the assumptions, (1) that the mechanical force on a substance suspended in an electrolyte through which an electric force acts is due to the charge on the suspended system, (2) that the direction of the force is determined by the sign of the charge, and (3) that there is no charge or potential difference relative to the electrolyte when, in an electric field, there is no mechanical force relative to the electrolyte. The method used consists in suspending a light metal needle, shaped like the needle of a quadrant electrometer, by a phosphor-bronze ribbon in an electrolyte containing such a concentration of the metal-ion that there is no electric double layer at their interface. This isoelectric condition is indicated by the absence of any mechanical forces when an electric field is applied through the electrolyte. The potential of the needle is at the same time compared with the potential of a standard half cell. On eliminating the liquid junction potential the measured *E.M.F.* is the absolute potential of the constant electrode. A full description of the apparatus and its method of use is given in the paper. Using a silver needle at its isoelectric point as the zero electrode, the absolute potential of a 0.1*N*-calomel electrode is found to be between -0.20 volt and -0.10 volt at 25° . This result is a confirmation of Billitzer's value of -0.13 volt, and it removes the objections which have been made to the method employed by Billitzer (*Z. Elektrochem.*, 1902, 8, 638). J. F. S.

The Polarisation of Electrodes. J. E. VERSCHAFFELT (*Rec. trav. chim.*, 1922, 41, 764—777; cf. Aten, A., 1916, ii, 370).—A mathematical argument in which the author develops views previously put forward (*Bull. Acad. roy. Belg.*, 1919, 441). The conclusion is drawn that the variation of potential due to the application of *E.M.F.* is mainly effective at the cathode in the case of two electrodes of a metal in contact with a solution of one of its own salts, whilst with the same salt but with electrodes of a more electropositive metal the anode potential undergoes the greater variation and thus only the anode is polarised. H. J. E.

Activity Coefficient of Hydrochloric Acid in Aqueous Salt Solutions. HERBERT S. HARNED and NORMAN J. BRUMBAUGH (*J. Amer. Chem. Soc.*, 1922, 44, 2729—2748).—*E.M.F.* measurements of cells of the following types have been carried out at the temperatures indicated: $H_2|MCl_2(c)|0.1N\ HCl|HgCl|Hg$ at 18° , 25° , and 30° , where *M* denotes barium, strontium, or calcium; $H_2|MCl_2$ in $0.1N\ HCl|KCl(sat.)|HgCl|Hg$ at 25° , where *M* signifies the same metal as before; $H_2|KCl(c)|HCl(c')|AgCl|Ag$, and $H_2|KCl(c)|HCl(c')|HgCl|Hg$, where *c'* is $0.01N$ and $0.001N$, at

18°, 25°, and 30°. From the data obtained, the decrease of free energy and the decrease of the heat content of the cell reaction have been calculated, as well as the changes in partial molecular free energy and heat content of hydrochloric acid in the mixtures. The mean activity coefficients of hydrochloric acid in solutions of potassium, sodium, lithium, barium, calcium, and strontium chlorides have also been calculated. By means of the formula $\log F_a' = \alpha'c_1 - \beta'\mu^{m'} + \alpha''(\mu - c_1)$, the values of the mean activity coefficients (F_a') of hydrochloric acid in the acid salt mixtures, containing acid at concentrations from 0.001*N* to *N*, may be calculated with considerable accuracy. In solutions of greater dilution of acid, it is necessary to add a term to the above equation which is a function of the salt to acid concentration ratio, thus: $\log F_a' = \alpha'c_1 - \beta'\mu^{m'} + \alpha''(\mu - c_1) + \gamma'[(\mu - c_1)/c_1]$ is approximately valid for solutions containing acid of concentration as low as 0.001*N*. Thus when $(\mu - c_1)/c_1$ is very high, a considerable increase in the value of F_a' is observed. In the above equations c_1 is the concentration of acid, α' , β' , α'' , m' are constants, and μ is the ionic strength and for uni-univalent electrolytes equals the sum of the concentrations of the salt and acid or $(c + c_1)$. It is pointed out that the effect mentioned above is probably due to an increase in activity of the hydrogen-ion. If, as is to be expected, the same phenomenon is observed in mixtures containing other ions, it will be of considerable importance, especially in dealing with the problem of the solubility of sparingly soluble salts in solutions of other salts. Evidence has been obtained which leads to the conclusion that in solutions of strong bivalent chlorides, at the same temperature and concentration, the chloride-ion will have the same activity, and also that the activity of the chloride-ion in uni-univalent chloride solutions is greater than in bivalent chloride solutions of the same ionic strength.

J. F. S.

Activities of the Ions of Potassium Hydroxide in Aqueous Solution. M. KNOBEL (*J. Amer. Chem. Soc.*, 1923, 45, 70—76).—The author has determined the *E.M.F.* of cells of the type $H_2|KOH(c_1)|KHg_x|KHg_x|KOH(c_2)|H_2$ at 25° for concentrations of potassium hydroxide ranging from 3*N* to 0.0001*N*. The activity coefficients of the ions of the solution at various concentrations and the free energy of dilution between various concentrations have been calculated and tabulated. The data given by Chow (*A.*, 1920, ii, 281) are found to be incorrect; differences of 2—8% are found between Chow's values and the present values. The relationship between the activity and concentration for potassium hydroxide has been found to be similar to that for other uni-univalent electrolytes.

J. F. S.

Degree of Ionisation of Ethyl Alcohol. I. From Measurements of Conductivity. PHILIP S. DANNER and JOEL H. HILDEBRAND (*J. Amer. Chem. Soc.*, 1922, 44, 2824—2831).—The methods available for the purification of ethyl alcohol are discussed as to their efficiency, and the following method has been adopted for the preparation of absolutely pure material. Commercial 95% alcohol

was distilled with 5 c.c. of concentrated sulphuric acid and 20 c.c. of water per litre and the distillate boiled for several hours with 10 g. of silver nitrate and 1 g. of potassium hydroxide per litre. This product was distilled on to commercial quicklime, 600—700 g. per litre and boiled for eight hours. The mixture was then shaken vigorously for twenty-four to thirty-six hours at the ordinary temperature and distilled on to specially prepared quicklime, made by burning the mixture of calcium hydroxide and carbonate such as is obtained by drying slaked lime in the air. This product was present in the quantity 100—150 g. per litre of alcohol and the mixture was boiled for four to six hours. The alcohol was then distilled into the vessel from which the final purification was to be made and at this stage had a specific conductivity 1.0×10^{-7} ohms⁻¹. Subsequent distillation in evacuated sealed apparatus gave a value 2.2×10^{-8} ohms⁻¹, but here the most volatile portion was not removed. Repeated vacuum distillation with removal of the most volatile portion gave a steadily decreasing value with each repetition until the tenth distillation gave the value 1.35×10^{-9} ohms⁻¹, and this is regarded as the value for the purest ethyl alcohol. The dissociation constant calculated from this figure is 2.89×10^{-16} for the ionisation $\text{C}_2\text{H}_5\cdot\text{OH} \rightleftharpoons \text{C}_2\text{H}_5\text{O}' + \text{H}'$; the molecular fraction ionised is 1.0×10^{-9} , which is comparable with the similar value for water, 1.8×10^{-9} .
J. F. S.

Degree of Ionisation of Ethyl Alcohol. II. From Measurements of Electromotive Force. PHILIP S. DANNER (*J. Amer. Chem. Soc.*, 1922, **44**, 2832—2841; cf. preceding abstract).—The *E.M.F.* of a series of cells of the types $\text{H}_2\text{Pt}|\text{HCl}, \text{HgCl}|\text{Hg}$, $\text{Hg}|\text{HgCl}, \text{NaCl}|\text{Na}$ (2-phase amalgam), and Na (2-phase amalgam)| $\text{C}_2\text{H}_5\cdot\text{ONa}|\text{PtH}_2$, all in pure ethyl alcohol (*loc. cit.*) have been measured at 25°. The cells were very slow in reaching an equilibrium value, but were reproducible to 0.0001 volt, and calculations based on the values obtained involve no assumptions as to the value of the potential at the boundary water/alcohol, since this is not present. The dissociation constant for the ionisation $\text{C}_2\text{H}_5\cdot\text{OH} \rightleftharpoons \text{C}_2\text{H}_5\text{O}' + \text{H}'$ is calculated to 7.28×10^{-20} and the molecular fraction dissociated to 1.6×10^{-11} . This indicates that ethyl alcohol is dissociated only to 1/100 of the amount to which water is dissociated. The discrepancy between the present results and those given in the previous paper (*loc. cit.*) is attributed to the assumptions involved in the interpretation of the conductivity measurements, since the maximum possible error of the *E.M.F.* measurements, 0.002 volt, would not produce a greater error than 10% in the value of the dissociation constant.
J. F. S.

The Ionisation of Water in Solutions of Electrolytes. E. DOUMER (*Bull. Soc. chim.*, 1923, [iv], **33**, 49—55).—Hittorf's assumption that water is only ionised in negligible proportions in solutions of electrolytes does not seem to be justified, especially in the case of acid electrolytes, and particularly of hydrochloric acid solutions. Evidence for the fact that the liberation of oxygen at the anode in the electrolysis of hydrochloric acid is a primary

effect, and not a secondary reaction due to the action of nascent chlorine on water, is furnished by electrolysis with a silver or mercury anode, when the amount of oxygen liberated is actually greater than with platinum anodes, whilst all the chlorine combines with the anode forming the metallic chloride. Initially the silver anode becomes covered with a brown film, which eventually becomes white, so that both chlorine and oxygen are apparently discharged simultaneously, the former then displacing oxygen from the oxide when free metal is no longer available on the surface of the anode. Experiments on the electrolysis of dilute hydrochloric acid showed that for 50 c.c. of hydrogen liberated at the cathode 16.55 c.c. of oxygen were formed at the anode, and it is therefore concluded that of the total hydrogen-ions discharged $2 \times 16.55/50$ were derived from ionised water, that is, about 66%. This surprisingly high proportion finds confirmation in a determination of the total loss of hydrochloric acid in the electrolyte compared with the theoretical loss had all the liberated hydrogen been derived from hydrogen chloride. Further, the molecular conductivity of hydrochloric acid solutions is about three times as great as that of alkali chloride solutions, and the explanation provided by the above hypothesis is that in such acid solutions there are in addition to hydrogen- and chlorine-ions about twice as many hydrogen- and hydroxyl-ions. G. F. M.

Theory of the Polarisation of the Electrolytic Generation of Oxygen. II. Anodic Behaviour of Manganese in Solutions of Alkali Hydroxides. G. GRUBE and H. METZGER (*Z. Elektrochem.*, 1923, 29, 17—30; cf. *ibid.*, 1922, 28, 568).—The anodic behaviour of pure manganese in solutions of sodium hydroxide has been investigated. It is shown that in hot concentrated solutions with small current densities, manganese passes into solution in the bivalent condition, with medium current densities (0.3—0.1 amp./dcm.²) in the tervalent condition, and with higher current densities in the sexavalent condition. The solution of manganous oxide thus produced is yellowish-red in colour, and that of the manganic oxide brownish-red. The sexavalent manganese forms manganate, the production of which is always accompanied by the liberation of oxygen. At ordinary temperatures and also in dilute hydroxide solution, manganese passes into solution in the septavalent condition, with liberation of oxygen. The potentials corresponding with the individual anode changes have been measured at various temperatures and concentrations of alkali. The polarisation of the electrolytic evolution of oxygen occurs because the manganese becomes covered with a thin film of dioxide which then forms permanganic acid according to the equation $\text{MnO}_2 + 2\text{H}_2\text{O} + 3\oplus \rightarrow \text{MnO}_4' + \text{H}^+$. This substance then decomposes completely at lower current densities in *N*-sodium hydroxide with the evolution of oxygen according to the equation $2\text{HMnO}_4 \rightarrow 2\text{MnO}_2 + \text{H}_2\text{O} + 3/2\text{O}_2$; at higher current densities only a portion decomposes in this way, whilst the other portion diffuses into the solution and forms sodium permanganate. The competition of the velocity

of the two reactions, the oxidation of manganese dioxide to permanganate, and the spontaneous decomposition of the permanganic acid with liberation of oxygen, determines the extent to which the current is used for the liberation of oxygen and the formation of permanganate and also the potential of the process. J. F. S.

Effect of Fluorine on Electrolytic Oxidations. A. RÍUS Y MIRÓ (*Anal. Fis. Quím.*, 1922, **20**, 644—661).—The electrolytic oxidation of chrome alum and potassium hydrogen phosphate is increased with increasing amounts of potassium fluoride. It is supposed that the fluoride-ions at the moment of their discharge at the anode react directly, or indirectly by means of a peroxide of platinum, with the electrolyte present. With water, ozone is formed, whilst in other cases per-compounds may be formed, for example, in the case of phosphates, perphosphoric acid. The theoretical objections to this theory are discussed. G. W. R.

Electrolysis with a Dropping Mercury Cathode. I. Deposition of Alkali and Alkaline-earth Metals. JAROSLAV HEYROVSKÝ (*Phil. Mag.*, 1923, [vi], **45**, 303—315).—The decomposition potentials of the alkali and alkaline-earth metals have been determined by means of a dropping mercury cathode. When the dropping electrode is made the cathode, it is found that in neutral or alkaline solution hydrogen is not evolved even with high polarisations, and hence this arrangement is convenient for the study of the cathodic deposition of the most positive metals, which are otherwise attacked by water. The decomposition potentials found by this method were: lithium —2.023, potassium —1.883, sodium —1.860, caesium —1.837, rubidium —1.796, ammonium —1.787, calcium —2.023, magnesium —1.903, strontium —1.862, and barium —1.814 volts. Assuming that the alkali metals form compounds with the mercury, it is possible to calculate the affinity of the metal for mercury, this being given by the equation $A = \pi_n - E.P.$, where π_n is the observed decomposition potential with the drop electrode, and $E.P.$ is the decomposition potential obtained by G. N. Lewis. The affinity for mercury increases with increasing atomic weight, but sodium occupies an anomalous position, behaving like a more noble metal. It is deduced that the $E.P.$ of caesium is —3.3 volt. W. E. G.

Transport Numbers of Potassium Hydroxide in Aqueous Solution. M. KNOBEL, D. K. WORCESTER, and F. B. BRIGGS (*J. Amer. Chem. Soc.*, 1923, **45**, 77—79).—The $E.M.F.$ of concentration cells of potassium hydroxide of the type $H_2|KOH(c_1)|KOH(c_2)|H_2$ have been measured at 25°, for concentrations between 3.0*N* and 0.01*N*. These values, combined with those obtained for cells without transport (see this vol., ii, 116) have been used to calculate the transport number of the potassium-ion in solutions of potassium hydroxide of various concentrations. The transport number of the potassium-ion is found to be constant and equal to 0.2633 over the whole range of concentration 3.0*N* to 0.01*N*, and to increase with decrease in concentration below this value to

0.274 at infinite dilution. The following values of the $E.M.F.$ are recorded for the cells measured: $c_1=3.0N$, $c_2=0.3N$, $\epsilon=0.03683\pm 0.00003$; $c_1=1.0N$, $c_2=0.1N$, $\epsilon=0.03104\pm 0.00003$; $c_1=0.3N$, $c_2=0.1N$, $\epsilon=0.01424\pm 0.00003$; $c_1=0.3N$, $c_2=0.03N$, $\epsilon=0.02916\pm 0.00003$; $c_1=0.1N$, $c_2=0.01N$, $\epsilon=0.03465\pm 0.00015$. J. F. S.

Possibility of Varying Intermediate Stages in the Kolbe Reaction and a Case of Anodic Ester Formation with Aromatic Acids. C. SCHALL (*Z. Elektrochem.*, 1922, 28, 506—511).—The electrolysis of molten lead acetate, manganous acetate in benzoic acid, and alkali benzoates in benzoic acetate has been investigated; it is shown that in the case of metals of constant valency the change takes place according to the equation $x\text{RCO}_2' + xF = x/2R.R + x\text{CO}_2$, but when the metal has a variable valency the primary change is represented by the equation $M(\text{RCO}_2)_x + x\text{RCO}_2' + xF = M(\text{RCO}_2)_{2x}$, and if the temperature is sufficiently high this reaction is followed by a secondary thermal action $M(\text{RCO}_2)_{2x} = M(\text{RCO}_2)_x + x/2R.R + x\text{CO}_2$. These equations indicate that intermediate compounds may be formed in the Kolbe reaction. When potassium benzoate containing benzoic acid is electrolysed, using a silver anode, phenyl benzoate is produced. This formation is due, at least in part, to the oxidation of the acid to phenol by the silver oxide produced on the anode. J. F. S.

The Anomalies of Strong Electrolytes with Special Reference to the Theories of J. C. Ghosh. II. HENRY J. S. SAND (*Phil. Mag.*, 1923, [vi], 45, 281—292; cf. this vol., ii, 55).—Alterations have been made in the subsidiary hypotheses of Ghosh, to bring them into line with the equation $\mu/\mu_\infty = e^{-G/NRT}$, where μ/μ_∞ is the ratio of the molecular conductivities and G the work required to separate one gram-mol. of ions. Although the theory is strengthened by these changes, the number of subsidiary hypotheses is so great that the above equation must be regarded as an empirical formula. The hindrances to conduction in a medium of uniform dielectric constant, by the electric fields of the ions, is of the nature of polarisation, and the conductivity should be greater with rapidly alternating currents and high potential gradients than with small, constant potential gradients. Since this conclusion is contrary to experiment, the idea of a solvent with uniform dielectric constant has been abandoned.

An explanation of ionisation is put forward based on the assumption that solvent molecules possess polar properties, the ionising media consisting of a number of bipoles, similar to those postulated by Debye in his explanation of the dielectric properties of the media. These bipoles, which are capable of rotation, are held when in the powerful electric field of the ion, and their rotation stopped and converted into vibrational motion. Each ion will thus consist of the simple charged atom or group in the centre of a number of polar water molecules, which is capable as a whole of rotatory or vibratory motion. The ions become bound when they meet other ions of different polarity, and are then only capable of vibration around a position of equilibrium and become incapable of

transmitting a current. These views lead to a formula similar to that of Ghosh. The Ghosh equation, whilst yielding satisfactory values for binary electrolytes, breaks down for salts like barium chloride. The introduction of the Milner virial into Ghosh's formulæ does not lead to any improvement. W. E. G.

Faraday's Law and the Action of the Electrical Discharge on Gases. A. DE HEMPTINNE (*Bull. Acad. roy. Belg.*, 1919, [v], 5, 521—527).—Faraday's law has been shown to hold, with fair approximation, for chemical effects produced by an electrical discharge on gases at low pressures. E. E. T.

Faraday's Law and the Chemical Action of the Electrical Discharge. A. DE HEMPTINNE (*Bull. Acad. roy. Belg.*, 1919, [v], 5, 161—177).—An investigation of the reduction of unsaturated oils by hydrogen, under the influence of an electrical discharge, the amount of reduction being followed by the change in iodine number of the oil. A large number of experiments, involving variations in thickness of dielectric, density of current, potential difference, etc., are described, and do not lend themselves to abbreviated description. The author concludes that Faraday's Laws of Electrolysis are obeyed, at any rate, roughly. E. E. T.

Faraday's Law and the Action of the Electrical Discharge on Metallic Oxides. II. III. IV. V. A. DE HEMPTINNE (*Bull. Acad. roy. Belg.*, 1919, [v], 5, 249—260; 1921, [v], 7, 146—155, 458—468, 590—595).—II. A study of the reduction of metallic oxides by hydrogen in presence of an electrical discharge. The results fall in line with those previously obtained with unsaturated oils (cf. preceding abstract). Lead peroxide is taken as a standard substance for reduction, and a large number of other metallic oxides and also chlorides and miscellaneous substances are compared with it. Carbon monoxide was found to be roughly as effective in reduction as hydrogen, the experiments being carried out at low pressures to avoid polymerisation, etc., of the monoxide.

III. The reduction of various substances by this method shows that, as a rule, it is unimportant whether the substance in question is in contact with the positive or with the negative electrode. Values are found for the ratio N/N' , where N is the number of hydrogen molecules disappearing during a reduction and N' the number of ions and electrons (calculated from the measured current). This ratio has a value ranging from zero in the case of difficultly reduced oxides such as zinc or magnesium to above unity in the case of lead peroxide and manganese dioxide, etc., the reducibility of an oxide being connected with the electrolytic potential of the corresponding metal. Potassium chlorate is almost unaffected under conditions sufficing for the reduction of most oxides, a fact which is attributed to the purely electrical nature of the process, no thermal effect being produced by the incidence of positive ions or electrons. Thus, in the case of oxides, the amount of reduction is approximately proportional to the amount of current passing.

IV. The reduction of lead peroxide, cupric oxide, and ferrosioferric oxide is effected in a dried atmosphere of hydrogen by

means of an electrical discharge, the oxide in question being placed in contact with one of the electrodes. By measuring the variation of pressure, of potential difference between the electrodes, and the current flowing, a relation is found between the number (N) of hydrogen molecules used in the reduction and the number of positive ions (N_i) and electrons (N_e). The point is raised as to whether in ionisation the hydrogen molecule loses one or two electrons. Activated hydrogen (H_2) offers another explanation, but the mechanism of the reduction remains in doubt. With lead peroxide in contact with the positive electrode, N/N_e has values from 0 to 1.1, and when in contact with the negative electrode, values of 2.7 to 1.4 for N/N_i are obtained. Similar results are obtained for other oxides. If the positive ions are formed by the loss of one electron from each hydrogen molecule, and if each electron liberates one atom of oxygen, which then combines with one molecule of hydrogen, N/N_i and N/N_e should be equal to unity. Values (for these ratios) of 0.5 will correspond with the loss of two electrons when hydrogen is ionised and so on.

V. In the earlier sections the loss of weight of oxides when submitted to the action of an electrical discharge in presence of hydrogen was not determined. It is now found that, in the reduction of lead peroxide, the weight of hydrogen absorbed (as measured by the diminution in pressure) is equivalent to the loss in weight of oxide, whether the latter is in contact with the positive or with the negative electrode. The oxide formed as a result of the reduction is probably lead suboxide. When nitrogen is substituted for hydrogen in these experiments, no change is observed in either gas or solid, except such as could be accounted for owing to defects in the apparatus. Carbon monoxide, under similar conditions, causes the lead peroxide to gain in weight, probably owing to the formation of a deposit of a lower oxide of carbon.

E. E. T.

Dissociation of Carbon in the Intensive Arc. LOUIS BELL and P. R. BASSETT (*Science*, 1922, **56**, 512).—In the spectrum of the "negative tongue" which appears in the carbon arc at currents of at least 100 amperes, there were found fifteen lines, of which seven were coincident with the most conspicuous helium lines, and two others with H_α and H_β . Some carbon nuclei are considered to dissociate into helium, and possibly further, although the hydrogen lines may be due to water vapour absorbed by the carbon.

CHEMICAL ABSTRACTS.

The Evolution of the Molecule of Ferric Hydroxide in Contact with Water. (MLLE) S. VEIL (*Compt. rend.*, 1923, **176**, 101—103).—The molecular coefficient of magnetisation, with reference to iron content, of the hydroxide and the oxide of iron depend, to a large extent, on the previous states through which the material has passed and the temperatures to which it has been heated.

W. G.

The Calculation of the Magneton Number of an Atom in Solution. J. H. SMITH (*Phil. Mag.*, 1923, [vi], **45**, 375—378).—The magnetic susceptibility of cobalt chloride in water is greater

than in alcoholic solutions, and this change is associated with a shift in the maximum of the light adsorption from 0.510μ to 0.65μ . Making the assumption that Wiedemann's law of the additivity of magnetic susceptibility holds for solutions, the magneton number of the cobalt-ion in aqueous solution is found to be 24.6. The difference between the magnetic susceptibility in water and in alcoholic solutions may be ascribed either to a change in the diamagnetic or the paramagnetic part of the atom. A reasonable conclusion is that the frequency of the paramagnetic part of the atom is diminished, and this view is supported by the decrease in the frequency of the light absorbers in the atom.

W. E. G.

Paramagnetism and the Structure of the Atom. B. CABRERA (*J. Phys. Radium*, 1922, 3, 443—460).—The property of paramagnetism is confined very largely to the elements in column VIII of the Mendeléev classification and to the rare earths. The magnetic susceptibilities of the elements from chromium to copper, following the order of the atomic numbers, have been seriously studied, and data are available to fix the magneton number (Weiss) of the metallic ions for many of the elements in their various stages of oxidation. For these elements, the Weiss magneton number is seen to be given by a series of whole numbers, which are independent of the degree of ionisation of the salt. A theoretical interpretation of this regularity in the Weiss magneton number is sought in the structure of the atom, and, in particular, in the N -level of electrons. This level is subdivided into N_1 and N_2 levels, the latter first making its appearance with titanium. The number of electrons in the N_1 level augments from Ti^{+++} to Cu^+ for which element it attains a maximum value. It is assumed that the number of electrons in the M level remains constant at 8 throughout. On plotting the magneton number of the ion against the number of electrons in the N_1 level, a symmetrical curve is obtained giving a maximum at Fe^{+++} , when the magneton number is 29, and $N_1 = 5$. Ions containing an identical number of electrons in the N_1 level give the same magneton numbers; thus Fe^{+++} , Mn^{++} , Mn^{+} , and Cr^{++} give the same values. The points corresponding with Co^{++} and Fe^{+} are somewhat displaced, but these elements give a variable magneton number. At Ti^{+++} and Cu^+ the magneton number is zero. The magnetic susceptibilities of the oxides of manganese, and the oxides and sulphides of titanium and vanadium, are in general agreement with the above curve. The metals offer considerable difficulties, for the number of electrons which bind together the atoms is unknown. The work of Urbain and Janesch (cf. A., 1909, ii, 116) has demonstrated the existence of two groups within the rare earths, in each of which the magneton moment attains a maximum and then decreases. Qualitatively, the changes in magneton number will be analogous to that of the group studied above. These results do not appear to be in accord with the modification of the M levels assumed by Bohr, for this structure should lead to discontinuities in the curve of the magnetic moment.

The results of Stern and Gerlach (*Z. Physik*, 1922, 9, 353) are not in opposition to the Weiss magneton. W. E. G.

Influence of the Pitch of Sound on the Measurement of the Relationship $k=c_p/c_v$ for Carbon Dioxide. BRUNO TORNAU (*Z. Physik*, 1923, 12, 48—57).—The ratio of the specific heats for carbon dioxide was found to be $K_0=1.3165\pm0.00032$. Variation in the pitch of the sound produced no change in the value of K_0 . W. E. G.

Atomic Heat of Simple Substances. EDM. VAN AUBEL (*Bull. Acad. roy. Belg.*, 1921, [v], 7, 155—159).—The validity of certain conclusions drawn by Michaud (A., 1920, ii, 532) is discussed, making use of existing data for the specific heats, etc., of silicon, boron, rhombic sulphur, thallium, magnesium, and chromium. Michaud's conclusions are shown to be untenable. E. E. T.

Third Law of Thermodynamics. Evidence from the Specific Heats of Glycerol that the Entropy of a Glass exceeds that of a Crystal at the Absolute Zero. G. E. GIBSON and W. F. GIAUQUE (*J. Amer. Chem. Soc.*, 1923, 45, 93—103).—An improved calorimetric apparatus is described for determinations at low temperatures. The specific heat of supercooled glycerol and the specific heat and heat of fusion of crystalline glycerol have been determined at temperatures down to $69.9^\circ K$. The specific heats of the glass and the crystals approach one another as the temperature is lowered and are almost identical below $140^\circ K$. The heat of fusion of glycerol at the melting point $291.00^\circ K$ is 47.50 cal./gram or 4370 cal./mol. and the entropy of fusion is 15.02 cal./degree per mol. or 1.073 cal./degree per gram. The entropy of supercooled liquid glycerol exceeds that of crystalline glycerol by 5.6 ± 0.1 cal./degree per mol. at $70^\circ K$, and it is concluded that this value will not be appreciably different at the absolute zero. J. F. S.

Mass Effect in the Entropy of Substances. E. D. EASTMAN (*J. Amer. Chem. Soc.*, 1923, 45, 80—83).—The hypothesis that the expression for the mass effect in the entropy of all substances in which equipartition holds takes the same form as for monatomic gases is tested for all cases for which data are available. The results show that there is much evidence in support of the hypothesis, and none definitely contradicting it. Several approximate equations are given for the calculation of the entropy of diatomic gases and metals. J. F. S.

Physical and Chemical Transformations of Gibbs's Systems. TH. DE DONDER (*Bull. Acad. roy. Belg.*, 1920, [v], 6, 315—328).—A thermodynamical treatment of systems consisting of phases as defined by Gibbs. The author adopts a point of view very slightly different from the usual one. E. E. T.

The Chemical Constants of the Halogens in the Monatomic and Diatomic Condition. F. A. HENGLEIN (*Z. Physik*, 1923, 12, 245—252).—The chemical constants of chlorine, bromine, and

iodine have been calculated from the dissociation and vaporisation equilibria of these gases, and the values are in good agreement with those derived by Stern and Tetrode. For the monatomic gases, the following results were obtained for the chemical constants: chlorine +0.72, bromine +1.26, iodine +1.56, and for the diatomic gases, chlorine +0.02, bromine +1.50, and for iodine +2.55. Bromine and iodine have the highest chemical constant of any element. The heat capacity of solid bromine has been determined, and a Debye function given for the calculation of its specific heat. The chemical constants of the halogens in the diatomic condition increase slightly as the temperature rises.

W. E. G.

Relation between the Absolute Melting, Boiling, and Critical Temperatures of Substances. EDM. VAN AUBEL (*Bull. Acad. roy. Belg.*, 1921, [v], 7, 469—472).—The value of r , a constant (according to Prud'homme, A., 1920, ii, 83, 84, 376; see also A., 1921, ii, 622) deduced from the absolute melting and boiling points and critical temperatures of various substances, has been calculated for a number of compounds, using existing data, and the following values of r have been obtained: Mercury 0.512, mercuric chloride 1.01, mercuric bromide 1.03, mercuric iodide 1.03, antimony trichloride 1.04, antimony tribromide 1.01, aluminium bromide 1.16, and aluminium iodide 1.10. All these substances, therefore, with the exception of mercury, give a normal value (*i.e.*, about unity) for r .

E. E. T.

Method for the Determination of the Melting Point of Difficultly Fusible Metals. MARCELLO PIRANI and HANS ALTERTHUM (*Z. Elektrochem.*, 1923, 29, 5—8).—The melting point of metals with high melting point may be determined by using a hole (6 mm. deep and 1 mm. diam.) bored at an angle to the axis of a 7 mm. square rod of the metal, as a black body for temperature determination. That the metal had melted was indicated by drops of it falling from the hole. The heating was effected by passing a 50-period alternating current, which could be varied by steps of 10 amp. to 1500 amp., through the bar. Using this method, the melting point of tungsten and molybdenum has been determined and the values $3660^{\circ} \pm 60^{\circ}$ and $2840^{\circ} \pm 40^{\circ}$, respectively, have been obtained. These values are in agreement with other recent determinations.

J. F. S.

Separation of Liquid Mixtures by Combined Distillation and Atmolysis. Preparation of Practically Pure Ethyl Alcohol and Nitric Acid. ÉDOUARD URBAIN and RÉMY URBAIN (*Compt. rend.*, 1923, 176, 166—168).—The apparatus consists of a distillation flask surmounted by a porous porcelain tube, which is jacketed with a glass tube in which the pressure can be reduced. The porous tube is fitted with a condenser on top, and is so arranged that the condensed vapours can be returned to the distillation flask or run into another vessel. With this apparatus, it is possible to obtain 99.8% alcohol by direct distillation. The water vapour passes through the wall of the porous tube, and the condensed

alcohol is returned to the distillation flask. In a similar manner, it is possible by means of this apparatus to prepare 99.6% nitric acid.

W. G.

The Heat of Oxidation of the Alkaline-earth Metals. A. GUNTZ and BENOIT (*Compt. rend.*, 1923, 176, 219—220).—The authors have made measurements of the heats of solution of calcium, strontium, and barium, respectively, in dilute hydrochloric acid, and from the results and the known heats of solution of their oxides in this acid have calculated the heats of oxidation of these metals to be 152.7, 141.8, and 134.04 cal., respectively.

W. G.

Berthelot's Normal Acids and the Theory of Ions. F. BOURION (*Compt. rend.*, 1923, 176, 95—98).—A theoretical discussion in which it is shown that in order to observe, in the progressive neutralisation of an acid by a base, differences between the values found and those calculated by proportionality by the current thermochemical methods, the affinity constant of the acid must not be greater than 10^{-10} with the usual order of magnitude of the heats of ionisation.

W. G.

The Phenomenon of Molecular Association. ETTORE CARDOSO and GABRIELE BATTISTA (*Anal. Fis. Quim.*, 1922, 20, 420—432).—From a combination of van der Waals's equation and the rule of Cailletet and Mathias, the densities of a liquid and its vapour, respectively, d_1 and d_3 , are connected with the critical constants by the relation $d_1 d_3 / d_c^2 = K(pT_c/p_c T)$, or more generally $d_1 d_3 / d_c^2 = f(pT_c/p_c T)$. Deviations of this function from a linear relationship are attributable to molecular association and are the more pronounced the greater is the difference between the degree of association of the coexisting phases. The liquid phase is invariably more complex than the coexistent vapour phase.

G. W. R.

Cohesion Pressure, Surface Activity, and the Tendency to the Formation of Submicrons. I. TRAUBE (*Kolloid Z.*, 1923, 32, 22—24; cf. A., 1912, ii, 858; 1915, i, 105).—It has been shown previously that salts of alkaloids are molecularly dispersed in aqueous solution (*loc. cit.*) and because of their ionic charge have a large cohesion pressure; they are therefore unable to form submicrons and have no surface activity. In every respect the reverse is the case for free, non-ionised alkaloids. It is now shown that the salts of fatty acids are similar to the salts of alkaloids in the above respects. With the exception of formic acid, the free fatty acids have a small cohesion pressure, and have a surface activity and from butyric acid upwards form submicrons. Here, as in the case of the alkaloids, the cohesion pressure decreases with increasing molecular weight, whilst the surface activity and the ability to form submicrons increases. The lower fatty acids, including propionic acid, do not form submicrons, whilst butyric acid forms many submicrons, and the higher fatty acids, such as nonoic, decoic, and undecic acids, exist in both a surface active and an inactive form. Substances such as amyl alcohol, octyl alcohol, phenol, cresol,

aniline, and xyloidine have a considerable cohesion pressure, and their concentrated solutions contain submicrons and molecular dispersed particles, whilst hydrocarbons and alkyl halides have small cohesion pressures, and in aqueous solutions exist mainly as submicrons. From the above facts, the author claims general validity for the rule previously put forward. The smaller the cohesion pressure, the greater is the surface activity and tendency to form submicrons.

J. F. S.

Films. Spreading of Liquids and the Spreading Coefficient. WILLIAM D. HARKINS and AARON FELDMAN (*J. Amer. Chem. Soc.*, 1922, 44, 2665—2685).—It is found that the spreading of films is, in general, related to what is defined thermodynamically as the spreading coefficient. Liquids for which the value of this coefficient, S , is positive will spread, whilst those for which it is negative will not spread. Actually, the value of the coefficient refers to the system, spreading liquid—substance on which the spreading occurs, and may be quite different when A spreads on B , from what it is when B spreads on A . For example, most organic liquids have positive coefficients with reference to spreading on water, and therefore will spread into a film; but water has a negative coefficient with reference to most organic liquids and will not spread over them. The value of the coefficient, S , is defined by the equation $S = W_A - W_c$, in which W_A is the work of adhesion for the interface of the two liquids, and W_c the work of cohesion of the liquid which is applied to the surface of the other liquid or solid on which the spreading might occur. Thus a liquid will not spread if its work of cohesion, which indicates its attraction for itself, is greater than the work of adhesion, which indicates its attraction for the substance on which the spreading will not occur. The values of W_A and W_c are given by the equations: $W_A = \gamma_a + \gamma_b - \gamma_{ab}$; $W_c = 2\gamma_b$, so that the value of the spreading coefficient may be entirely defined in experimental terms by the equation $S = \gamma_a - (\gamma_b + \gamma_{ab})$, where a indicates the liquid which is spreading on the liquid or solid represented by b . A large number of experiments have been made on the spreading of organic liquids on the surface of water, on the spreading of water on the surface of organic liquids, and on the spreading of water and organic liquids on the surface of mercury. The results show the importance of the spreading coefficient as a criterion of spreading. Unimolecular films are produced on water only when the spreading coefficient has a relatively high value. Since these high values seem to occur only when the spreading substance contains a polar group in its molecules, it is concluded that the presence of such groups is essential for spreading on water to a unimolecular film, but not at all essential for the production of a film which is thicker than this. Contrary to the generally held opinion, benzene is found to spread on a clean water surface. The non-spreading of organic liquids on water is brought about by the presence in the organic molecule of chlorine, bromine, iodine, doubly-linked sulphur, phenyl, and the group =CS . Liquids which do not spread on water are insoluble in it, but insoluble

liquids may spread on water. The addition of camphor to water appears to reduce the value of the spreading coefficient; so that many liquids which have small positive coefficients on water will not spread on water containing camphor, but those which have coefficients sufficiently high are found to spread. The values of the spreading coefficients of water and organic liquids on mercury are, in every case investigated, found to be positive. Water and twenty-two of the other liquids were tested with reference to their spreading on pure mercury, and in agreement with their positive coefficients were found to spread. The coefficients for the spreading of mercury on water and organic liquids are all negative. This corresponds with the fact that mercury will not spread on their surface. Since the free surface energy of almost all inorganic solids is high, their work of cohesion is high, and the work of adhesion is also high with reference to practically all liquid substances. Since the work of cohesion in water and organic liquids is in general low, the values of the coefficients of spreading of these liquids on such solids should be positive and in general the value should be high. Thus the spreading of these liquids should occur on such solids when the surfaces are pure. The frequently occurring phenomenon of non-spreading is thus indicated to be due to the presence of an already existent film on the solid substance. The removal of such films may be brought about by vaporisation, or by the more common process of substituting one film for another. This is the ordinary function of soap, soap solutions, and other cleansing agents. It is difficult for petroleum to penetrate sands which have been wetted by water, and for water to penetrate sands which have been wetted by petroleum, although either substitution may be effected in time. Many oil wells cease to produce petroleum because the sand becomes wet with water. Lubrication and many other phenomena depend on the wetting of solids by films. J. F. S.

Measurement of Adsorption Processes by Means of an Interferometer. OTTOMAR WOLFF (*Kolloid Z.*, 1923, 32, 17—19).—Experiments are described to show that for industrial purposes an interferometer may be used to ascertain the amount of colloid adsorbed from solutions by any given adsorbent. J. F. S.

General Theory of the Adsorption of Solutions. WOLFGANG OSTWALD and RAMON DE IZAGUIRRE (*Kolloid Z.*, 1923, 32, 57—64).—In answer to the criticisms of Gustaver (this vol., ii, 57), the authors admit that in their recent paper they have interchanged the values u and u_0 as used by Williams (*Medd. Nobel-Inst.*, 1919, 2, No. 27, 1) owing to want of clearness in that paper. The authors deny that the equation which is put forward in their paper is the same as that due to Williams. The equation put forward by Williams is special and relates to a single case only whilst that due to the authors applies to three cases. In the best investigated case, the adsorption of acetic acid solutions by charcoal, the deduction made by Williams that $u_0 = -\infty$ when $c=1$ does not hold. The new equation furnishes more and other results than that of Williams. The necessity of differentiating between relative and absolute

thicknesses of layers in the investigation of adsorption layers is emphasised. In the adsorption of colloid particles the adsorption layer cannot be unimolecular in thickness; it must be at least unimicellar. The adsorption layer may have very different thicknesses, depending on the size of the absorbed particles and on the amount of water which is adsorbed at the same time. The assumption of Gustaver that the adsorption layer has a maximum thickness of one molecule is further refuted by the ultramicroscopic observations of Traube and Klein (A., 1921, ii, 683) on adsorption layers of surface active emulsoids, which vary up to 0.01 mm. thick.

J. F. S.

The Sorption of Iodine by Carbons Prepared from Carbohydrates. JAMES BRIERLEY FIRTH (T., 1923, 123, 323—327).

The Absorption of Moisture by Coal (and other Fuels).
I. A Relation between Degree of Humidity in the Air and Moisture Content of Coal. BURROWS MOORE and FRANK STURDY SINNATT (T., 1923, 123, 275—279).

Adsorption of Toluene Vapour on Plane Glass Surfaces. EMMETT K. CARVER (*J. Amer. Chem. Soc.*, 1923, 45, 63—67).—Isotherms for the adsorption of toluene vapour on plane glass surfaces at 0° have been obtained. The glass used was, after thorough cleaning, kept at 200° in a vacuum for twelve hours and any gas set free removed by a mercury vapour pump. Pressure measurements were made with the author's modified Shrader and Ryder optical lever manometer (this vol., ii, 148). The results are generally in agreement with Langmuir's adsorption formula (A., 1918, ii, 430), and indicate that the adsorbed layer is not more than one molecule thick.

J. F. S.

Fixing of Organic Dyes by Inorganic Substrates. H. RHEINBOLDT and E. WEDEKIND (*Koll. Chem. Beihefte*, 1923, 17, 115—188).—The literature dealing with the fixing of organic dyes by insoluble inorganic substances has been collected and discussed. It is shown that acidic and basic dyes exhibit a different behaviour toward similar substrates. In particular, substrates of acidic character are only fast dyed by basic dyes, whilst acidic dyes only fast dye basic substrates. The results of various authors which appear to be at variance with the above rule are in reality not so, since they do not refer exactly to the same thing. A large number of experiments with many dyes and inorganic gels have been carried out and give results entirely in agreement with the above rule. This rule is not only true for acidic and basic oxides, of which the following were examined: silica and tin, titanium, zirconium, thorium, and cerium dioxides; aluminium, chromium, and iron sesquioxides; and glucinum, zinc, magnesium, and lead monoxides; but also for sulphides (arsenic, antimony, and cadmium), and silver chloride. In no case was a dye from both classes fixed, with the single exception of amorphous carbon. The electro-endosmotic migration of the dyes and inorganic substrates was investigated, and it is found that fast dyeing only takes place between substrate and dye when

they are oppositely charged. The authors are of the opinion that the unsaturated valency forces of the crystal lattice of the absorbent are responsible for the fixing of the dye. Since these valencies are identical with the normal chemical valency, the behaviour of the substrate is explained. And since the valencies are of an electrostatic character, the parallelism of the electro-endosmosis and the adsorption is understandable. The fixing therefore consists in the binding of the dye to the substrate to form a unimolecular layer of a molecular additive compound. This process the authors term *adsorption by electro-affinity*. It is held that the adsorption by electro-affinity is not restricted to substances which have ordered crystal lattices, and the charge of sols, gels, and other colloidal material is attributed to the action of the same surface valencies.

J. F. S.

Exact Process for the Determination of the Coefficient of Diffusion in any Solvent. ERNST COHEN and H. R. BRUINS (*Z. physikal. Chem.*, 1923, **103**, 349—403).—The authors have summarised and criticised the method available for the determination of the coefficient of diffusion. A process for the exact determination of the diffusion coefficient has been devised. The apparatus consists of six thick glass plates of the same diameter, which fit exactly on a firm central axis. The four middle plates are firmly fixed and three holes bored through them so that in each plate there are three holes relatively in the same position. These plates are placed between the other two, which constitute a base and a cover plate. The hole in the lowest bored plate is filled with the liquid of which the diffusion is to be measured, by means of a small hole which can be brought above it by rotating the necessary plates. The other three plates with holes are brought into such a position that the holes in them are above one another, but not above the hole in the lowest plate, and filled with the solvent. The arrangement now is that of two tubes filled with liquids, which by rotation of the bottom bored plate may be brought into contact. When the whole apparatus has reached the required temperature, the liquids are brought into contact and the diffusion commences. After a sufficiently long period, the plates are twisted so as to cut the column of liquid into four isolated parts and the composition of each is estimated by the Rayleigh Löwe interferometer. It is claimed for the apparatus that it may be used for all types of liquids, of which only small quantities are necessary. It may be used at any temperature over a wide range, and there is no error due to vibration or shaking when the liquids are brought into contact. By the use of an air thermostat, the temperature is known, and may be kept constant to 0.03° . The error of the method is not greater than 0.3%, and individual measurements are reproducible to 0.1—0.3%.

J. F. S.

Validity of the Stokes-Einstein Law for Diffusing Molecules. ERNST COHEN and H. R. BRUINS (*Z. physikal. Chem.*, 1923, **103**, 404—450).—The validity of the Stokes-Einstein equation for the diffusion in solutions at various temperatures has been investigated by means of the diffusion apparatus previously

described (preceding abstract). The pair of liquids tetrabromoethane and tetrachloroethane has been used and the diffusion velocity measured at temperatures from 0° to 50°. The viscosity of tetrachloroethane has been determined over the same temperature range with a maximum error of 0.05%. Divergences from the Stokes-Einstein law have been observed which are at least three times as great as the experimental error. The divergences are in the sense that the temperature coefficient of the velocity of diffusion is smaller than would be expected. The following values of the relative viscosity of tetrachloroethane are recorded: 0°, 1.6219, 10.0°, 1.3113, 15°, 1.1924, 25°, 1.0000, 35°, 0.8541 and 50°, 0.6917. The absolute fluidity of tetrachloroethane is given by the formula $\eta/T = 0.13796 (1 + 0.019171\theta + 0.00000925\theta^2)$. J. F. S.

The Capabilities of the Rapid Dialyser. A. GUTBIER, J. HUBER, and W. SCHIEBER (*Chem. Ztg.*, 1923, 47, 109—110).—Further investigation of the rapid dialyser described previously (A., 1922, ii, 551). The effect of using tap water instead of distilled water for the outer liquid was studied, and it was found that 80—90% of the electrolytes can advantageously be removed from colloidal solutions by dialysing against tap water, after which point distilled water must be used. Experiments indicated that dialysis was more efficient the greater the speed of rotation of the membrane and stirrer; 100 revolutions per minute was satisfactory, with slightly greater efficiency at 150 per minute. Generally, a flow of 5 litres of water per hour in the outer vessel is sufficient. The use of more than 10 litres per hour produced no corresponding increase in the rate of dialysis. G. F. M.

The Law of Solution. PAUL MONDAIN-MONVAL (*Compt. rend.*, 1923, 176, 301—304).—Measurements made with a very soluble salt, sodium nitrate, show that it obeys very exactly the equation established by Le Chatelier for the solubility of salts in water (A., 1885, 340; 1894, ii, 272). W. G.

Solubility and Chemical Constitution. H. J. PRINS (*Rec. trav. chim.*, 1923, 42, 25—28).—It has been concluded by Harkins (A., 1921, ii, 242) and by Langmuir (A., 1917, ii, 19) that adsorption and solubility are closely related. Both authors attribute orientation phenomena exhibited by organic substances with water to the tendency of the polar group to dissolve in water. It is pointed out that the arbitrary circumstance that these researches were carried out with water and an organic substance containing a group more or less similar to water may lead to erroneous conclusions. With organic acids and water, solubility and adsorption are both caused by the same group, but this is not generally the case. A number of examples are given showing that solubility in hydrocarbons such as light petroleum depends, not on polar groups, but on saturated hydrocarbon groups. Solubility depends in general on similarity in kind and number of atoms present in the molecules of the substances in question. Adsorption represents a case of hetero-complex formation, whilst in solution the complexes have the character of homo-compounds. E. H. R.

Contraction on Solution of Various Substances in Water.

JITENDRA NATH RAKSHIT (*Reprint Indian Assoc. Cultivation Sci.*, 1917, 3, pp. 1—21).—Making use of data from Landolt and Börnstein's tables, the author has calculated the contraction which takes place when 100 g. of various substances are dissolved in various quantities of water. The values have been calculated for sulphuric acid, nitric acid, formic acid, stannic chloride, acetic acid, methyl, ethyl, propyl, isobutyl, and isoamyl alcohols, glycerol, acetonitrile, acetone, nicotene, ammonia, hydrogen chloride, sodium and potassium hydroxides, sodium chloride, tartaric acid, chloral hydrate, phenol, sucrose, lævulose, dextrose, maltose, and invert-sugar. In some cases, the contraction increases with increasing dilution, whilst in others the contraction increases, passes through a maximum, and then decreases with increasing dilution. J. F. S.

Effect of Scratching the Wall of a Vessel with a Glass Rod.

L. DEDE (*Z. Elektrochem.*, 1922, 28, 543); ROBERT FRICKE (*ibid.*, 1923, 29, 44—46).—A continuation of the controversy on the cause of crystallisation when the walls of a tube containing a solution are rubbed with a glass rod (cf. A., 1922, ii, 692, 744).

J. F. S.

Viscosimetric Researches on Lyophilic Sols. H. G.

BUNGENBERG DE JONG (*Rec. trav. chim.*, 1923, 42, 1—24).—The greater proportion of viscosity measurements recorded in the literature cannot claim an accuracy of more than a few per cent. The conditions necessary to attain an accuracy of 0.1 to 0.2% are discussed, and in particular the two most important sources of error, the systematic error of the viscosimeter and the method of setting the instrument. For a given capillary, there is a maximum average rate of flow for a given liquid so that the deviation from Poiseuille's law shall not be greater than 0.1%. A formula for calculating this rate was given by Grüneisen (*Wiss. Abh. Phys. Tech. Reichsanstalt*, 1905, 4, 151). By means of this formula, the systematic error of the viscosimeter and the necessary length and fineness of capillary can be calculated. The error of setting can be minimised by fixing the instrument so that the line joining the centres of the upper and lower reservoirs in the Ostwald viscosimeter is vertical, instead of one of the limbs. Measurements of viscosity recorded in the literature are subjected to a general criticism and in particular the work of Hatschek on the viscosity of gelatin sols (A., 1911, ii, 98; 1913, ii, 835), and that of Rothlin (A., 1920, ii, 18), is discussed. Hatschek observed with a number of lyophilic sols that the viscosity depends on the rate of flow or shear, and he supposes that this phenomenon supports the theory of a dodecahedral structure of concentrated lyophilic sols. Rothlin divides lyophilic sols into two groups, one of which follows Poiseuille's law, whilst the other does not. These deviations are to be ascribed to the formation of larger aggregates in the sol through gelation; these aggregates, according to the conditions of flow, can be broken down to different extents, and so give rise to the observed irregularities. This explains the fact, in the case of both Hatschek's and Rothlin's abnormal sols, that the

viscosity increased with time, due to progressive gelation. At higher pressures, such systems would approximate more and more closely to Poiseuille's law, as Rothlin found. It is concluded that, for viscosimetric measurements to have any value, the system under examination must not only follow Poiseuille's law, but the disperse phase must retain its stability. Experiments with agar sols show that at 50°, that is, above the gelation temperature, agar sols follow Poiseuille's law within 0.2%, although at 27° deviations of more than 100% are shown. Moreover, above the gelation temperature all hysteresis phenomena are absent, and mechanical treatment has no influence on the viscosity. The only alteration in viscosity with time shown by these sols is a slight decrease due to hydrolysis of the disperse phase. When such an agar sol is diluted with electrolytes, a final equilibrium is reached immediately.

It is suggested that the term sol should exclude all liquid systems (1) which show deviations from Poiseuille's law; (2) where the viscosity is influenced by mechanical treatment, (3) where gelation, coagulation, and ageing phenomena generally are present.

E. H. R.

Topo-chemical Reactions. Crystal Formation in Colloidal Metals. V. KOHLSCHÜTTER and K. STECK (*Z. Elektrochem.*, 1922, 28, 554—568).—The frequent formation of silver crystals in solutions of colloidal silver has been explained partly on thermodynamic grounds as the result of solubility differences between silver particles of different sizes and partly as a result of the formation of crystal aggregates of the ultramicroscopic crystalline particles due to action of a molecular field. Both views are open to criticism; on the one hand, on account of the excessively small solubility of metallic silver, and, on the other, because of the constitution of the surface of colloidal particles. The author is of the opinion that chemical reactions are responsible for the crystallisation. It is shown that in eighteen months definite silver crystals form in Lea's sol, but in pure sols, prepared by the reduction of silver oxide with hydrogen, no silver crystals were visible until the sol had been kept for twelve years; the same applies to gels which are free from electrolytes and protective colloids and are preserved under water. Well-formed polyhedra are produced by the action of ferric-ions or silver-ions on coagulated gels and other forms of colloidal silver. Also the reduction of a silver-ion solution with ferrous-ions, within a definite range of concentration, produces a transient colloiddally-dispersed metal which speedily forms crystals. The localisation of the reaction, by adding a solid ferrous salt to a solution of silver-ions or by adding a solid silver salt to a solution of ferrous-ions, accelerates the crystal formation. In keeping with the experimental results, the formation of crystals from colloidal solutions is to be regarded as due to a maturing process in consequence of the silver of the micellæ entering into the reversible reactions $\text{Ag} + \text{Fe}^{+++} \rightleftharpoons \text{Ag}^+ + \text{Fe}^{++}$ and $\text{Ag} + \text{Ag}^+ \rightleftharpoons \text{Ag}_2^+$, whereby the pressing together of the reaction products in and on the colloidal particles is probably determinative of the commencement of the reaction and also of the specific form-

ation of the crystalline silver. Observations on various oxides and sulphides lead to the view that, in the formation of crystals in colloidal systems, electromotive actions play a part. These are due to the formation of concentration cells in the colloidal systems.

J. F. S.

The Constitution of Colloidal Gels. J. DUCLAUX (*Bull. Soc. chim.*, 1923, [iv], **33**, 36—43).—A theory of the constitution of reversible gels is developed in which it is suggested that they are composed of three elements: the fluid which may be water or some other solvent, an insoluble solid forming with the fluid an irreversible gel, or sponge-like structure of ultra-microscopic cells, and a soluble solid dissolved in the solvent of the gel. The molecules or micellæ of this substance, which may be either crystalloid or colloid, are too large to be able to escape from the cellules of the sponge, but they are small enough for their solution to have a certain osmotic pressure in relation to the pure solvent. This solution is the "plasm" of the gel, and its swelling and expansion in a solvent are due to the osmotic pressure of the plasm. The limit of expansion is reached when equilibrium is attained between this osmotic pressure and the cohesion of the cellular structure of the gel. If the osmotic forces are strong enough, continued inflation of the cellules may result in the dissolution of the gel, and the separation of the soluble and insoluble constituents. The mechanical properties of the gel will evidently depend on the relative proportion of the two solid constituents, in gum arabic, or nitro-cellulose solutions prepared in the warm; the insoluble constituent is almost absent, and the tendency to gel formation is a minimum, but in gum-tragacanth, or cellulose-nitrate solutions prepared in the cold, the insoluble constituent dominates and manifests itself by gel formation or high viscosity. G. F. M.

The Influence of a Dissolved Crystalloid on the Rigidity of Gels. F. MICHAUD (*Compt. rend.*, 1922, **175**, 1196—1198).—By means of a method recently described (*ibid.*, 1922, **174**, 1282), the author has measured the rigidity of gels the moduli of which were less than any previously measured. The dissolved substances were added in solution to the liquid gel, the whole being allowed to set. The rigidity of gelose or gelatin gels is considerably decreased by the presence of acids or bases. In the case of gelatin, a strong acid exerts a more marked effect than a strong base, whilst the converse is the case if the gel is dilute. The curves obtained show that the action of the acid is a linear function of the concentration of the gel; that of the base is parabolic, so that addition to a gel of increasing quantities of base or acid eventually causes the base to exhibit a greater influence than the acid for equimolecular quantities. The disposition of the curves obtained for gelose is in the inverse sense. The author suggests that these results are consistent with the amphoteric properties of gelatin, and that, by analogy, gelose should be regarded as amphoteric, its basic being stronger than its acid function. The action of salts on the gel depends primarily on the amount hydrolysed: for those which

are not hydrolysed, the molecular lowering of rigidity is about one-tenth that of an acid or base. The action of organic substances is variable; sugars and glycerol have practically no effect, urea, urethane, and acetamide act similarly to mineral salts, whilst resorcinol, quinol, and, above all, tannin bring about a very much greater decrease than an acid or base. H. J. E.

Colloid Chemistry of Urate Jellies. E. KEESER and H. ZOCHER (*Koll. Chem. Beihefte*, 1923, 17, 189—217).—An investigation of urate jellies, particularly those of lithium and sodium. It is shown that the jelly-forming urates belong to the class of electrolyte colloids and have properties which are parallel with those of soaps and similar substances. Microscopic examination of lithium urate jellies shows the presence of long, optically anisotropic, negative doubly refracting jelly particles and also of radial structures which extend into the rest of the jelly mass. The addition of methylene-blue to the long jelly particles produces a dichroic coloration, and the structure becomes fibrous. The dispersion of the double refraction is abnormal. The long structure of the particles cannot be confirmed by ultramicroscopic examination because of their size. Solutions of urates cannot be obtained in a viscous state like the anisotropic sols of vanadium pentoxide and benzopurpurin, neither do the urate solutions show streaming double refraction nor magnetic double refraction. Before lithium urate solutions pass into jellies, they become turbid, and after the jelly has formed, the turbidity, for the most part, disappears. It is suggested that the turbidity is due to droplets formed by an unmixing of the solution. Mechanically effected changes in the jellies are irreversible, that is, after displacement the jelly does not resume its original form when the displacing force is removed. The residue obtained by subjecting the jellies to pressure shows but slight swelling power. The rigidity of the jellies increases with increasing concentration of the solution of lithium urate from which they are formed. The rigidity of jellies of constant composition increases with increasing addition of a lithium salt, and the transformation into the crystalline condition takes place more slowly the more rigid the jelly. In all cases, crystallisation commences at a number of isolated but equally distributed points throughout the jelly mass. The addition of non-electrolytes such as carbamide, sugar, glycerol, or alcohols reduces the rigidity of the gels increasingly with increasing concentration, and retards the crystallisation generally. Carbamide is exceptional, inasmuch as it accelerates the crystallisation. Protective colloids are without effect on the jellies. Examination of the jellies by X-rays shows that particles of sufficient size to produce Röntgen interference figures are absent, whereas a similar examination of crystalline lithium urate gives very broad interference bands, which shows that the true size of the particles is considerably less than that of the needles visible in the microscope. Lithium urate is a negatively charged colloid. The residues obtained by drying the jellies are colloidal in character and have the power of adsorbing

gases. Thus 1 g. of lithium urate will adsorb 0.5 c.c. of nitrogen at atmospheric pressure. J. F. S.

Interfacial Tension between Gelatin Solutions and Toluene. S. E. SHEPPARD and G. S. SWEET (*J. Amer. Chem. Soc.*, 1922, **44**, 2797—2805).—The general relationship of the orientation of specific atom groups in the molecule to the emulsoid colloid state is discussed. A number of experiments on the separation of gelatin at a benzene-water interface have been carried out; these consisted in shaking 1.0%, 0.1%, and 0.01% aqueous solutions of gelatin with an equal volume of benzene at 30°, 40°, and 50° and measuring the volumes of the resulting benzene, water, and foam phases. The foam or interfacial layer consists of benzene dispersed in and protected by hydrated and aërated gelatin, and is partly stabilised. In further experiments, air was excluded and toluene substituted for benzene, and here it was found possible to shake the liquid without much separation of the gelatin in the toluene, although a considerable amount of toluene was emulsified in the gelatin solution. The stability of the gelatin foam at various hydrogen-ion concentrations was found to increase from both sides of the isoelectric point and to be most stable at this point. The interfacial tension of gelatin solutions of varying hydrogen-ion concentrations has been determined at 30°, 35°, and 40° by measuring the drop number of the solution. The drop number-hydrogen-ion concentration curves all lie above the corresponding curves for water, and all the gelatin solution curves show a characteristic break near the isoelectric point, the maximum reduction of interfacial tension being at $p_H=4.8$. J. F. S.

Classification of Disperse Systems in Connexion with the Mechanism of True and Colloidal Solution and Precipitation. P. P. VON WEIMARN (*Koll. Chem. Beihefte*, 1923, **32**, 72—114).—A survey of dispersoid chemistry in which classifications of disperse systems according to the state of aggregation of the particles and according to the "external" degree of dispersion are put forward. The imperfect nature of the static classification is pointed out, and a large number of tables are given of the appearance of precipitates of sparingly soluble substances at various times after their formation. J. F. S.

Velocity of Flocculation of Selenium Sols. H. R. KRUYT and A. E. VAN ARKEL (*Kolloid Z.*, 1923, **32**, 29—36).—The velocity of flocculation of selenium sols of various concentrations by solutions of potassium chloride and barium chloride of various concentrations has been determined at a series of temperatures from 15° to 20°. It is shown that the region of rapid flocculation for potassium and barium chloride lies at very high concentrations of these electrolytes. This result has been confirmed by measurements of the boundary charge of the sols. The results show that Smoluchowski's theory is valid in the region where the velocity of flocculation is not far removed from that obtaining when the colloidal particles are totally discharged. The results deviate

strongly from this theory when smaller concentrations of electrolytes are used; the divergence consists in a continuously decreasing velocity of flocculation. The boundary charge of the sols has been determined in the presence of a solution of various concentrations of potassium chloride, barium chloride, potassium hydroxide, and hexamminecobaltic chloride. It is shown that the addition of hydrazine increases the boundary potential, and that after the addition of ten m.mols. of barium chloride the particles still possess a charge. The addition of potassium hydroxide increases the boundary potential, and it is therefore suggested that the like action with hydrazine is due to hydroxyl-ions. J. F. S.

Colloidal Phenomena in Paintings. CH. COFFIGNIER (*Bull. Soc. chim.*, 1923, [iv], 33, 128—132).—The thickening or swelling of the paint in oil paintings is a colloidal phenomenon, and is attributable to the action of the resin acids in the varnish on the lead or other heavy metal compounds used in the paint, whereby a colloidal metallic complex is formed which behaves as a reversible gel. The phenomenon is particularly noticeable and rapid with colophony varnishes, but it also occurs with other materials possessing free acidity. Congo and kauri gums, for example, whilst not behaving in this way with white lead, show the reaction with litharge or zinc white, but it can be prevented in all cases by eliminating the free acidity of the resin or gum. For this purpose, neutralisation with calcium carbonate or hydroxide is not so satisfactory as esterification, as the "neutralised" material has still a certain acid value which is not reduced to zero even by calcium hydroxide. Esterification of the gum or colophony with glycerol furnishes a material from which a neutral varnish can be prepared, and the troublesome phenomena above referred to then no longer occur, even with litharge or zinc white. G. F. M.

General Nephelometry. M. U. C. AL. LEDNICKÝ (*Kolloid Z.*, 1923, 32, 12—17).—A general discussion of the application of nephelometry to colloidal solutions. It is shown that in comparisons it is essential that the illumination should be uniform and symmetrical; the beam of light should be horizontal and parallel. The surfaces of the solutions should be the same height and the concentration such that Beer's law holds, and so low that the boundaries of the Tyndall cone are sharp. The light should be monochromatic, and in the case where the two solutions have not the same colour a filter must be used before the light reaches the eye. J. F. S.

Non-, Uni-, and Bi-variant Equilibria. XXII. F. A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1923, 25, 341—353).—In continuation of previous work (A., 1922, ii, 430), the author has investigated mathematically the condition determining the equilibrium of n components in a system comprising $n+1$ phases, when the quantity of one of the components is infinitesimally small, and has examined more especially the effect of a small quantity of added substance on a non-variant equilibrium. Expressions are derived for the partition of the added substance

between the various phases and for the temperature and pressure changes respectively occurring on such addition. F , L , and G representing the respective phases, it is shown that when a substance x is added to a system in non-variant unary equilibrium, $E(x=0)=F+L+G$, an equilibrium arises which is represented on the P - T diagram by a curve commencing at the non-variant point of the equilibrium $E(x=0)$. When the added substance occurs in the liquid phase only, this curve corresponds with the curve $L=F+G$ of the system $E(x=0)$. If the added substance occurs both as liquid and vapour, then the equilibrium curve is situated in region F , and its direction is determined by the partition of x between the vapour and liquid phases. When the added substance occurs both in the liquid and solid phases, the curve is situated in the region G , and its initial direction is determined by its partition between mixed crystals and liquid. In the case when the added substance occurs in the three phases, the curve may be situated in any of the three regions L , F , or G . Its direction is then defined by the partition of the added substance between the three phases.

J. S. G. T.

Determination of the Chemical Equilibria between Various Stages of Oxidation by Means of Electrometric Measurements. I. The Equilibrium between the Sulphates of Bi-, Ter-, and Quadri-valent Manganese in Sulphuric Acid Solution. G. GRUBE and K. HUBERICH (*Z. Elektrochem.*, 1923, 29, 8—17).—Oxidation potential measurements of mixtures of the sulphates of manganese in sulphuric acid of various concentrations have been made for a large number of solutions at 12°. It is found that in a solution which contains 0.05 g. atom of manganese in a litre of 15*N*-sulphuric acid when at 12° the ratio of the stages of oxidation is 1:1, the following oxidation potentials exist: $\epsilon^{\circ}_{\text{Mn}^{\text{II}} \rightarrow \text{Mn}^{\text{III}}} = 1.511$ volts, $\epsilon^{\circ}_{\text{Mn}^{\text{III}} \rightarrow \text{Mn}^{\text{IV}}} = 1.642$ volts, and $\epsilon^{\circ}_{\text{Mn}^{\text{II}} \rightarrow \text{Mn}^{\text{IV}}} = 1.577$ volts. These potentials are slightly dependent on the total concentration of manganese, but strongly dependent on the concentration of the acid. Increasing concentration of acid displaces the values to less positive potentials. Using the measured potentials, the equilibrium constant of the reaction $\text{Mn}_2(\text{SO}_4)_3 \rightleftharpoons \text{MnSO}_4 + \text{Mn}(\text{SO}_4)_2$ was calculated. This value also changes with the acidity and the total concentration of manganese, and has been determined for a total manganese concentration of 0.05 g. atom per litre in concentrations of sulphuric acid varying between 9.1*N* and 24.2*N*. From the determinations, it is shown that a 0.05*M*-solution of manganic sulphate in 9.1*N*-sulphuric acid decomposes according to the above equation to the extent of 36%, but in 24.2*N*-sulphuric acid to the extent of 6.7%, that is, the equilibrium is displaced toward the left of the equation with increasing concentration of acid. The existence of this equilibrium is the cause of the abnormal behaviour of manganic sulphate on hydrolysis. With this substance, hydrolysis produces manganous sulphate and a hydroxide of quadrivalent manganese. This is due to the fact that of the components of the equilibrium, quadri-

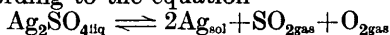
valent manganese sulphate, $\text{Mn}(\text{SO}_4)_2$, is most easily hydrolysed, whereby the equilibrium is disturbed and still more sulphate is produced, so that the reaction takes place completely from left to right.

J. F. S.

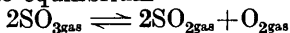
Equilibrium Gelatin-Hydrochloric Acid. R. DE IZAGUIRRE (*Kolloid Z.*, 1923, 32, 47—51).—It is shown that the view put forward by Lloyd and Mayes (A., 1922, i, 280) on the basis of measurements of the hydrogen-ion concentration in solutions of gelatin containing hydrochloric acid, that at concentrations below 0.04*N* the hydrochloric acid is attached to the amino-group and at higher concentrations to the nitrogen atom of the polypeptide group, cannot be substantiated from the measurements. So far as the accuracy of the measurements permits, it must be held that they point rather to a continuous curve for the hydrogen-ion combination curve. But from this it does not follow that a chemical combination has taken place between the hydrochloric acid and the gelatin, for a logarithmic equation similar to the adsorption equation leads to a similar curve. It is also shown that the change of the electric charge of an adsorbent during an adsorption process can lead to curves of the most divergent type. Since such changes do take place during the adsorption of ions, the point has to be settled whether the combination with ions is to be regarded as a chemical process or merely as an adsorptive process.

J. F. S.

The Dissociation of Silver Sulphate. (MLLE) G. MARCHAL (*Compt. rend.*, 1923, 176, 299—301).—The decomposition of silver sulphate under the influence of heat gives rise to an equilibrium reaction forming a bivariant system which becomes univariant if care is taken to have in the gaseous phase only the gases coming from the decomposition. The author has made a study of this equilibrium under these conditions. Above 660°, silver sulphate decomposes according to the equation



and there exists in the gaseous phase a small amount of sulphur trioxide to satisfy the equilibrium



Using the equation $q = [4.57(\log K_2 - \log K_1)T_1T_2]/(T_2 - T_1)$, the heat absorbed in the decomposition is calculated as 82.4 cal. between 820° and 1000°. Using Nernst's equation, the values obtained are 103.9 cal. at 820° and 103.2 cal. at 1000°. By means of the experimental results it is possible to calculate the state of equilibrium of the bivariant system for each temperature if it is arranged for the pressure of the oxygen at equilibrium to be equal to 1/5 atmos. pressure of the oxygen in the air.

W. G.

Equilibrium of the Reaction between Metallic Silver, Cupric Chloride in Aqueous Solution, and Solid Cuprous and Silver Chlorides. GRAHAM EDGAR and LAWRENCE S. CANNON (*J. Amer. Chem. Soc.*, 1922, 44, 2842—2849).—The reaction $\text{CuCl} + \text{AgCl} + \text{H}_2\text{O} = \text{CuCl}_2 + \text{H}_2\text{O} + \text{Ag}$ has been investigated in the presence of hydrochloric acid of various concentrations

at 25° and 40°. The equilibrium constant has been obtained from both sides. The method is to shake the reagents together in coloured bottles and analyse the solution after equilibrium has been attained. The equilibrium constants have been calculated, making use of the principle of "ionic strength" and the values 1.86×10^{-6} for 25° and 1.61×10^{-6} for 40° obtained. From these values, the increase in the heat content of the system is calculated by means of the expression $\Delta H = RT^2 d \log_e K / dT$ and the value -1755 cal. obtained. The increase of free energy of the system is calculated for 25° and the value $\Delta F = 7820$ cal. obtained. These values have been compared with the values obtained by Noyes and Ellis (A., 1918, ii, 27), Lewis and Lacey (A., 1914, ii, 521), and Noyes and Chow (A., 1918, ii, 214), and a moderate agreement has been found between the two sets of values. The present data afford a measure of support for the methods employed by Lewis and Randall (A., 1913, ii, 29) in calculating the activities of mixed electrolytes.

J. F. S.

Liesegang Rings. I. Silver Chromate in Gelatin and Colloidal Gold in Silicic Acid Gel. EARL C. H. DAVIES (*J. Amer. Chem. Soc.*, 1922, 44, 2698—2704).—The author has investigated the influence of gravity and light on the formation of silver chromate rings in gelatin and gold rings in silicic acid gel. A jelly composed of 0.14 g. of potassium dichromate, 4 g. of gelatin, and 120 g. of water was brought into contact with a solution of 8.5 g. of silver nitrate in 100 c.c. of water, the jelly being held in various positions so that diffusion could occur vertically downward and upward and also horizontally. It is found that diffusion is slowest when it operates against gravity, but the effect of gravity may be counterbalanced by hydrostatic pressure. The mechanism of the ring formation is as follows. The silver nitrate diffuses into the gelatin and gives what appears to be an opaque region which in reality consists of opaque bands; these preliminary bands are further apart as the distance from the surface increases. These preliminary bands are due to the unequal rate of diffusion of the nitric acid and potassium nitrate produced in the reaction. The groups of silver chromate-potassium nitrate crystals, which are seen microscopically to form, are gradually broken up as the potassium nitrate diffuses away and the silver chromate particles become larger because of the oncoming silver nitrate. Hence the small bands lose their identity and the large bands are formed. Colloidal gold in silicic acid gel produced no rings when kept at 0° in the dark for nine days, but only isolated gold crystals. On placing these tubes in a powerful beam of light for an hour a band 1.5 cm. thick was formed. The band did not commence as a thin line and grow, but the whole area developed a faint yellow colour at once, and this grew in intensity as the exposure proceeded. A further tube of colloidal gold in silicic acid gel was covered with black paper and at distances of 9 cm., 2 cm. bands were cut away. The tube was placed in a dark room and the light from an 80 watt lamp fell on it for nine days, when slightly green colloidal bands

developed at the openings. A similar tube showed no bands after keeping for six days in the dark, but on exposure for a few minutes to an arc light bands developed at the openings in the paper, but no bands appeared between the openings. The tube was kept for for a further seven days in the dark at 0° . The paper was then entirely removed and the tube exposed to an arc light for three hours, when a slight blue colour developed between the original bands.

J. F. S.

Liesegang Rings. II. Rhythmic Bands of Dyes on Filter-paper and Cloth by Evaporation. Refractivity, Surface Tension, Conductivity, Viscosity, and Brownian Movement of Dye Solutions. EARL C. H. DAVIES (*J. Amer. Chem. Soc.*, 1922, **44**, 2705—2709; cf. preceding abstract).—Rhythmic bands of dyes have been produced on filter-paper, cotton cloth, and unglazed porcelain by regulated evaporation. Solutions of some sixty-two dyes were used in 0.04% and 0.005% concentrations with several varieties of filter-paper. A table is given in which the following physical properties of the 0.04% solutions are recorded: refractive index, surface tension, electrical conductivity, viscosity, and Brownian movement. The Tyndall cone and band formation are also investigated and the data recorded. It is shown that a uniform temperature and a gradual decrease in the rate of flow are the important factors in the formation of bands. It is probable that just before the band forms a film of oriented molecules is present.

J. F. S.

Calculation of Velocity Constants. A. L. TH. MOESVELD (*Z. physikal. Chem.*, 1923, **103**, 481—486).—The author describes a method of calculating the velocity constant of a reaction which is more accurate and less arbitrary than the generally adopted method. The velocity equation for a reaction of the n th order can be written in the form $1/(A-x)^n = k't + 1/A^n$, where x is the concentration at time t and A at $t=0$. The method consists in inserting the values of $A-x$ and t in the equation for each measurement and so obtaining a series of equations with two unknowns, k' and $1/A^n$. When these equations are solved by the method of least squares, the value of k' is obtained which corresponds most nearly with the whole of the experimental results. Further, from the divergence of the experimental value of $1/(A-x)^n$ and the value calculated from k' , it is at once shown whether the equation chosen is the correct one for the case under examination. A simplified method of working out the rather complicated calculations is given.

J. F. S.

The Speed of the Uniform Movement of Flame in Mixtures of the Paraffins with Air. WALTER MASON (*T.*, 1923, **123**, 200—214).

The Roaring of the Bunsen Burner Flame. KARL GLASER (*Z. angew. Chem.*, 1923, **36**, 38).—The phenomenon of the roaring of the flame of the Bunsen burner is not a peculiarity of any particular gas, but can be caused with any gas by sufficiently

increasing the pressure above the normal, whereby a corresponding increase occurs in the velocity of flow, other things remaining equal. The conditions governing the phenomena may be expressed as follows, where v is the velocity of flow, c the velocity of the propagation of flame for the gas in question, v' a factor depending on the buoyancy of the gas, and c' on the preliminary heating to which the gas is subjected in the burner: when $v+v' < -(c+c')$ the flame strikes back; when $v+v' = -(c+c')$ the burner burns normally, and when $v+v' > -(c+c')$ the flame roars. G. F. M.

Piezo-chemical Studies. XVII. Influence of Pressure on the Velocity of Reaction in Homogeneous Liquid Systems. A. L. TH. MOESVELD (*Z. physikal. Chem.*, 1923, 103, 486—504).—The pressure coefficient of the velocity of reaction of the change $5\text{HBr} + \text{HBrO}_3 = 3\text{Br}_2 + 2\text{H}_2\text{O}$ between the temperatures 1° and 39° has been determined. It is shown that for the temperature range examined it is independent of the temperature. The velocity of reaction at a pressure of 1500 atm. is 15.4% less than that at 1 atm. pressure. The pressure influence is therefore negative and very much smaller than that observed in cases of hydrolysis carried out under approximately similar conditions. From this it is to be concluded that pressure exerts a specific influence on the velocity of reaction, and this is not changed by changing the external conditions under which the reaction is taking place.

J. F. S.

Regularities in the Velocity of Vaporisation. W. HERZ (*Z. Elektrochem.*, 1922, 28, 526—527).—It has been shown recently by Volmer and Estermann that the velocity of vaporisation, G , is given by the equation $G = 1/\sqrt{2\pi R} \times p\sqrt{M/T}$, where p is a constant, M the molecular weight, and T the boiling point in absolute degrees (A., 1922, ii, 193). This indicates that $\sqrt{M/T}$ is proportional to G . The author has calculated the values of $\sqrt{M/T}$ for a large number of substances, and finds that the value increases steadily with the molecular weight in homologous series; it also increases with the replacement of hydrogen by chlorine. The removal of two hydrogen atoms and consequent formation of a double linking reduces the value, whilst the formation of a treble linking causes a still further and much larger decrease. Ethers generally have much larger values than the corresponding saturated hydrocarbons. J. F. S.

Solubility and Specific Rates of Hydrolysis of $\beta\beta'$ -Dichlorodiethyl Sulphide in Water. ROBERT E. WILSON, E. W. FULLER, and M. O. SCHUR (*J. Amer. Chem. Soc.*, 1922, 44, 2867—2878).—The hydrolysis of $\beta\beta'$ -dichlorodiethyl sulphide in water has been investigated. It is shown that the hydrolysis in contact with water is a two-phase reaction which affects only the molecules dissolved in the aqueous phase. The rate of the first stage of the reaction determines that of the second stage. Once steady conditions are established, the concentration of the intermediate compound automatically increases or decreases, keeping the rate of the second stage just equal to that of the first stage. The

amount of intermediate compound present at any time is extremely small, and the time required to build up the equilibrium concentration is generally negligible. The simplest expression for the rate of hydrolysis at 25° in alkaline solutions, where there is no tendency toward reversal, is $dc/dt = 2K_1(M) = 0.304(M)$, where dc/dt is the rate of hydrolysis in millimols. of hydrogen chloride produced per litre per minute and (M) is the concentration of gas in millimols. per litre. The second stage of the hydrolysis is substantially non-reversible except in very concentrated hydrochloric acid solutions. The first stage is, however, reversible to a considerable extent even in the presence of dilute acids. This reversibility of one stage serves to retard, but not to stop, the reaction, because the intermediate compound of the hydrolysis is being continually destroyed by the irreversible second stage. Indirect evidence indicates that the second stage of the reaction is catalysed in direct proportion to the hydrogen-ion concentration in acid solutions. Since the rate is also very rapid in alkaline solutions, it is very likely catalysed also by hydroxyl-ions. The mathematical expression for the rate of hydrolysis in acid solutions is $dc/dt = K_1(M) - k_1(I)(H')(Cl') + k_2'(I)(H')$. A simpler but less obviously rational form of this equation is $dc/dt = 2k_1(M)/(1 + k_3(Cl')) = 0.304(M)/(1 + 6.14(Cl'))$. This equation has been found satisfactory for a wide range of acid concentrations. The solubility of $\beta\beta'$ -dichlorodiethyl sulphide in water at 25° is 0.0043 mol./litre, and on substituting this value in the equations above the rate of hydrolysis in saturated solutions is obtained.

J. F. S.

Velocity of Hydrolysis of Methoxymethyl Acetate. ANTON SKRABAL and MARIA BELAVIĆ (*Z. physikal. Chem.*, 1923, **103**, 451—460).—The velocity of hydrolysis of methoxymethyl acetate in 0.1*M*-solution by 0.1, 0.05, 0.02, and 0.01*N*-hydrochloric acid, 0.1*N*-sodium carbonate, and 0.1*N*-sodium metaborate has been determined at 25° and the values obtained have been compared with the values previously obtained (A., 1921, ii, 134) for the simple acetals, methylal, and methylene diacetate. The mixed acetal is hydrolysed much more rapidly in acid solution than the two simple acetals, whilst the velocity in alkaline solution lies between that of the two simple acetals.

J. F. S.

Energetics of Sucrose Inversion. THOMAS MORAN and HENRY AUSTIN TAYLOR (*J. Amer. Chem. Soc.*, 1922, **44**, 2886—2892).—The effect of temperature on the potential difference of the normal hydrogen electrode is discussed, and it is shown from *E.M.F.* measurements with acetic acid that it is approximately proportional to the absolute temperature. Measurements have been made on the very short ultra-red absorption of aqueous solutions of sucrose, dextrose, and lævulose in the region 0.75—1.0 μ . Sucrose and lævulose show a band at 0.875 μ which is not present with dextrose. The bearing of these results on the critical increment of sucrose dihydrate and on the mechanism of the inversion of sucrose has been discussed.

J. F. S.

Process for Studying the Velocity of Formation of Precipitates. ROGER G. BOUSSU (*Compt. rend.*, 1923, 176, 93—95).—A modified form of Jolibois's apparatus for studying the mixture of liquids (A., 1920, ii, 107) is used. The bottom limb of the Y-tube is cut off, and the two side limbs are so adjusted that their orifices are 1 cm. apart. The liquids necessary to form the precipitate are run at the same rate down the side tubes and mix almost immediately. The resulting mixture is allowed to flow into a large volume of water saturated with respect to the precipitate the formation of which it is desired to study. This volume of liquid is held at different distances below the point of mixing, and thus the time for the formation of the precipitate is varied. The diluted mixture is filtered at once and the precipitate collected and weighed. The errors do not exceed 5%. W. G.

Catalysts and Chemical Equilibrium. J. CLARENS (*Bull. Soc. chim.*, 1923, [iv], 33, 43—48).—Polemical. A reply to Durand's criticism (A., 1922, ii, 701) of the author's original paper (A., 1922, ii, 436). G. F. M.

The Catalytic Action of Hydrogen-ions in the Hydrolysis of Esters. S. C. J. OLIVIER and G. BERGER (*Rec. trav. chim.*, 1922, 41, [ii], 637—645).—An examination of the rate of hydrolysis, under various conditions, of benzyl chloride, α -chlorohydrin, ethyl nitrate, and methyl trichloroacetate showed that the presence of hydrogen-ions has practically no effect on the speed of the reaction in the case of the two first-named substances, a very small effect with ethyl nitrate, and a small but quite definite catalytic action with methyl trichloroacetate. The facts observed together with those described by Cavalier (A., 1899, ii, 13), Wegscheider (A., 1902, ii, 493), and Klemenc (A., 1918, i, 220), lead to the conclusion that hydrogen-ions have little or no effect on the hydrolysis of esters of strong acids. In a brief discussion of the mechanism of the reaction, the authors state that theories based on the supposed activation of the water by the acid (Rohland, A., 1901, ii, 152; Noyes and Sammet, A., 1902, ii, 498) are not satisfactory, as water should also be activated in the case of esters derived from strong acids. The theory of formation of oxonium salts put forward by Stieglitz (A., 1908, ii, 167) is preferred, because an increase in the negative character of the group R in $R\cdot CO\cdot O\cdot R'$ decreases the basic character of the oxygen and consequently diminishes the tendency to form such salts (cf. Kendall and Booge, A., 1916, i, 707). It is uncertain whether the hydrolysis is effected by the ion $R'\cdot CO_2R'\cdot H$, or by activation of the ester at the moment of conversion into oxonium salt. H. J. E.

Catalase Action of Peroxydase. E. ABEL (*Z. Elektrochem.*, 1922, 28, 489—496).—It is shown that peroxydase catalyses the reaction between potassium iodide and hydrogen peroxide only in the presence of hydrogen-ions; in faintly alkaline solution, there is no acceleration of the velocity of reaction. The peroxydase

was obtained from horse-radish, and is seen in the above-mentioned reaction to exercise the action of a catalase (cf. A., 1920, ii, 35, 180).
J. F. S.

The Fine Structure of Atomic Nuclei, and the Deviation from Coulomb's Law in the Interior of the Nucleus. I. The Atomic Nuclei of Lithium and isoHelium. MAXIMILIAN CAMILLO NEUBERGER (*Ann. Physik*, 1923, [iv], 68, 574—582).—A theoretical paper in which it is shown that the deviations from Coulomb's law become smaller as the atomic number increases (cf. Smekal, *Sitzungsber. Akad. Wiss. Wien*, 1920, 130, 149—157). In this paper the atoms of lithium (atomic weight=6) and *iso*helium are examined. The lithium atom is assumed to consist of two α -particles (*iso*helium) rotating in a ring around a β -particle. This arrangement is stable, and making allowance for the deviation from Coulomb's law, it is shown that the heat of formation of one gram-atom of $\text{Li}^6 = 4.72 \times 10^7$ Cal. The heat of formation of *iso*helium from three hydrogen atoms is $Q = 4.72 \times 10^8$ Cal. The deviation from Coulomb's law is considerably greater for *iso*helium than for the Li^6 nucleus. It is shown that B^9 is unstable, which is in agreement with Aston's work on the isotopes of boron. The upper radius for the Li^6 nucleus is 2.53×10^{-13} cm., and for *iso*helium 1.45×10^{-13} cm.
W. E. G.

The Stability of Atomic Nuclei, the Separation of Isotopes, and the Whole Number Rule. WILLIAM D. HARKINS (*J. Franklin Inst.*, 1922, 194, 329—356, 521—535, 645—681, 783—814; 195, 67—106; cf. A., 1922, ii, 702).—A summary of previous work on the stability and methods of separation of isotopes, and a review of the theory of Harkins and Wilson (A., 1915, ii, 543, 544) of the evolution of atomic species from hydrogen atoms and α -particles, and the experimental evidence in its favour. From the relative abundance of the different atomic species in meteorites and in the earth's crust, deductions are made as to the relative atomic stabilities and the part played by the ratio of the number of protons to electrons in the nucleus in determining the order of stability (cf. A., 1922, ii, 490). Five stability principles are enunciated, (1) no nucleus is stable unless the number of electrons it contains is equal to, or greater than, one-half the number of protons ($N/P > 0.5$), (2) as the nucleus becomes more positive with reference to its net content of protons, it is essential for stability that it shall become more negative with respect to its relative content of electrons, (3) the number of electrons in most nuclei is even, (4) atomic nuclei, and groups of protons and electrons in atomic nuclei, are in general more stable when they contain an even, rather than an odd, number of protons, and (5) elements of an even atomic number are much more abundant than those of odd atomic number. The determining factor for stability is the ratio N/P . The principles for the prediction of isotopes from the chemical or mean atomic weights are illustrated by means of the element lithium, for which isotopes with atomic weights 6 and 7 should exist. For the hypothetical atom with atomic

weight 5, $N/P=0.4$, and for that with atomic weight 8, $N/P=0.625$, which is higher than the ratio for any known atomic species. Hence it is concluded that these forms of lithium are incapable of existence. The principle that the most abundant isotopes of elements with even atomic weights will also possess even atomic weights has received support from the work of Dempster on the isotopes of zinc, and of Aston on the isotopes of tin. In general, the most abundant isotope of an element has a charge and a mass equal to a whole number times the charge and mass of an α -particle. The original theory of Rutherford, that the light atoms are built up mostly of particles of mass 3, was not justified. The mode of disintegration of the light atoms by the Rutherford method and the disintegration of the radioactive elements are discussed. Calculations are made of the energy of disintegration of the radioactive elements. In conjunction with Lunn, the loss of electromagnetic mass due to the approach of protons to electrons has been derived (cf. A., 1922, ii, 703). The possibility of distinguishing between isotopes by spectroscopic measurements is considered, and it is concluded that isotopes should differ chemically. A summary is given of the methods previously employed in the separation of the isotopes of neon, chlorine, and mercury, and of the efficiencies of the processes of distillation, diffusion, and liquid centrifuging. Evidence is submitted of the separation of cadmium and zinc, by a distillation method, to the extent of 0.04 to 0.05 of a unit of the atomic weight.

W. E. G.

A Relation between the Atomic Numbers and the Atomic Weights of the Chemical Elements. F. LOEWINSON-LESSING (*Compt. rend.*, 1923, 176, 307—309).—The sum of the atomic numbers of two adjacent elements starting from helium give the following relationships: for the first twenty elements the atomic weight is equal to $+$ or -1 to the sum of the atomic numbers of the element and of that which immediately follows it. Starting from scandium this atomic difference between the atomic weight in round numbers and the sum of the atomic numbers increases and reaches a value of 51 at the finish, but in certain groups of elements its value remains almost constant. There is in the horizontal rows of the periodic system a certain regularity in its increase. This correlation allows the atomic weights of the five elements not yet discovered to be foretold and atomic weights of certain elements to be corrected.

W. G.

Radicles and the Periodic Classification of the Elements. A. RIUS Y MIRÓ (*Anal. Fis. Quím.*, 1922, 20, 496—500).—The atomic number of a radicle may be obtained by subtracting from the sum of the atomic numbers of its constituent elements twice the number of valencies concerned in its formation. For example, in the case of ammonium the atomic number is $7+(4 \times 1)-(2 \times 4)=3$, equal to the atomic number of lithium. Atomic numbers for other radicles calculated in the same way enable them to be assigned to appropriate positions in the periodic classification.

G. W. R.

The Ångström System of Units. T. M. LOWRY (*Rec. trav. chim.*, 1923, 42, 29).—The proposal of Centnerszwer for the introduction of a unit of atomic mass (*ibid.*, 1922, 41, 580) has been anticipated by Sir W. H. Bragg (*Proc. Phys. Soc.*, 1921, 34, 35), who proposed that the Ångström unit of length, 10^{-8} cm., should be made the basis of a unit of area 10^{-16} cm.², of volume 10^{-24} cm.³, and of mass 10^{-24} g. The mass of an atom in Ångström units is then 1.65 times its atomic weight. E. H. R.

Molecular Dimensions, Molecular Structure, and the Viscosity of the Halogens and their Hydrides. HARRY SCHMIDT (*Z. Physik*, 1923, 12, 24—27).—An extension of the equations of Chapman (A., 1916, ii, 416). The mean molecular collision area of chlorine, bromine, and iodine have been derived by Rankine (A., 1921, ii, 192) from viscosity determinations, and from these values, on the assumption that the halogen molecule consists of two atoms in contact, the atomic radii have been calculated. From these figures and the radius of the hydrogen atom, given by the Bohr theory, the mean collision area of the hydrogen halides is derived, and compared with data based on viscosity measurements. The agreement is satisfactory. On the other hand, measurements of the viscosity of hydrogen give values for the mean collision area which are not in accord with the assumption that the hydrogen molecule consists of two hydrogen atoms in contact. W. E. G.

Magnetic Valency and the Radiation Hypothesis. F. T. PEIRCE (*Phil. Mag.*, 1923, [vi], 45, 317—323).—An inquiry into a possible mechanism of chemical change which would assign an effective rôle to radiation of a definite frequency. A theory of the valency bond is put forward which is based on the work of Oxley (cf. A., 1921, ii, 82). The valency bond is due to the magnetic attraction between two ring or vortical electrons, and can only be destroyed by the influence of radiation of the right frequency. The effects of temperature radiation and external illumination are discussed and compared, and the conclusion is drawn that photocatalysis should be observable only where the rate of reaction is determined by a dissociation. W. E. G.

Transformations in Unsaturated Compounds. Negative Migration. A New Theory of the Conjugated System C:C:C:C. ALFRED GILLET (*Bull. Soc. chim. Belg.*, 1922, 31, 365—375; cf. A., 1921, i, 490, 533, 761).—A theoretical discussion in which the author maintains that by generalising two or three types of transformation of which several cases are known, the properties of conjugated double bonds may be explained without assuming the existence of partial valencies. H. J. E.

The Metallurgical Applications of Physical Chemistry. CECIL HENRY DESCH (T., 1923, 123, 280—294).—A lecture delivered before the Chemical Society on December 14th, 1922.

The Identity of Geber. E. J. HOLMYARD (*Nature*, 1923, **111**, 191—193).—A criticism of Berthelot's view, now commonly held, that Geber's works are European forgeries of the thirteenth century; the author considers the identity of Geber with Jābir ibn Haiyān (eighth century A.D.) to be extremely probable. A. A. E.

The Identity of Geber. J. R. PARTINGTON (*Nature*, 1923, **111**, 219—220; cf. preceding abstract).—An historical discussion in support of the probable authenticity of the Latin works ascribed to Geber. A. A. E.

Improved Optical Lever Manometer. EMMETT K. CARVER (*J. Amer. Chem. Soc.*, 1923, **45**, 59—63).—The optical lever manometer described by Shrader and Ryder (*Physical Rev.*, 1919, **13**, 321) has been slightly modified, whereby the sensitivity has been increased to 0.0001 mm. with an accuracy of about 0.0002 mm. of mercury. The modifications introduced are: a tube of 44 mm. diam. instead of narrow as in the original apparatus; this eliminates the error due to clinging of the mercury to the walls; a steel float instead of glass, which eliminates irregular wetting of the float; the knife edges are replaced by steel points, which prevent the changes which occur in the seating of the mirror support and so prevent a shift of zero; temperature changes were eliminated by placing the manometer in a thermostat with an optical glass window. J. F. S.

The Production of Coloured Flames for Use with Spectrophotometers and Polarimeters. J. J. MANLEY (*Phil. Mag.*, 1923, [vi], **45**, 336—337).—An apparatus is described for the introduction of aqueous solutions of salts, acidified with hydrochloric acid, into the Bunsen flame. This consists of a glass bulb of 20—30 c.c. capacity blown in the middle of a glass tube 1 cm. in diameter. The tube below the bulb is drawn out, bent at right angles, and cemented on to a vitrosil tube 5 mm. in diameter with a bore of 1 mm. Three or four platinum wires 0.3 mm. diameter are placed within the pipe of vitrosil, and constitute a wick extending out in a horizontal direction. The salt solutions when placed in the bulb are fed into the flame by capillary action along the platinum wires, and the rate of introduction can be adequately controlled by varying the inclination of the tube. W. E. G.

A Simple Automatic Apparatus for Delivering Drops and Keeping a Constant Level in Washing with Acids. FRITZ REIMANN (*Biochem. Z.*, 1922, **133**, 112—113).—An apparatus is described on the syphon principle which delivers a slow current of liquid drop by drop at a constant rate. W. O. K.

Inorganic Chemistry.

Active Chlorine. Y. VENKATARAMAIAH (*J. Physical Chem.*, 1923, 27, 74—80).—Pure chlorine, prepared by heating gold chloride, was activated by the silent electric discharge, by electrical discharge at 20 mm. pressure, by ultra-violet light, or thermally. The active variety combines with ozone to form chlorine monoxide, with sulphur to form sulphur monochloride, with tellurium to form tellurium dichloride, and with benzene in the dark to form benzene hexachloride. It does not react with carbon, and is unstable above 50°. The activation of chlorine is accompanied by a contraction in volume, indicating that the activity is probably due to the presence of complex molecules. J. S. G. T.

Some Fundamental Atomic Weights. E. MOLES and J. M. CLAVERA (*Anal. Fis. Quim.*, 1922, 20, 550—554).—Revised values are given for the atomic weights of fluorine (19·000), chlorine (35·457), bromine (79·926), nitrogen (14·008), carbon (12·000), and sodium (22·998). G. W. R.

A Class of Hydrates but little Stable, called Hydrates of Gases. A. BOUZAT (*Compt. rend.*, 1923, 176, 253—255).—The author has calculated as accurately as possible the values of Q and q , the heats of formation of the hydrates from liquid water and solid water, respectively, in the cases of chlorine, bromine, and sulphur dioxide, and the values obtained give as the general formula for the hydrates M_6H_2O , which is in agreement with the experimental results and the hypothesis of Villard (A., 1897, ii, 151). W. G.

Solubility of Iodine Pentoxide in Sulphuric Acid. ARTHUR B. LAMB and A. W. PHILLIPS (*J. Amer. Chem. Soc.*, 1923, 45, 108—112).—The solubility of iodine pentoxide has been determined at 24·77° in sulphuric acid of concentrations 50—106%, and is found to decrease up to 77% acid, and from this point upwards the initial solubility increases. However, a slow transformation of the solid phase begins at this point, with the formation of a less soluble solid substance. This substance has a maximum solubility at 104% acid. There is also evidence of a third solid substance in equilibrium with acids of intermediate concentrations. A possible explanation of these facts is that the main solubility curve (the initial curve) represents the solubility of iodic acid, whilst the second and probably the third curves represent solubilities of iodine pentoxide and of anhydro-iodic acid (HI_3O_5). J. F. S.

The Activation of Oxygen and Hydrogen Peroxide by Palladium Hydride. N. D. ZELINSKY and P. P. BORISSOW (*Ber.*, 1923, 56, [B], 396—406).—The decolorisation of indigotin in faintly acid solution in the presence of palladium foil saturated with hydrogen occurs after the same time, whether air or oxygen is passed through the solution, although the production of hydrogen

peroxide is considerably greater in the latter circumstances. The amount of hydrogen peroxide, therefore, has little influence on the oxidation of indigotin.

The formation of hydrogen peroxide when air or oxygen is rapidly passed through water containing palladium foil thoroughly saturated with hydrogen takes place to a greater extent than has been previously supposed and attains a maximum concentration of 0.646 g. per litre. The oxidation of indigotin, however, under the experimental conditions cannot be attributed to this unexpectedly high concentration of hydrogen peroxide, since the effect is produced only after a much longer period by solutions of the technical agent of considerably greater concentration.

Decolorisation of indigotin proceeds much more rapidly under otherwise similar conditions in the absence of acid, and is observed when solutions of technical hydrogen peroxide and indigotin are brought into contact with palladium hydride and kept agitated by a current of carbon dioxide. Under these conditions, it is not possible for fission of the oxygen molecule or formation of a higher oxide of hydrogen to take place; the only possible explanation is to be found in the mutual action of palladium hydride and hydrogen peroxide.

Palladium hydride by itself has a marked reducing action towards indigotin; conversely, in the presence of hydrogen peroxide the oxidising action of the latter is catalytically accelerated by palladium hydride.

If air is passed through water in which palladium hydride is immersed and the latter is then removed, a solution is obtained which contains hydrogen peroxide, but is much more active towards indigotin than a solution of similar concentration which has been prepared from the technical peroxide. A similarly active solution can be obtained from palladium hydride, hydrogen peroxide, and carbon dioxide. If, however, the passage of the carbon dioxide is prolonged, the hydrogen peroxide is completely destroyed, and the solution does not react with potassium permanganate or zinc iodide-starch, even in the presence of ferrous sulphate; the activity is, however, rapidly restored by the addition of a little hydrogen peroxide. An active solution cannot be obtained from palladium and hydrogen peroxide, or from palladium hydride and water. The essential condition appears to consist of the presence of palladium hydride and hydrogen peroxide. The solution does not lose its activity when it is distilled, filtered, or preserved in a closed vessel during eight months. The presence of traces of palladium or of its compounds cannot be detected. Apparently, the effect is due to unusually minute traces of a substance with the properties of an inorganic peroxydase, which, for the present, cannot be detected analytically. The formation and decomposition of the possible compound may conceivably be expressed as follows: $\text{Pd}_3\text{H}_2 + \text{H}_2\text{O}_2 \rightarrow \text{Pd}_3\text{H}_2(\text{OH})_2 \rightarrow \text{O} + \text{H}_2\text{O} + \text{Pd}_3\text{H}_2$. The liberated oxygen atom affects the oxidation. This hypothesis explains the labile condition of hydrogen peroxide in the presence of palladium hydride.

H. W.

Ozone and Allotropy. P. DE PAUW (*Chem. Weekblad*, 1923, 20, 26).—The conception of ozone as an allotrope of oxygen conflicts with the definitions of allotropy, since (1) both are gases, (2) their chemical reactions do not always yield identical products; the action of ozone on unsaturated organic compounds yields ozonides, which cannot be obtained from oxygen, (3) their solutions are not identical. Ozone, therefore, should not be selected as an example of allotropy; a more suitable example would be grey tin, which on heating passes over into the white form at constant temperature.

S. I. L.

Forms of Sulphur in Coke. Physico-chemical Study of the Sulphur held by Carbon at High Temperatures. ALFRED R. POWELL (*J. Amer. Chem. Soc.*, 1923, 45, 1—16).—A phase-rule investigation of the carbon-sulphur complex which exists with carbon at high temperatures shows that the sulphur is present in two forms, adsorbed free sulphur and sulphur in solid solution in the carbon or held on the surface of the carbon in such a manner that it cannot be distinguished from a solid solution. Coke produced in the laboratory by heating coal rapidly contains sulphur in three forms, adsorbed free sulphur, sulphur in solid solution in the carbonaceous mass, or held on the surface in such a form as to exhibit all the properties of a solid solution and ferrous sulphide, together with much smaller quantities of calcium and magnesium sulphide. When this coke is maintained at a red heat for several hours, the adsorbed sulphur slowly passes into solid solution. Coke made by the usual commercial process of carbonisation over a comparatively long period contains, before it is cooled, only two forms of sulphur, sulphur in solid solution, as above, and ferrous sulphide with smaller quantities of other sulphides, the absorbed sulphur being absent or present in inappreciable quantities. When coke cools, even with limited access to the air, oxidation of ferrous sulphide takes place according to the equation $4\text{FeS} + 3\text{O}_2 = 2\text{Fe}_2\text{O}_3 + 4\text{S}$. When coke is quenched as in ordinary coke manufacture, the decomposition of ferrous sulphide is incomplete; this is due to the speed with which the temperature of the coke is carried below that necessary for oxidation. Coke kept at a temperature about 500° , even with a limited supply of air, shows an almost complete oxidation of the ferrous sulphide. When hydrogen or gas containing hydrogen is led through red-hot coke in a coking oven, the sulphur removed as hydrogen sulphide comes from the decomposition of the ferrous sulphide, because this compound has the highest dissociation pressure of all the forms of sulphur in coke.

J. F. S.

The Desulphuration of Metals by Lime. B. BOGITCH (*Compt. rend.*, 1923, 176, 103—105).—If the metal is rich in sulphur a considerable amount of the sulphur is removed by calcium oxide at 1500 — 1600° , but if the sulphur content is low the desulphuration by lime or by a basic slag is extremely slow, and at this temperature the slag ceases to absorb sulphur when the sulphur content of the slag reaches about 22%, although there may still be some unaltered

calcium oxide present. If the proportion of calcium fluoride in the slag is increased, the absorption of sulphur continues until the whole of the oxide is converted into sulphide. W. G.

Vapour Pressures of Sulphur Dioxide. W. MUND (*Bull. Acad. roy. Belg.*, 1919, [v], 5, 529—543).—The author has determined, by the static method, the vapour pressures of sulphur dioxide corresponding with temperatures between -42° and 0° . The errors common to such determinations are examined and eliminated by methods for the description of which the original paper should be consulted. The vapour pressure of sulphur dioxide at 0° was found to be 1163.98 mm. or 1.53 atmos., other determinations being made at the temperature of fusion of certain eutectic mixtures (cf. Bruylants and Mund, *ibid.*, 113). E. E. T.

Acidity and Electrolytic Dissociation of Hydrogen Selenide. M. DE HLASKO (*Bull. Acad. Polonaise Sci. Lettres*, 1921, [A], 18—25; from *Chem. Zentr.*, 1923, i, 16).—The equivalent conductivity of the ion HSe' , calculated by the Kohlrausch formula, from measurements of the conductivity of aqueous solutions of hydrogen selenide is 70. The value 1.88×10^{-4} was obtained for the dissociation constant of hydrogen selenide. G. W. R.

Selenium Nitride. WILHELM STRECKER and LUDWIG CLAUS (*Ber.*, 1923, 56, [B], 362—383).—Selenium nitride, SeN , has been obtained previously as an amorphous, pale orange-yellow, extremely explosive powder by the action of gaseous ammonia on a number of compounds of selenium. In the hope of securing a better-regulated course of the change, the action of liquid ammonia has now been investigated.

The action of liquid ammonia on diselenium dichloride is exceedingly vigorous, and results in the deposition of red selenium; a similar result is obtained if the chloride is mixed with chloroform or anhydrous benzene, only traces of the nitride being produced. In ethereal solution, on the other hand, a pale brown, amorphous compound, Se_2NCl , is formed. Selenium tetrachloride in the absence of solvent behaves similarly to the lower chloride towards liquid ammonia; in the presence of carbon disulphide it is converted into a pale yellow, amorphous material which could not be satisfactorily purified. Selenyl chloride is transformed by liquid ammonia in the presence of ether in open vessels into the primary product, $\text{SeOCl}_2 \cdot 4\text{NH}_3$, which is decomposed by water into selenium, selenium nitride, ammonium chloride and selenite, and selenious acid, whereas in a sealed tube it gives selenium nitride in comparatively good yield.

Diselenium dibromide reacts with gaseous ammonia in the same manner as the corresponding chloride; with liquid ammonia in the presence of ether, it gives the compound, $\text{Se}_2\text{N}_2\text{Br}$. The reaction of selenium tetrabromide towards liquid ammonia resembles closely that of the tetrachloride. On the other hand, the action of these substances in the presence of carbon disulphide proceeds more quietly than when the chloride is used, and gives

better yields of the nitride. The change follows a similar course in the presence of benzene.

It therefore appears that the selenium tetrahalides are the best initial materials for the preparation of selenium nitride; the small amounts of the latter which are produced when the lower halides or the oxy-compounds are employed appear to be derived from intermediately formed tetrahalide.

Selenium nitride is an amorphous, orange-coloured powder which is considerably more sensitive than mercury fulminate to shock or blow; it explodes with certainty when heated at 160° . According to Verneuil, its formation from the tetrachloride and ammonia is expressible by the equation: $3\text{SeCl}_4 + 16\text{NH}_3 = 3\text{SeN} + 12\text{NH}_4\text{Cl} + \text{N}$. In the case of the bromide in the presence of carbon disulphide, the volume of nitrogen evolved is far in excess of that required by a similar equation, whereas in the presence of benzene the reaction $3\text{SeBr}_4 + 16\text{NH}_3 = 2\text{SeN} + \text{Se} + \text{N}_2 + 12\text{NH}_4\text{Br}$ appears to take place.

Chlorine and bromine react explosively with selenium nitride. In the presence of carbon disulphide, the action of bromine leads to the formation of a brownish-green, hygroscopic *substance*, SeN_2Br_4 . Bromine vapour diluted with carbon dioxide transforms solid selenium nitride into ammonium selenohexabromide, $(\text{NH}_4)_2\text{SeBr}_6$, the formation of which appears to be due to the action of atmospheric moisture on a primary additive product of bromine and the nitride. Chlorine, in similar circumstances, gives the *product* SeNCl_3 . Bromination of the compound $\text{Se}_2\text{N}_2\text{Br}$ yields the substance SeN_2Br_4 , whereas exhaustive chlorination of the product Se_2NCl yields Se_2NCl_6 , which possibly is not quite homogeneous.

Selenium nitride is not affected by solid iodine or by a solution of the halogen in ether or chloroform.

The constitution of selenium nitride is discussed at some length; unfortunately, a suitable solvent is not available for the determination of the molecular weight, but reasons are advanced in favour of a cyclic structure of the molecule Se_4N_4 .

The possibility that selenium nitride is a derivative of azoimide has been examined, but this does not appear to be the case. Diselenium dibromide reacts with silver azide suspended in benzene with the formation of silver chloride and selenium; similar changes occur with lead and sodium azides. Selenium tetrabromide and silver azide give a pale yellow compound, which becomes bluish-black when exposed to light. Selenium oxychloride and sodium azide in the presence of benzene gives nitrogen and the *compound* $2\text{NaCl}, \text{SeO}_2, \text{H}_2\text{O}$.
H. W.

New Method of Determination of the Atomic Weight of Tellurium. P. BRUYLANTS and J. MICHIELSEN (*Bull. Acad. roy. Belg.*, 1919, [v], 5, 119—130).—The ratio $\text{Te} : \text{H}_2$ and $\text{Te} : \text{H}_2\text{O}$ have been measured. Hydrogen telluride, prepared by the electrolysis of dilute sulphuric acid, using a tellurium cathode, was purified by fractional distillation, etc., from the accompanying hydrides

of sulphur, selenium, and antimony, and decomposed into its elements at a temperature of 200–220°. The tellurium was weighed as such, and the hydrogen oxidised to water by means of cupric oxide. A marked difference obtained between the ratio $\text{Te}:\text{H}_2$ measured directly, and that measured indirectly through water, was traced to incomplete decomposition of the hydrogen telluride, and, correcting for this, the authors obtain the figure 127.8 for the atomic weight of tellurium. E. E. T.

The Allotropy of Tellurium. A DAMIENS (*Ann. Chim.*, 1922, [ix], 18, 282–312).—A detailed description of work which has been previously published (*A.*, 1922, ii, 498, 562). The general conclusion is drawn that the analogy between the allotropy of sulphur and tellurium cannot be accepted, as the latter element is clearly differentiated by the existence of a single crystalline form. H. J. E.

Properties of Hydrogen Telluride. P. BRUYLANTS (*Bull. Acad. roy. Belg.*, 1920, [v], 6, 472–478).—Pure hydrogen telluride was prepared by a modification of the process used previously Bruylants and Michielsen, *ibid.*, 1919, 119–130; this vol., ii, 153), and various constants were determined. The triple point has for co-ordinates t -45.4° , p 102 mm. The density is d_0 2.65. The vapour-pressure curve was compared with the curves for ethyl alcohol and carbon disulphide, whence the b. p. at 760 mm. was calculated as -2.2° , using the Ramsay-Young equation. The actual b. p. found by experiment was -1.8° . The calculated latent heat of vaporisation was found to be L 5.7 cal., whence, by Trouton's Rule, $L/T=20.9$. The critical temperature of the hydride lies in the region of 200°, if the Guldberg-Guye relation holds. E. E. T.

Acidity of Hydrogen Telluride. Electrolytic Dissociation of Hydrogen Telluride. M. DE HLASKO (*Bull. Acad. Polonaise Sci. Lettres*, 1919, [A], 73–78; from *Chem. Zentr.*, 1923, i, 15–16).—The electrical conductivity of aqueous solutions of hydrogen telluride was determined. The value 61 was obtained for the equivalent conductivity of the ion HTe' . The value $K=2.27 \times 10^{-3}$ was obtained for the dissociation constant of hydrogen telluride in aqueous solution. G. W. R.

The After-glow of Activated Nitrogen. MARCELLO PIRANI and ELLEN LAX (*Wiss. Veröffentl. Siemens-Konzern*, 1922, 2, 203–207; from *Chem. Zentr.*, 1923, i, 17; cf. *A.*, 1921, ii, 197–198).—Highly purified nitrogen in sealed glass vessels was submitted to high frequency discharge of about 100,000 periods per second. The discharge occurs in the form of bright threads joining up with the walls of the vessel. At pressures varying from 2–700 mm. with an optimum at 60–200 mm., a pale blue glow was produced. Contamination by gas given off from the walls of the vessels during discharge amounted to less than $5 \times 10^{-50}\%$. In experiments at pressures of 150 to 180 mm., nitrogen always showed luminescence either at once or after longer discharge (ten minutes). The glow

spreads from those parts of the walls of the vessels receiving the greatest impact of electrons. The luminescence occurs when the nitrogen is contaminated with gases evolved from the hygroscopic moisture on the glass walls of the vessels. These may amount at 150 mm. pressure to 10^{-5} to $10^{-4}\%$. Inert gases and electro-positive gases such as hydrogen have little effect. Electronegative gases such as oxygen, water vapour, and iodine vapour give in concentration of about 1.5×10^{-3} a maximum after-luminescence; with 6 to $8 \times 10^{-3}\%$, the luminescence is inhibited. Perfectly pure nitrogen does not show luminescence. It is supposed that an active form of nitrogen is produced which decomposes in the presence of small quantities of electronegative gases with emission of light. Electronegative gases increase the point discharge and thereby the number of active molecules and the rate of decomposition. With larger amounts of impurity, the point discharge is decreased whilst the rate of decomposition is so much increased that luminescence only occurs in the region of the lines of discharge. With still greater quantities of impurity, for example, $10^{-2}\%$ of oxygen, the decomposition within the region of the lines of discharge is so rapid that luminescence is no longer visible.

G. W. R.

The Catalytic Oxidation of Ammonia by Air in Contact with Platinum. EUGÈNE DECARRIÈRE (*Ann. Chim.*, 1922, [ix], 18, 312—388).—A detailed description of work previously published. Fuller particulars are given of the author's work of the action on the catalyst of certain gaseous impurities (A., 1921, ii, 503, 546; 1922, ii, 284) and also of work carried out in collaboration with Pascal on the effect of variations in the form of the catalyst (A., 1919, ii, 463).

H. J. E.

The Crystal Structure of Hydrazine Dihydrochloride. RALPH W. G. WYCKOFF (*Amer. J. Sci.*, 1923, 5, 15—22).—Using Laue photographic and spectrographic data, the structure of hydrazine dihydrochloride has been shown to be based on the paramorphic hemihedry of the cubic system. The crystal unit consists of a cell, 7.89 Å. in length, containing four chemical molecules. An approximate placing of the atoms in the unit cube has been made, and the arrangement is analogous to that obtaining in crystals of the alkaline-earth nitrates, the hydrazine groups occupying positions analogous to those held by the alkaline-earth metals, and the chlorine atoms replacing the nitrate groups. The distance between adjacent chlorine atoms is approximately 3.96 Å.; between chlorine and nitrogen atoms, about 3.14 Å. These results are at variance with the hypothesis of constant atomic radii.

W. E. G.

The Preparation of Hydroxylamine Hydrochloride and Acetoxime. WALDO L. SEMON (*J. Amer. Chem. Soc.*, 1923, 45, 188—190).—A modification of Divers's method (T., 1896, 69, 1665), in which the conversion of the sodium carbonate first into a mixture of hydrogen carbonate and hydrogen sulphite and then

into hydrogen sulphite alone is carried out prior to the addition of the sodium nitrite, as a result of which the time required for the complete operation and the amount of cooling necessary are considerably reduced. Further, the sodium hydroxylaminedisulphonate is converted directly into acetoxime (cf. Raschig, A., 1887, 549, 635) and this is then hydrolysed by hydrochloric acid and the required hydroxylamine hydrochloride obtained after distilling off the acetone (cf. Janny, A., 1883, 580, 581). Under these conditions, a product is obtained free from ammonium salts and with a yield of 53—77%.
W. G.

Black Colloidal Suspensions in Phosphorus. CLAUDE HAINES HALL, jun. (*J. Amer. Chem. Soc.*, 1923, 45, 67—69).—The literature relating to black phosphorus is quoted and discussed, and it is shown that Thénard's black phosphorus is a colloidal suspension of mercury in the phosphorus, whilst the black phosphorus obtained by Bridgman (A., 1914, ii, 647) is a true allotropic modification of phosphorus. Using Svedberg's method of colloidisation, the author has dispersed copper and mercury in molten phosphorus to form colloidal suspensions of these metals. The material obtained with copper and mercury was homogeneous, readily inflammable, and had d 1.9. When extracted with carbon disulphide, tiny, black crystals of copper phosphide were obtained in the case of copper, but with mercury droplets of mercury; a few red flakes of amorphous phosphorus were obtained in each case.
J. F. S.

Action of Light on Arsenic Trisulphide Hydrosol. RAY V. MURPHY and J. HOWARD MATHEWS (*J. Amer. Chem. Soc.*, 1923, 45, 16—22).—The effect of exposing arsenic trisulphide sols of varying concentrations to the light of a condensed filament lamp for various periods at constant temperature has been investigated by measuring the electrical conductivity of the solutions after each exposure. The results show that the electrical conductivity increases on exposing the sols to light, the rate of change increasing with decreasing concentration of the colloid. This is explained as due to the increased photochemical activity of the colloid per unit mass of arsenic trisulphide, brought about by the greater dispersion of the more dilute sol. The reaction is explained, according to the suggestion of Freundlich and Nathanson (A., 1921, ii, 494), as one of a two-stage photochemical oxidation of hydrogen sulphide to colloidal sulphur and a thionic acid, accompanied by a reaction between hydrogen sulphide and the thionic acid, which serve as stabilising electrolytes for the micellæ of arsenic trisulphide and sulphur, respectively. Removal of the stabilising electrolytes produces a de-stabilisation of the two colloids which are consequently precipitated. The increase in electrical conductivity is explained as due to the building up of a concentration of the thionic acid sufficient to serve as the stabilising electrolyte for the colloidal sulphur, the reaction between hydrogen sulphide and the thionic acid then proceeding at such a rate that the equilibrium is maintained between the several components of

the system, further change in the electrical conductivity thus being prevented. J. F. S.

Estimation of the Atomic Weight of Boron. ALFRED STOCK and ERNST KUSS (*Ber.*, 1923, 56, [B], 314—316).—A preliminary account. The full details of the work will be published elsewhere.

The method adopted consists in the decomposition of weighed amounts of diborane, B_2H_6 (cf. Stock and Massenez, A., 1913, ii, 44), by water in accordance with the equation $B_2H_6 + 6H_2O = 2H_3BO_3 + 6H_2$, and measurement of the evolved hydrogen. As mean value of six determinations, the atomic weight of boron is found to be 10.8055 ($H=1.0077$), the mean error of the individual experiments being ± 0.0036 and of the average value ± 0.0015 . The figure is slightly lower than that obtained (10.82—10.84) from the analysis of boron trichloride by Hönigschmid and by Baxter and Scott, but agrees with that predicted by Aston (10.75 ± 0.07) from observations of the mass spectrum.

The atomic weight of silicon has been estimated similarly by decomposing monosilane with sodium hydroxide. Preliminary results are 28.15, 28.16, and 28.14, which, however, are given with reserve. It is certain that the usually adopted figure for the atomic weight of silicon (28.3) is considerably too high. H. W.

Absorption of Carbon Monoxide by Cuprous Ammonium Carbonate and Formate Solutions. ALFRED T. LARSON and CLARK S. TEITSWORTH (*J. Amer. Chem. Soc.*, 1922, 44, 2878—2885).—A static method for investigating the absorption capacity of liquid absorbents for carbon monoxide is described, and has been used with various solutions of cuprous ammonium formate and cuprous ammonium carbonate for this purpose. It is shown that for equivalent concentrations the formate and carbonate solutions have essentially the same absorption capacity for carbon monoxide under the same conditions of temperature and partial pressure of carbon monoxide. At low temperatures (0°), the results indicate the formation of a complex or additive compound containing 1 mol. of carbon monoxide per mol. of copper, which is largely decomposed at slightly elevated temperatures (60°). Small variations in the concentration of total carbonate or formate have no appreciable effect on the solubility of carbon monoxide, but the solubility is proportional to the copper concentration of the solution. The carbonate solutions are much less stable than the formate solutions; the former deposits copper at 60° . The maximum permissible copper concentration of any solution is fixed by the temperature at which the solution is to be regenerated. High copper concentration is accompanied by increased precipitation of free copper as the temperature is raised. High pressures of carbon monoxide also tend to increase the precipitation of copper. Solutions of cuprous ammonium formate are preferable to cuprous ammonium carbonate, because the deposition of copper at the regeneration temperature is very much less. J. F. S.

Formation of Carbon Disulphide by the Action of Sulphur Dioxide on Carbon. B. RASSOW and K. HOFFMANN (*J. pr. Chem.*, 1922, [ii], **104**, 207—240).—When sulphur dioxide is led over red-hot carbon, the following reactions can occur: (i) $2\text{SO}_2 + 2\text{C} = 2\text{CO}_2 + \text{S}_2$. (ii) $\text{S}_2 + \text{C} \rightleftharpoons \text{CS}_2$. (iii) $\text{CO}_2 + \text{C} \rightleftharpoons 2\text{CO}$. (iv) $\text{S}_2 + 2\text{CO}_2 \rightleftharpoons \text{COS} + \text{CO} + \text{SO}_2$. (v) $\text{S}_2 + 2\text{CO} \rightleftharpoons 2\text{COS}$. (vi) $\text{CS}_2 + \text{CO}_2 \rightleftharpoons 2\text{CO} + \text{S}_2 \rightleftharpoons 2\text{COS}$. (vii) $2\text{SO}_2 + 4\text{C} \rightleftharpoons 4\text{CO} + \text{S}_2$. The mutual influence of these reactions and the influence of temperature are discussed in detail, the conclusion being that an increase in the reaction temperature can lead only to an optimum formation of carbon disulphide. This prediction has been verified experimentally.

Sulphur dioxide was led over red-hot beechwood charcoal previously freed from hydrogen by heating in a current of chlorine. Free sulphur in the issuing gas was collected by condensation and filtration through glass wool; carbon disulphide vapour was next absorbed by means of ethereal triethylphosphine, the precipitated additive product being collected and weighed. Carbon dioxide and carbon oxysulphide were absorbed in ammoniacal calcium chloride solution, the total carbon in the liquid being determined by oxidation with hydrogen peroxide, followed by filtration and titration of the precipitated calcium carbonate, whilst the sulphur in the filtrate was estimated as barium sulphate. The remaining gas was finally collected over water, and the carbon monoxide estimated in the usual way.

At 700°, only traces of carbon disulphide are produced; the amount formed increases with rising temperature, the product containing also carbon oxysulphide, carbon dioxide, free sulphur, and small amounts of carbon monoxide. The maximum formation of carbon disulphide occurs at 850—900°, the sulphur from the sulphur dioxide being then distributed as follows: 35% as carbon disulphide, 55% as carbon oxysulphide, and 10% as free sulphur, whilst carbon monoxide and a small amount of carbon dioxide constitute the rest of the gas mixture. Above 900°, the proportion of free sulphur increases at the expense of both carbon disulphide and carbon oxysulphide; the oxygen from the sulphur dioxide appears almost exclusively as carbon monoxide. Above 1100°, free sulphur and carbon monoxide are the only products. The formation of carbon oxysulphide decreases continuously with increasing temperature; the free sulphur produced is a minimum at about 850°.

It is concluded that the process is useless as a technical method of making carbon disulphide.

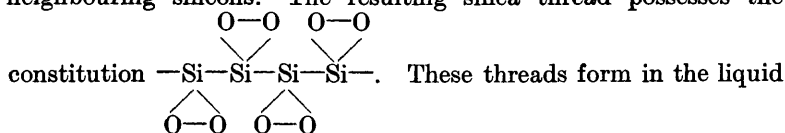
W. S. N.

Absorption of Carbon Disulphide Vapour by Aqueous Solutions of Sodium Trinitride [Azide]. A. J. CURRIER and A. W. BROWNE (*J. Amer. Chem. Soc.*, 1922, **44**, 2849—2854).—The absorption of carbon disulphide vapour from gaseous mixtures by solutions of sodium azide in water has been investigated. It is shown that a 1% solution of sodium azide absorbs the theoretical amount of carbon disulphide vapour from gaseous mixtures, but that a further amount may also be absorbed at a much slower

rate. The absorption of carbon disulphide by a 1% aqueous solution of sodium azide amounts to about 3.5 times the volume of the absorbing liquid, and takes place irreversibly with the quantitative formation of sodium azidodithiocarbonate, $\text{NaN}_3 + \text{CS}_2 = \text{NaS} \cdot \text{CSN}_3$. Various mixtures of carbon disulphide vapour with air, oxygen, nitrogen, hydrogen, methane, and carbon monoxide have been analysed, using a 5% or a saturated aqueous solution of sodium azide as absorbent with exceedingly good results. The solution of the salt produced by the interaction of the absorbent and vapour has been found to possess no dangerously explosive properties, but to decompose very slowly after keeping for long periods, with the formation of nitrogen, sulphur, and sodium thiocyanate. J. F. S.

A Theory of the Structure and Polymorphism of Silica.

ROBERT B. SOSMAN (*J. Franklin Inst.*, 1922, 194, 741—764).—A set of hypotheses is put forward to explain in a consistent manner the wide variety of experimental data on the modifications of silica. It is assumed that the silica atom triplet, SiO_2 , maintains its individuality in all the forms of quartz and silicates, and that the silica molecules aggregate themselves in chains in which the silicon atoms share a pair of electrons with each oxygen, and the oxygen atoms share a pair of electrons between them. At the same time, the silicon shares one pair of electrons with each of two neighbouring silicons. The resulting silica thread possesses the



state or even in the vapour. In the liquid they are in a constant state of vibration and movement, with the oxygen atoms in haphazard orientation relative to the thread. On this view, solid silica glass is analogous to a compressed pad of wires. The thread structure is believed to persist in the crystalline state, and the three principal crystalline modifications (cristobalite, tridymite, and quartz) are built up by combining the threads through the oxygen atoms. The high to low inversions (α — β) in all three forms are considered to be due to a change in the state of motion of certain electron orbits resulting from increased thermal vibration of the atoms. These changes produce sudden alterations in the shape of the silica triplet and the relative positions of the two oxygen atoms. In cristobalite, the oxygen atoms of the silica threads are incompletely fixed, some of the threads being capable of rotation about the silica axis. This explains the variable inversion point of this form of quartz. The theory of the polymorphism of silica is extended to silicate systems, and to the oxides of other elements in group IV of the periodic classification. This view of the structure of the silica complex is in agreement with the minimum in the temperature volume curve of silica glass, and the relations between the specific heats of the various forms of quartz.

W. E. G.

Silicon Hydrides. XII. Disiloxan, $(\text{SiH}_3)_2\text{O}$. ALFRED STOCK and CARL SOMIESKI (*Ber.*, 1923, 56, [B], 132—135).—Unsuccessful attempts are described to convert disiloxan (Stock, Somieski, and Wintgen, A., 1918, ii, 110) into disilene, Si_2H_4 .

Disiloxan is not sensibly affected when heated at 300° ; at 400° , it yields small amounts of hydrogen, monosilane, and polymeric prosiloxan, but the greater portion of the original substance remains unchanged. Phosphoric oxide decomposes disiloxan at the atmospheric temperature, giving a little hydrogen, much monosilane, and polymeric prosiloxan. The initial reaction appears to consist in a slight hydrolysis in accordance with the equation $(\text{SiH}_3)_2\text{O} + \text{H}_2\text{O} = 2\text{SiH}_2\text{O} + 2\text{H}_2$, followed by a polymerisation of the volatile prosiloxan to its non-volatile polymeride. The liberated hydrogen is largely utilised in the reduction of disiloxan to monosilane, $(\text{SiH}_3)_2\text{O} + 2\text{H}_2 = 2\text{SiH}_4 + \text{H}_2\text{O}$. The water which is thus set free hydrolyses a further quantity of disiloxan, and thus the change continues until it is brought to a gradual conclusion by the absorption of water by the excess of dry phosphoric oxide. H. W.

Silicon Hydrides. XIII. Some Reactions of Chloromonosilane and Disilane. ALFRED STOCK and CARL SOMIESKI (*Ber.*, 1923, 56, [B], 247—252).—Disilane is very stable towards heat, but at not too high a temperature (about 500°) suffers decomposition which resembles the cracking of hydrocarbons. In addition to silicon, large volumes of monosilane are obtained, the production of which depends on the reducing action of primarily liberated hydrogen on unchanged disilane. Higher hydrides are not produced in sufficient quantity to make the method practicable for their preparation. At a higher temperature, the fission of disilane into silicon and hydrogen predominates.

Chloromonosilane and silver cyanide at 150° yield hydrogen cyanide and cyanogen as gaseous products. At 300° , chloromonosilane is decomposed by silver sulphide into non-volatile silicon compounds, hydrogen, and hydrogen sulphide. Monochlorosilane and hydrogen sulphide at 150° in the presence of aluminium chloride give hydrogen, dichloromonosilane, and a volatile compound containing sulphur [possibly $\text{SiH}_3\cdot\text{SH}$ or $(\text{SiH}_3)_2\text{S}$], which has not been investigated completely.

The main products of the action of sodium amalgam on dichloromonosilane are monosilane and the unsaturated, yellow, polymerised hydride, $(\text{SiH})_x$. The course of the reaction is represented by the equations $\text{SiH}_2\text{Cl}_2 + 4\text{Na} = \text{SiH}_2\text{Na}_2 + 2\text{NaCl}$; $\text{SiH}_2\text{Na}_2 + \text{mercury} \rightarrow \text{SiH}_2 + \text{sodium amalgam}$; $3\text{SiH}_2 \rightarrow \text{SiH}_4 + 2(\text{SiH})_x$.

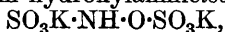
The following tensions have been measured for hydrogen sulphide prepared from iron sulphide and hydrochloric acid and purified by fractional distillation in a vacuum: -130° , 3 mm.; -120° , 7 mm.; -110° , 20 mm.; -100° , 54 mm.; -90° , 117 mm.; -80° , 247 mm.; -70° , 440 mm.; -59.1° , 778 mm. The pure dry gas can be preserved unchanged over mercury. H. W.

The Densities of Dilute Solutions of Potassium Salts and the Volume Changes Occurring on Solution. HAROLD HARTLEY and WILLIAM HENRY BARRETT (*T.*, 1923, 123, 398—401).

The Formation of Pyramidal Crystals by Alkali Halides.

HERMANN KUNZ-KRAUSE (*Ber. Deut. pharm. Ges.*, 1922, 32, 329—334).—The crystallisation of sodium chloride in pyramidal crystals previously observed from time to time by various workers has been shown to take place also with potassium iodide. Photographs are shown of such crystals of both these salts, and their mode of formation is indicated by diagrams of crystal growth at the surface of a saturated solution. P. M.

The Preparation of Potassium Hydroxylamineisodisulphonate. F. RASCHIG (*Ber.*, 1923, 56, [B], 206—208).—The preparation of potassium hydroxylamineisodisulphonate,



has previously been a matter of some difficulty, mainly owing to the poor yields and unstable nature of the intermediately formed trisulphonate. A convenient process for preparing the latter is now described.

Sodium hydrogen sulphite solution (5*N*, 1200 c.c.) is added with continuous stirring to a mixture of ice (1000 g.) and technical sodium nitrite (150 g.), whereby the temperature is not allowed to rise above 5°. One c.c. of the solution, when tested after the addition has been finished for ten minutes, should react with about 17 c.c. of *N*/10-iodine solution, and subsequently require 14—15 c.c. of *N*/10-sodium hydroxide for neutralisation in the presence of methyl-orange. Any ice particles are removed and the solution is treated whilst being vigorously shaken with lead peroxide (600 g.). It is subsequently warmed on the water-bath, frequent agitation being required to prevent the oxidising agent from becoming aggregated. The conclusion of the oxidation is reached when 1 c.c. of the solution neutralises about 9 c.c. of *N*/10-hydrochloric acid and subsequently does not react with more than 1 c.c. of *N*/10-iodine solution. The solution is filtered and the residue washed with hot water (200 c.c.). The filtrate is warmed with technical potassium chloride (800 g.) until the precipitated lead chloride forms coarse particles, which are removed. The filtrate, after remaining for three days in an ice-chest, deposits potassium hydroxylaminetrisulphonate (790 g.) in large monosymmetric prisms. It is filtered, dried on porous earthenware, and subsequently over calcium chloride. The finely-divided, dry salt (423 g.) is agitated with boiling water (800 c.c.) containing 1 c.c. of dilute hydrochloric acid until solution is complete; the small amount of lead sulphate which separates is removed. The filtrate deposits potassium hydroxylamineisodisulphonate in colourless crystals, the yield being about 90% of that theoretically possible. H. W.

The Alkali Permanganates. M. CRESPI and E. MOLES (*Anal. Fis. Quim.*, 1922, 20, 555—562).—The alkali permanganates, with the exception of sodium permanganate and ammonium permanganate, which are relatively unstable, decompose at temperatures which increase almost proportionally to their molecular weights. The densities are closely correlated with molecular weights. The thermal decomposition is similar throughout the series, and is

represented, for example, in the case of potassium permanganate, by the equation $10\text{KMnO}_4 = 2\text{K}_2\text{MnO}_3 + (3\text{K}_2\text{MnO}_4, 5\text{MnO}_2) + 6\text{O}_2$.

G. W. R.

The Dissociation of Potassium Chloroiridiate. G. GIRE (*Compt. rend.*, 1923, 176, 241—244).—The author has studied the decomposition of potassium chloroiridiate in the same manner as that used for barium chloroplatinate (A., 1922, ii, 551), and from his results calculates the heat of fusion of a molecule of potassium chloride to be -4.92 cal., which is in close agreement with the value obtained by Schemtschuschny and Rambach (A., 1910, ii, 204).

W. G.

Molecular Weight of the Sodium-Tellurium Complex in Liquid Ammonia as Derived from Vapour Pressure Measurements. CHARLES A. KRAUS and EDWARD H. ZEITFUCHS (*J. Amer. Chem. Soc.*, 1922, 44, 2714—2728).—The lowering of the vapour pressure of liquid ammonia, at temperatures of 17.9° to 20.6° , due to the complex sodium-tellurium compound, has been measured at a series of concentrations down to $0.03N$. It is shown that when the values of $\Delta P/P$ are plotted against the values of $n/n+N$, where n is the number of atoms of sodium in the mixture, a curve is obtained which, for dilute solutions, approaches very closely to a straight line, and for which the value $(\Delta P/P) / (n/n+N)$ is equal to 0.5 . Apparently solutions of the complex telluride in liquid ammonia very nearly follow Raoult's law; and from the value of the above ratio it follows that two atoms of sodium are present in each molecule of the complex telluride present in the solution. The complex telluride-ion, therefore, carries two negative charges. The formation of the complex telluride consists in the addition of tellurium atoms to the normal telluride-ion, the valency of the telluride-ion undergoing no change under these conditions. The bearing of this result on the present-day conceptions of the nature of other complexes in ammonia solution and of metallic alloys in general is discussed.

J. F. S.

The Position of the Atoms in the Optically Active Crystals, NaClO_3 and NaBrO_3 . L. VEGARD (*Z. Physik*, 1922, 12, 289—303).—By the employment of the Debye powder method, the positions of the atoms in the chlorate and bromate crystals have been determined. The parameter values lead to a very simple grouping of the atoms in space which is in agreement with the volume conditions. As was recognised by Bragg, the space lattices are based on the face-centred cube, but none of the atom centres themselves lies in a face-centred arrangement. The atoms lie about trigonal axes, with the halogen and the three oxygen atoms forming a pyramid group. The halogen, which forms the apex of this group, is attached to a sodium atom along the vertical axis of the pyramid. Each oxygen atom is in contact with two other oxygen atoms, and the halogen atom in the same molecule, and with two sodium atoms from neighbouring molecules. The halogen atom is not in contact with the sodium atom. The following distances

obtain between the atoms in contact, $D_{\text{Na-O}}=2.36 \text{ \AA.}$; $D_{\text{Br-O}}=1.89 \text{ \AA.}$; $D_{\text{O-O}}=1.20 \text{ \AA.}$, whereas, according to Bragg, these distances should be 2.42 \AA. , 1.84 \AA. , and 1.30 \AA. , respectively. The arrangement of the oxygen atoms is quite different from that ascribed to them by Koltmeijer, Bijvoet, and Karssen (*K. Akad. Wetensch. Amsterdam*, 1921, 23, 644—653). The intensities of the lines calculated on the basis of the above structure is, however, in agreement with the experimental values.

Both the chlorine and sodium atoms are displaced towards the angles of the unit cube, and this involves a rotation of the pyramid group about the pyramidal axis. Since this rotation can occur in two directions, the occurrence of optical activity is accounted for. This rotation does not occur in the isomorphous group of nitrates, although these crystallise in the same system as the chlorate and bromate. These substances are, however, inactive. Formulæ based on the assumption that contact between the atoms in the crystal indicates the positions of the valency forces are not in accordance with chemical ideas. It is therefore concluded that crystal structure gives very little clue to chemical constitution. The volume conditions governing the packing of the atoms in the crystal, and not the chemical forces, are the deciding factor in the atomic arrangement.

W. E. G.

The System Sodium Sulphate-Sodium Chromate-Water.

II. YUKICHI OSAKA and RYOHEI YOSHIDA (*Mem. Coll. Sci. Kyoto*, 1922, 6, 49—54).—This work is a continuation of that of Takeuchi (A., 1916, ii, 31), and the equilibrium of the sodium sulphate-sodium chromate system has now been studied at 28° , 31° , and 33° . At 28° and 31° , the chromate exists as tetrahydrate and its solubility in the sulphate as decahydrate decreases as the temperature rises, the molar fraction being 0.16 at 28° and 0.04 at 31° . The solid solution obtained by Takeuchi at 25° having the composition $2\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CrO}_4 \cdot 30\text{H}_2\text{O}$ was not a definite compound. At 33° , no solid solution of the decahydrates exists.

E. H. R.

Some Slags from the Clausthal Silver Furnaces. A New Family of Silicates of Composition $\text{R}_3\text{Si}_2\text{O}_7$. KURT HOFMANN-DEGEN (*Sitzungsber. Heidelberger Akad. Wiss.*, 1919, [A. 14]; from *Chem. Zentr.*, 1922, iii, 1248—1249).—Cavities of slag from the Clausthal silver works contain a zinc bearing iron-calcium olivine (Fe_2SiO_4 50.9%, Zn_2SiO_4 2.7%, Mg_2SiO_4 5.1%, Ca_2SiO_4 41.2%) having $a : b : c = 0.4371 : 1 : 0.5768$, and refractive indices γ_D 1.7430, β_D 1.7340, and α_D 1.6958, and also a tetragonal silicate mineral called "justite." *Justite* has the composition $(\text{Mg}, \text{Fe}, \text{Zn}, \text{Mn}, \text{Ca})_3\text{Si}_2\text{O}_7$, where $\text{Ca} : (\text{Mg}, \text{Fe}, \text{Zn}, \text{Mn}) = 1 : 1$. Its refractive indices are $\epsilon_D = 1.6581$ and ω_D 1.6712. It resembles the naturally occurring hardystonite, $(\text{Ca}, \text{Zn})_3\text{Si}_2\text{O}_7$. A slag from Bochum consisted of tetragonal crystals of the composition $(\text{Ca}, \text{Mg}, \text{Fe}, \text{Mn})_3\text{Si}_2\text{O}_7$, where $\text{Ca} : (\text{Mg}, \text{Fe}, \text{Mn}) = 2 : 1$. The tetragonal slag silicates including hardystonite form a well-defined isomorphous group of the type $\text{R}_3\text{Si}_2\text{O}_7$.

G. W. R.

Binary Lead Alloys. J. GOEBEL (*Z. Metallk.*, 1922, 14, 357—366, 388—394, 425—432, 449—456).—The hardness and density of alloys of lead with sodium, magnesium, arsenic, antimony, cadmium, tin, mercury, and bismuth have been determined. The hardening effect of small quantities of these elements decreases in the order named. Very small quantities of sodium and magnesium have a considerable effect in increasing the hardness of lead, the solid solution of sodium in lead containing about 1% of sodium having a Brinell number of 35 against 5 for pure lead (cf. *J.S.C.I.*, 1923, March).
A. R. P.

Topochemical Processes. The Conditions of Formation and the Forms of Lead Oxide. V. KOHLSCHÜTTER and H. ROESTI (*Ber.*, 1923, 56, [B], 275—288).—The formation of the yellow and red modifications of lead oxide during the course of the following reactions has been studied: (i) precipitations in which a change in the nature of the product may be expected as a consequence of alteration of the temperature, concentration, and nature of the solution; (ii) the oxidation of metallic lead beneath water by oxygen; (iii) the pseudomorphic transformation of solid lead salts; (iv) the thermal decomposition of compounds of lead oxide, and (v) the oxidation of lead vapour and rapid condensation of the product.

The yellow variety of lead oxide is produced when the compound is immediately formed from molecular solutions or by the oxidation of lead vapour. On the other hand, the red modification is obtained by reactions in which water plays a part through the hydrate, $3\text{PbO}\cdot\text{H}_2\text{O}$, and thus through a solid compound. This reaction is observed only when the hydrate is in a suitably disperse condition in which a certain spatial compression appears to be essential; it does not occur with the recognisably crystalline hydrate. The process therefore involves a well-marked topochemical factor. The formation of the red variety by the thermal decomposition of lead oxide or hydrate can be explained from the same point of view, if it is assumed that the oxide molecules, after rupture of the molecules, more readily form complexes by reason of their proximity to one another than they arrange themselves to the elements of the yellow variety which is favoured by separation from solution or from the gaseous phase.

The formation of the red variety through the hydrate appears to indicate a difference in the complexity of the molecules of the two forms. The assumption is made that the condensed molecule which is already present in the hydrate, $3\text{PbO}\cdot\text{H}_2\text{O}$, remains intact during the formation of the red oxide. When, therefore, the latter is produced by the dissociation of a solid compound, a coalescence of several molecules must have occurred which is favoured by topochemical conditions. In solution, on the other hand, the simple lead hydroxide, $\text{Pb}(\text{OH})_2$, is present, and hence a simpler molecular formula may be assigned to the yellow lead oxide obtained therefrom.

The simultaneous production of the two oxides from solution

depends on the dehydration and amphoteric ionisation of the bivalent metallic hydroxide (cf. von Euler, A., 1922, ii, 831, who has discussed the analogous case of copper hydroxide). The production of the yellow variety is due to the dehydration of lead hydroxide in accordance with the scheme $\text{Pb}(\text{OH})_2 \rightarrow \text{PbO} + \text{H}^+ + \text{OH}^-$ whilst that of the red modification is due to the preliminary condensation of several simple molecules to the complex $2\text{PbO}, \text{Pb}(\text{OH})_2$.
H. W.

The System Copper-Oxygen. E. MOLES and M. PAYÁ (*Anal. Fis. Quím.*, 1922, 20, 563—570).—The initial temperature of absorption of oxygen by copper is about 350° ; at this temperature also the dissociation of cupric oxide begins. Copper oxide wire commonly used in analysis is a solid solution of cuprous oxide in cupric oxide. Powdered cupric oxide undergoes contraction on heating, and a decrease in dissociation pressure takes place. The change is superficial.
G. W. R.

Topochemical Reactions. Homologous and Substituted Forms of Production. V. KOHLSCHÜTTER and VL. SEDELINOVICH (*Z. Elektrochem.*, 1923, 29, 30—44; cf. this vol., ii, 133).—Specimens of electrolytic copper hydroxide have been examined with the object of ascertaining to what extent the form is maintained in which the hydroxide was produced when topochemical changes take place. Nine varieties of copper hydroxide were investigated and as topochemical changes leading directly to new substances the following reactions were examined. Spontaneous formation of oxide, conversion into sulphide by means of hydrogen sulphide, and the further conversion to cuprous sulphide, the action of hydrogen peroxide, which through a peroxide forms cupric oxide with the liberation of oxygen, the reduction to cuprous oxide with hydrazine, and the formation of basic salts by the action of concentrated solutions of potassium chloride. The various forms of copper oxide were identified by the velocity of the change into oxide, and by their behaviour as suspensions. The observation of the velocity of sedimentation served also for the investigation of the products of the reactions. It is shown that there is a definite connexion between the form of the initial material, the course of the reaction, and the form of the product. The form of the initial material is conditioned largely by the velocity of formation. The forms of a substance obtained by changing the determining conditions of a reaction constitute a *form-homologous series*, from which by means of topochemical reactions other form-homologous series may be produced. The members of these series correspond with those of the first in behaviour and form.
J. F. S.

Cuprous Compounds. J. ERRERA (*Bull. Acad. roy. Belg.*, 1921, [v], 7, 361—386).—The electrolysis of solutions of chlorine-free sodium hydrogen carbonate, using a copper anode, gives rise to the basic carbonate, $2\text{CuCO}_3, 2\text{Cu}(\text{OH})_2, \text{H}_2\text{O}$, which is superimposed upon a layer of cuprous oxide. Deville's salt, $\text{Na}_2\text{CO}_3, \text{CuCO}_3, 3\text{H}_2\text{O}$, is probably an active complex in solution during electrolysis. The

change of anode potential was followed by means of a normal electrode, $\text{Hg}|\text{HgO}|\text{NaHCO}_3$ (46 g. per litre), for which the constant potential ($E_{\text{H}-0}$) is 0.433 volt at 15° .

The electrolysis of a solution of carbon dioxide (saturated at 20 atmospheres pressure), using a copper anode, results in the formation of a green carbonate. No azurite is formed. "Black copper," an unstable modification of the metal which rapidly passes into red copper, particularly in presence of acid, is deposited on the cathode.

The electrolysis of a solution of sodium silicate, using a copper anode, gives an insoluble silicate superimposed upon cuprous oxide. The formation of the latter was not prevented by using a water-cooled anode, and was therefore not due to secondary changes resulting from local heating.

The formation of cuprous salts by a reversible reaction occurring in solutions of cupric sulphate also occurs with cupric nitrate. The latter, in the presence of metallic copper, in the cold and under the influence of an electrical current, or at higher temperatures in the absence of a current, gives rise to a cuprous salt, oxidisable with potassium permanganate. For a $N/5$ -solution at 97° , the concentration of cuprous ions is 5×10^{-4} g. per litre, and $[\text{Cu}^{+}]/[\text{Cu}^{+2}] = 5 \times 10^5$. Such solutions regenerate the oxide $2\text{CuNO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{Cu}_2\text{O} + 2\text{HNO}_3$. A similar hydrolysis seems to occur when copper is in contact with the cupric salts of a weak acid, which may explain the formation of cuprous oxide on the anodes as described above.

When copper is left in contact with an aqueous suspension of its carbonate in a closed vessel in complete absence of air, etc., cuprous oxide is formed after a short time in the cold. (This points to the intermediate formation of cuprous salts, and may explain the occurrence of cuprite in minerals containing native copper and malachite.) Copper silicate and copper, under similar conditions, also give rise to small but appreciable quantities of cuprous oxide.

E. E. T.

Surface Tension of Mercury in Contact with Oxygen.

J. PALACIOS and E. LASALA (*Anal. Fis. Quím.*, 1922, 20, 505—508; cf. A., 1921, ii, 304).—The surface tension of freshly-distilled mercury in contact with oxygen does not decrease and is practically the same as in a vacuum. In contact with air, however, the surface tension gradually decreases.

G. W. R.

Separation of Mercury into Isotopes in a Steel Apparatus.

WILLIAM D. HARKINS and S. L. MADORSKY (*Nature*, 1923, 111, 148).—An apparatus is figured and described by means of which long-continued and repeated fractional vaporisation from a steel trough in a vacuum at low pressures can be effected. It has thus been found possible to obtain a difference of 0.1 unit in the atomic weight of mercury. Cooling by ice was employed.

A. A. E.

Dilatometric Study of the Alloys of Aluminium with Magnesium and Silicon. A. PORTEVIN and P. CHEVENARD (*Compt. rend.*, 1923, 176, 296—298).—The dilatometric curves

have been obtained for an alloy containing 0.95% of magnesium and 1.25% of silicon, the alloy having been originally annealed and then submitted to ten successive thermal cycles. The final temperature of each successive heating was increased until at the seventh heating the alloy commenced to melt. In curves three to six, at temperatures above 350°, there was a contraction of the alloy due to gradual solution of magnesium silicide, and on cooling precipitation of the silicide is marked by a progressive expansion, which is, however, retarded and incomplete, so that there is a residual contraction, which is greater the higher the temperature to which the alloy was heated. After these thermal cycles, therefore, there is, in increasing amount, an excess of silicide in solution, resulting in a more and more accentuated tempering effect.

The phenomenon of spontaneous return at the ordinary temperature can also be studied by means of a differential dilatometer, and curves are given for the above alloy. Experiments conducted between 20° and 80° show that the velocity of precipitation of the silicide increases according to an exponential law of the temperature and doubles for an interval of about 10°. W. G.

Hydrates and Hydrogels. I. Aluminium Hydroxide.

RICHARD WILLSTÄTTER and HEINRICH KRAUT (*Ber.*, 1923, 56, [B], 149—162).—During the application of aluminium hydroxide in the adsorption of enzymes, variations in activity are observed which do not appear to be simply related to the dispersivity of the hydrogel. The present investigation is concerned with the possibility that the varieties of aluminium hydroxide obtained by precipitation from the salts are different hydrates of aluminium oxide, and the relationship between the chemical properties of the varieties and their adsorptive capacity for enzymes.

Aluminium hydroxide has been obtained by four different methods, for the full details of which the original communication must be consulted. Variety *A* is prepared by precipitating aluminium sulphate solution with concentrated ammonia and protracted heating of the precipitate with ammonia; it is a pale yellow, plastic mass. Variety *B*, a very pale yellow, plastic, viscous mass, is obtained similarly to *A*, but the protracted heating is omitted. (An intermediate variety *b* is prepared by the dialysis of aluminium chloride with frequent addition of small quantities of ammonia against running water; it is related chemically to *B*, but in adsorptive capacity more closely resembles *A*.) Variety *C* is pure white in colour, voluminous, and very finely divided; it is obtained by precipitating aluminium sulphate solution with dilute ammonia without protracted heating. Variety *D*, which is pure white in colour and coarsely powdered, is obtained by passing a slow stream of carbon dioxide into a solution of potassium aluminate. The chemical behaviour of the different varieties towards sodium hydroxide (1%), warm acetic acid (12%), and hydrochloric acid (1%, 15%, and 35%) is described in detail. Variety *B* appears to be the most decidedly acidic, but loses this property to a considerable degree when subjected to protracted heating, owing to

conversion into *A*. Basic properties are most pronounced in *D*. The differences in behaviour cannot be explained on purely chemical or purely chemico-colloidal grounds. Different chemical types certainly exist, but their behaviour is as yet insufficiently elucidated.

The desiccation of the varieties when preserved in a desiccator over sulphuric acid has been studied; the process takes place very slowly. It is only possible to state that it is thus shown that the different gels contain a number of different chemical hydrates. The step-wise dehydration at gradually increasing temperatures has also been examined, and for this purpose a special form of apparatus is figured and described in the text. Definite steps in the dehydration appear to be indicated.

The adsorptive capacity of the different varieties for invertin and lipase has been examined. This appears to be affected to a very marked extent by the dilution of the solution. Invertin is accompanied by substances which greatly inhibit adsorption from concentrated solution, but have a much less pronounced action in dilute solution. A similar reaction is not shown by the companions of lipase. Invertin is only adsorbed to a slight extent by variety *D*, as would be expected from the physical properties of the micro-crystalline, coarse material. Whereas, however, *A* and *B* are very similar with regard to dispersivity, the latter, which is the more active chemically, is the more highly absorbent. The most surprising result is the high adsorptive capacity of *C*, which, in spite of its finely divided, non-plastic character, is superior to either *A* or *B*. A simple relationship does not exist between the colloidal properties of the aluminium hydroxides and their adsorptive capacities. Two different factors, the surface action and the differing chemical properties of the products, appear to be involved. These two factors, however, have not the same influence with all enzymes, since the relative activity of the aluminium hydroxide preparations towards invertin is not the same as towards lipase.

H. W.

Cobalt Complexes. Werner's Formulæ and their Experimental Signification. P. JOB (*Bull. Soc. chim.*, 1923, [iv], 33, 6—21).—A lecture delivered before the Société Chimique de France.

G. F. M.

The Catalytic Decomposition of Hexamminecobaltichloride. ROBERT SCHWARZ and WALTER KRÖNIG (*Ber.*, 1923, 56, [B], 208—214).—In a previous communication, Schwarz and Bausch (*A.*, 1921, ii, 404) have drawn the conclusion that the interaction of hexamminecobalti- and chloropentamminecobalti-chloride solutions on alkali silicates is accompanied by the displacement of the ammine groups by the silicate complex. This conclusion is now found to be due to an analytical error. The process only causes the formation of silicates and the silicato-compounds which have been described should be deleted from the literature. Slow decomposition of hexamminecobaltichloride solutions is caused by silicic acid gels, but the quantitative nature of the process is difficult to follow, and the change is more readily observed in the presence of

charcoal. The solutions are slowly decomposed in the presence of the latter at 20°, cobalt and ammonia being adsorbed, leaving a mixture of unchanged hexamminecobaltchloride and chloropentamminecobaltchloride in solution, which, however, is free from cobaltous salts. The reactions which occur may be represented by the equations: $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3 = [\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2 + \text{NH}_3$; $[\text{Co}(\text{NH}_3)_6]^{+++} = \text{Co}^{+++} + 6\text{NH}_3$; $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3 + 3\text{H}_2\text{O} \rightarrow \text{Co}(\text{OH})_3 + 3\text{NH}_4\text{Cl} + 3\text{NH}_3$. The change indicated by the second equation occurs readily also when aqueous solutions of the luteochloride are exposed to the light of a mercury lamp. Like the action of charcoal, it is inhibited by feeble acidity of the solution.

The maximum formation of the purpureochloride is observed in 1% solution; at higher concentrations, the ion, $[\text{Co}(\text{NH}_3)_6]^{+++}$, becomes more stable, whereas in more dilute solution reaction III preponderates. With an increased amount of carbon, the cobalt is completely adsorbed from a 0.5% solution of the luteochloride, and a solution of ammonia remains. With increasing concentration of the solution, the quantities of adsorbed cobalt diminish, whereas those of ammonia rapidly become constant. Contrary to the usual adsorptive process, the absolute amounts of adsorbed cobalt diminish with increasing concentration of the solution; the phenomenon is explained by the increased extent of the hydrolysis (equation III) in dilute solution.

H. W.

Effect of Masked Anions on the Magnetic Susceptibility of Chromic and Chromyl Salts. B. CABRERA and S. PIÑA DE RUBIES (*Anal. Fís. Quím.*, 1922, 20, 509—518; cf. A., 1922, ii, 612).—Solutions of chromic sulphate which when freshly prepared give no sulphate reaction undergo change on keeping, whereby electrical conductivity and sulphate reaction show a parallel increase. No appreciable variation in magnetic susceptibility, however, is observed. In the case of solutions of chromyl sulphate, on the other hand, an increase in magnetic susceptibility is observed. The change is supposed to consist of two successive unimolecular reactions, namely, $[(\text{SO}_4)_2\text{Cr}_2\text{O}] \rightarrow \text{SO}_4[\text{SO}_4\text{Cr}_2\text{O}] \rightarrow (\text{SO}_4)_2[\text{Cr}_2\text{O}]$. The quantitative aspect of these reactions is discussed.

G. W. R.

Determinations of the Density of Metals and Alloys at High Temperatures. III. The System Tin-Bismuth. K. BORNEMANN and PAUL SIEBE (*Z. Metallk.*, 1922, 14, 329—334).—The specific volumes of tin, bismuth, and tin-bismuth alloys have been determined at temperatures up to 900°. In every case, the volume is directly proportional to the temperature. Tin expands 2.8% during melting, and bismuth contracts 3% (cf. *J.S.C.I.*, 1923, 229A).

A. R. P.

The System Tin-Arsenic. QASIM ALI MANSURI (*T.*, 1923, 123, 214—223).

Complex Compounds of Tin. Hydrolysis of Stannic Chloride and Chlorostannates. J. DE LA PUENTE (*Anal. Fís. Quím.*, 1922, 20, 486—495).—Stannic chloride reacts with four mole-

cules of sodium hydroxide, giving a complex of the composition $[\text{SnCl}_2(\text{OH})_4]\text{Na}_2$, which can also be obtained by the reaction of one molecule of orthostannic acid with two molecules of hydrochloric acid and sodium hydroxide. Potassium chlorostannate in 1% solution is completely dissociated into stannic chloride and potassium chloride. The dissociation is partly prevented by the presence of a large excess of potassium chloride. Attention is directed to the possibility of a series of complexes intermediate between chlorostannic acid, H_2SnCl_6 , and the hydrated stannic acid, $\text{H}_2\text{Sn}(\text{OH})_6$.
G. W. R.

Preparation of Pure Zirconium Oxide. HERMANN VON SIEMENS and HERBERT ZANDER (*Wiss. Veröffentl. Siemens Konzern*, 1922, 2, 484—488; from *Chem. Zentr.*, 1923, i, 21).—A Brazilian zircon mineral containing ZrO_2 67.8%, SiO_2 22.2%, Fe_2O_3 , TiO_2 8.7%, is mixed with 25% of carbon and treated with a stream of chlorine at 1000—1200°. From the mixture of chlorides thus formed, zirconium oxychloride is obtained by crystallisation from aqueous solution. Ignition of this in air yields zirconium oxide.
G. W. R.

Purification and Analysis of Zirconium Dioxide. F. G. JACKSON and L. I. SHAW (*J. Amer. Chem. Soc.*, 1922, 44, 2712—2714).—With the object of purifying zirconia for the investigation of this substance as a refractory, and particularly with the object of removing low melting impurities, the authors have investigated methods of purification. It is found that zirconia is best dissolved by fusion with a mixture of borax and sodium carbonate. The fusion, after treatment with dilute hydrochloric acid, cannot be separated from the insoluble residue by direct filtration. It is found that by precipitating the zirconium and other metals as hydroxides in the unfiltered solution the insoluble residue is entangled in the precipitate and may then be filtered and washed. The hydroxide can then be dissolved on the filter-paper by warm dilute hydrochloric acid and on repeatedly pouring the filtrate through the filter-paper a clear filtrate may be obtained. This contains all the iron, aluminium, and zirconium and most of the titanium present in the original material. The solution of chlorides is diluted, and treated with the calculated amount of sulphuric acid. A gelatinous precipitate of basic sulphates of zirconium and titanium is obtained, whilst the whole of the iron and aluminium, and some of the titanium and zirconium, remain in solution. The solution is heated, but not boiled, with constant stirring to coagulate the precipitate, which is filtered and washed until the washings give no reaction for iron with ammonium thiocyanate. This process, which is slow and tedious, is efficient for removing iron, aluminium, and silica, but does not remove much of the titanium.
J. F. S.

Reaction of Methane and of Acetylene with Zirconium Tetrachloride. F. P. VENABLE and R. O. DEITZ (*J. Elisha Mitchell Sci. Soc.*, 1922, 38, 74—75).—Zirconium tetrachloride

reacts with ammonia, phosphine, and hydrogen sulphide, forming compounds which, when heated, yield zirconium nitride, phosphide, and sulphide, respectively. Zirconia reacts with carbon at a high temperature, forming the carbide ZrC . The interaction of zirconium tetrachloride with methane gives rise to three distinct solid products, namely, black particles, light brown particles, and colourless masses with black inclusions. The first, which was present in small quantity, contained 32.09% C. The reaction with acetylene begins on gentle heating and is exothermic.

CHEMICAL ABSTRACTS.

Isolation of the Oxide of a New Element. ALEXANDER SCOTT (T., 1923, 123, 311—312).

The New Element Hafnium. D. COSTER and G. HEVESY (*Nature*, 1923, 111, 182; cf. this vol., ii, 80).—In order more accurately to estimate the amount of hafnium in the samples examined, a known quantity of tantalum (73) was added and the intensities of the lines were compared. A large number of zirconium minerals have been examined, and all have been found to contain between 5 and 10% of hafnium. Moreover, a chemical method of separation (details of which are not given in the present brief communication) has resulted in the production, on the one hand, of a substance containing about 50% of hafnium, and, on the other, of zirconium which did not yield any hafnium lines.

A. A. E.

The Element of Atomic Number 72. G. URBAIN (*Compt. rend.*, 1923, 176, 469—470); G. URBAIN and A. DAUVILLIER (*Nature*, 1923, 111, 218; cf. this vol., ii, 80, and preceding abstract).—The lines observed in the high-frequency spectra of zirconium minerals by Coster and Hevesy appear to be identical with those previously observed in the case of ytterbia by Urbain (A., 1911, ii, 115; see also A., 1922, ii, 505, and Dauvillier, A., 1922, ii, 463). Priority is therefore claimed for the name "celtium," then given to the element producing the lines in question, as against "hafnium." It is, however, admitted that to celtium was incorrectly ascribed properties intermediate between those of lutecium and scandium. Moreover, other cases are quoted in support of the contention that it is not impossible for a quadrivalent element, such as that under consideration, to be present in the mother-liquors after fractionation of the rare earths.

A. A. E.

The New Element Hafnium. D. COSTER and G. HEVESY (*Nature*, 1923, 111, 252).—A reply to Urbain and Dauvillier (preceding abstract).—Hafnium is considered to differ from celtium in that there is no difficulty in separating the former from contents of rare earths, nor does it appear to yield the characteristic optical spectrum ascribed by Urbain to celtium. It is maintained that the X-ray spectrum of hafnium is not coincident with that described by Dauvillier. The hafnium content of the earth's crust is estimated to be more than 1 part per 100,000.

A. A. E.

Germanium. IV. Germanium Tetraiodide. L. M. DENNIS and F. E. HANCE (*J. Amer. Chem. Soc.*, 1922, **44**, 2854—2860; cf. A., 1922, ii, 150, 302).—Germanium tetraiodide is prepared by passing iodine vapour in a current of carbon dioxide over crystalline germanium heated at 250—360°. The tetraiodide sublimes and a deposit of yellow and red crystals and a red liquid are formed in the cooler parts of the tube. Between the boat containing the germanium and the red iodide a small deposit of yellow crystals formed; these are germanous iodide, GeI_2 , which crystallises in the hexagonal system with angles of 120°. Germanium tetraiodide at the ordinary temperature is of the colour of coral when in lump form; when powdered, it has an orange colour. The colour depends on the temperature, at -185° it is canary-yellow; -50° , buff; -10° , orange; $+35^\circ$, salmon; $+50^\circ$, brick-red; $+90^\circ$, red, and $+144^\circ$, ruby red. It melts sharply at 144° to a ruby-coloured liquid. It forms regular octahedra and has $d_{20}^{25} 4.3215$. Concentrated sulphuric acid has no action on it, and since all other liquids examined either dissolve or decompose it, the density was determined by means of sulphuric acid. Germanium tetraiodide sublimes at temperatures just above the melting point without dissociation, but at 440° dissociation occurs according to the equation $\text{GeI}_4 \rightleftharpoons \text{GeI}_2 + \text{I}_2$. It is practically unchanged when exposed to air for five months, but is decomposed by a small quantity of water, giving germanium dioxide. Cold concentrated sulphuric acid produces no change in it in twenty-four hours, but on heating at 80° there is a slow liberation of iodine. It is slowly dissolved by cold 1:4-potassium hydroxide, concentrated nitric acid turns it black with liberation of nitrogen dioxide, and concentrated hydrochloric acid dissolves it very slowly. Concentrated ammonia solution decomposes it to form a white solid which is soluble in water, whilst dry gaseous ammonia slowly converts it into a white powder which is soluble in water. Germanium tetraiodide dissolves in the following solvents, giving solutions of the colours named; in all cases the solutions were quite unchanged after keeping for four months: benzene, reddish-orange; carbon disulphide, reddish-orange; methyl alcohol, deep orange; ethylene dichloride, light orange; chlorobenzene, reddish-orange; carbon tetrachloride, light orange; ethylene glycol, light yellow, and ethylene chlorohydrin, light yellow. It is also dissolved by the following solvents, giving solutions varying in colour from deep orange to pale yellow, but in every case a slow decomposition takes place: hexane, amyl alcohol, chloroform, nitrobenzene, light petroleum, butanol, and acetic acid. Many solvents decompose it at once.

J. F. S.

Measurements of the Density of Metals and Alloys, at High Temperatures. IV. The Systems Antimony-Zinc and Aluminium-Antimony and the Metals Silver and Magnesium. F. SAUERWALD (*Z. Metallk.*, 1922, **14**, 457—461).—The specific volumes of zinc-antimony alloys are greater than the values calculated from those of the two metals, both at

ordinary and at elevated temperatures, and a maximum value is obtained at a composition corresponding with Zn_3Sb_2 . Aluminium-antimony alloys show deviations from the calculated values only at the ordinary temperature, an abrupt change occurring at the composition corresponding with AlSb . At 1000° , this compound is decomposed and the specific volume of any alloy may then be calculated from those of its constituents. The specific volumes of silver at temperatures up to 1100° and of magnesium at 780° have been determined [cf. *J.S.C.I.*, 1923, 229A]. A. R. P.

Examination of the Alleged Antimonious Hydroxides. CHARLES LEA and JOHN KERFOOT WOOD (T., 1923, 123, 259—265).

The Crystal Structure of Bismuth. L. W. MCKEEHAN (*J. Franklin Inst.*, 1922, 195, 59—66).—New data have been obtained using the powder method and the X -rays of molybdenum. The results are best explained by means of a simple rhombohedral space lattice, with a set of rhombohedral axes, mutually inclined at $57^\circ 16'$. From the absence of any planes attributable to $(422)'$, $(330)'$, and $(411)'$, it is deduced that the bismuth atoms are not uniformly placed along the trigonal axis. The distances between adjacent atom centres have been calculated, and are shown in a diagram. W. E. G.

The Anode Oxidation of Gold. III. FR. JIRSA and OT. BURYÁNEK (*Chem. Listy*, 1922, 16, 328—330; cf. A., 1922, ii, 713, this vol., ii, 80).—It is concluded that the oxidation of gold anodes in dilute sulphuric acid takes place in four stages. The first, which requires the least *E.M.F.*, is the solution of gold in sulphuric acid, to form aurous sulphate. This is hydrolysed in the second stage to auric hydroxide, $2\text{Au}_2\text{SO}_4 + 2\text{H}_2\text{O} \rightarrow 2\text{Au}(\text{OH})\text{SO}_4 + \text{H}_2\text{SO}_4 + 2\text{Au}$; $\text{Au}(\text{OH})\text{SO}_4 \rightarrow \text{Au}(\text{OH})_3 + \text{H}_2\text{SO}_4$. In the third stage, the gold again dissolves in the acid, this time forming auric sulphate, which also undergoes hydrolysis in dilute solution, going first into the basic sulphate and then into auric hydroxide, as before. In the fourth stage, the tervalent gold becomes quadrivalent, forming AuO_2 . Since at the ordinary temperature the dissociation pressure of this oxide is above one atmosphere, it decomposes, liberating oxygen and forming auric oxide. The four stages may be thus shown: I. $\text{Au} \rightarrow \text{Au}'$; II. $3\text{Au}' \rightarrow \text{Au}''' + 2\text{Au}$; III. $\text{Au} \rightarrow \text{Au}'''$; IV. $\text{Au}''' \rightarrow \text{Au}'''' \rightarrow \text{Au}'''$.

The hydrolysis of the aurous sulphate explains why oxidation to bivalent gold does not take place. It is found, generally, that a gold anode in dilute sulphuric acid exhibits typical passivity, and that oxidation to auric oxide proceeds without the formation to any appreciable extent of intermediate products. The speed with which gold anodes, in the presence of lower degrees of oxidation, become passive is so great that it is impossible to isolate any intermediate oxidation product. The solubility of auric hydroxide increases with the concentration of the acid, whilst the passivity of a rotating gold anode decreases. Since with a stationary

anode the final passivity in concentrated acid is greater than in dilute, it is only possible to show the existence of the intermediate stages Au^+ and Au^{+++} if a rotating anode is used. The existence of auric dioxide (AuO_2) is proved beyond doubt by the discharge curve and the depolarisation curve given in the original. R. T.

Mineralogical Chemistry.

Parsonsite, a New Radioactive Mineral. ALFRED SCHOEP (*Compt. rend.*, 1923, 176, 171—173).—The green colour of some specimens of torbernite from Kasolo, Katanga, Belgian Congo (A., 1922, ii, 155), is obscured by a brown powder. This is readily separated by washing in water, and consists of minute crystals (monoclinic or triclinic) with $d^{17} 6.23$, $n > 1.99$. When heated, it turns yellow and fuses to a black bead; it is readily soluble in acids. Analysis gave:

PbO.	CuO.	UO ₃ .	P ₂ O ₅ .	TeO ₃ .	MoO ₃ .	CaO.
44.71	0.25	29.67	15.08	3.01	0.43	0.63
Al ₂ O ₃ .	CO ₂ .	Insol.	H ₂ O.	Total.		
1.23	1.19	1.51	1.56	99.47		

Deducting impurities (copper due to admixed torbernite) the formula is $2\text{PbO} \cdot \text{UO}_3 \cdot \text{P}_2\text{O}_5 \cdot \text{H}_2\text{O}$. Tellurium and molybdenum were detected also in the torbernite; and the pitchblende from Kasolo contains selenium and molybdenum. L. J. S.

Presence of the Element No. 72 (Hafnium) in Malacon and Alvite. V. M. GOLDSCHMIDT and L. THOMASSEN (*Norsk Geologisk Tidsskrift*, 1923, 7, 61—68).—The relation of element 72 to zirconium suggested the examination of some anomalous zircon-like minerals by the method of X-ray spectrum analysis (A. Hadding, A., 1922, ii, 780, 855), using a rock-salt crystal turned by clockwork. Malacon from Hitterö, Norway, showed the lines of zirconium, element 72, iron, manganese, yttrium, and trace of tungsten. Alvite from Kragerö, Norway, showed the lines of zirconium, strong 72, iron, manganese, aldebaranium, yttrium, weak thorium, and perhaps traces of cerium and tungsten. The formula of alvite is written as $(\text{Zr}, 72, \text{Th})\text{O}_2 \cdot \text{SiO}_2$. L. J. S.

Meteoric Iron from Glasgow, Kentucky. GEORGE P. MERRILL (*Amer. J. Sci.*, 1923, [v], 5, 63—64; *Chem. News*, 1923, 126, 63—64).—Two much-oxidised masses weighing about 25 and 20 lb. were recently ploughed up. The structure is that of a coarse octahedrite. Analysis by J. E. WHITFIELD gave:

Fe.	Ni.	Co.	S.	P.	C.	Cl.
70.63	7.27	0.62	0.11	0.12	0.06	0.36
	Fe, Ni oxides.	SiO ₂ .	Ign.	Total.		
	19.22	trace	1.65	100.04		

The percentage of chlorine corresponds with 0·62% of lawrencite (FeCl_2). This is high and accounts for the ready disintegration of the material which is difficult to arrest.

L. J. S.

Meteoric Iron from Somerset County, Pennsylvania.

GEORGE P. MERRILL (*Amer. J. Sci.*, 1923, [v], 5, 175—176).—An oxidised mass of about 18 kg. was ploughed up in 1922 on Allegheny Mountain, and is called the New Baltimore iron. It is an irregularly granular mass, readily breaking into fragments; and it therefore probably belongs to the same fall as the Mt. Joy iron found 90 miles away. Analysis by J. E. WHITFIELD gave :

Fe.	Ni.	Co.	P.	Si.	C.	Total.
93·256	6·420	0·325	0·037	0·010	0·015	100·063

Copper, manganese, and sulphur are absent.

L. J. S.

Analytical Chemistry.

New Vessel for Electrometric Titration. W. T. BOVIE (*J. Amer. Chem. Soc.*, 1922, **44**, 2892—2893).—A new form of glass vessel for use in electrometric titrations is described. The vessel has a capacity of about 150 c.c.; it is oviform in shape and at its wider end is fitted with four tubulures, one in the exact centre being for the burette jet and the other three situated at equidistant points on a circle being for the hydrogen electrode, calomel electrode and hydrogen inlet, respectively. The vessel is attached to a stout glass rod at its lowest point which slips into a hole in a heavy support. J. F. S.

Some Applications of Oxygen Electrode, Air Electrode, and Oxidation Potential Measurements to Acidimetry and Alkalimetry. N. HOWELL FURMAN (*J. Amer. Chem. Soc.*, 1922, **44**, 2685—2697).—An oxygen or air electrode, constructed in the manner generally adopted for a hydrogen electrode, may be used for the titration of the acid or alkali in the presence of oxidising agents such as potassium dichromate or potassium permanganate. The method yields accurate results, and by using an empirical scale the *E.M.F.* readings of the cells are built up as indicated. Platinised platinum|oxygen||acid or alkaline solution of an oxidising agent|calomel-electrode; will serve to give a quantitative indication of the hydrogen-ion concentration. J. F. S.

Mixtures of Tartrates and Phosphates as Buffers. Antagonistic Action of Calcium Chloride. L. J. SIMON and L. ZIVY (*Compt. rend.*, 1923, **176**, 136—138; cf. A., 1922, ii, 880).—The addition of calcium chloride exerts inverse effects in the neutralisation of tartaric acid and phosphoric acid. In the case of tartaric acid, the neutral zone, as between helianthin and phenolphthalein

as indicators, tends to disappear, whilst in the case of phosphoric acid it is doubled. This phenomenon is additive, and if the two acids are mixed in equimolecular proportions the neutral zone and the correlative buffer effect are invariable. W. G.

Method for the Micro-estimation of Chlorine in Blood. PAUL IVERSEN and M. J. SCHIERBECK (*Ugeskr. læger*, **84**, 454—456; from *Chem. Zentr.*, 1922, iv, 1076).—0.1 C.c. of blood is added to 0.8 c.c. of 0.1*N*-sodium hydroxide and 4 c.c. of 0.45% zinc sulphate solution. After heating for three minutes, the liquid is filtered and treated with 0.2 c.c. of 29% nitric acid and 1 c.c. of 0.01*N*-silver nitrate solution. When the precipitate has settled, the clear supernatant liquid is titrated with 0.005*N*-ammonium thiocyanate in the presence of one drop of saturated iron ammonium alum solution. G. W. R.

Bang's Method for the Micro-estimation of Chlorine. PAUL IVERSEN (*Ugeskr. læger*, **84**, 456—458; from *Chem. Zentr.*, 1922, iv, 1076).—Discordant results in the micro-estimation of chlorine are attributed to variations in the amount of ethyl alcohol used for the extraction of blood and in the method of extraction. G. W. R.

The Reaction between Hypochlorite and Potassium Iodide. I. M. KOLTHOFF (*Rec. trav. chim.*, 1922, **41**, 615—626; cf. following abstract).—Hypochlorous acid to which a solution of sodium hydrogen carbonate has been added reacts with potassium iodide according to the equation $3\text{HClO} + \text{I}' \rightarrow \text{IO}_3' + 3\text{H}' + 3\text{Cl}'$, the formation of hypiodite being a preliminary stage in the oxidation of the iodine. When the quantities of each substance are equivalent, the hypiodite reacts with iodide, liberating iodine. The rate of transformation of hypiodite into iodate depends on the hydrogen-ion concentration of the solution. In the presence of mineral acids, the end-point cannot be ascertained by means of starch, as no iodine-ions remain in the solution; moreover, iodate may be transformed into chloro-compounds of iodine in solutions containing sulphuric or hydrochloric acid. It is stated that Klimenko's method of estimation of hypochlorite and chlorine in presence of each other (*A.*, 1904, ii, 205) is untrustworthy. Chlorine in sodium hydrogen carbonate solution may be titrated in a similar manner to iodine. H. J. E.

The Titration of Hypochlorite. I. M. KOLTHOFF (*Rec. trav. chim.*, 1922, **41**, 740—750).—Solutions of hypochlorites on being kept are transformed into chloride, chlorate, and also into chlorite. In estimating hypochlorite in bleaching powder by means of potassium iodide in sulphuric acid solution, the presence of chlorite introduces an error, as it reacts according to the equation $\text{ClO}_2' + 4\text{I}' + 4\text{H}' \rightarrow 2\text{I}_2 + \text{Cl}' + \text{H}_2\text{O}$, although chlorates have no such influence. Chlorite reacts very slowly, if at all, with arsenious acid or with potassium iodide in sodium hydrogen carbonate solution, so that the titration of hypochlorite may be carried out accurately with either of these reagents according to Treadwell's

method. In effecting the titration by Pontius's method, the operation must be carried out slowly in presence of a large excess of sodium bicarbonate (cf. *J.S.C.I.*, 1923, 181A). H. J. E.

Detection of Hypochlorites and Chloroamines in Milk and Cream. PHILIP RUPP (*U.S. Dept. Agr. Bull.*, 1922, 1114, 1—5).—Five c.c. of the milk or cream, 1.5 c.c. of a 7% solution of potassium iodide, and 4 c.c. of hydrochloric acid (1:2) are heated in a water-bath at 85° for ten minutes, cooled, and 0.5 to 1 c.c. of starch solution is added. The presence of available chlorine in amounts as low as 1 in 50,000 is indicated by the pale yellow colour of the milk below the curd changing to a light reddish-purple, passing through reddish-purple to a deep bluish-purple as the amount of chlorine is increased. Milk pasteurised, after the addition of hypochlorites, at 63° for thirty minutes reacts in the same way as raw milk. CHEMICAL ABSTRACTS.

Analytical Investigation of Chlorates. P. POCH (*Anal. F's. Quim.*, 1922, 20, 662—666).—The reactions for chlorates are discussed. Potassium chlorate and ammonium thiocyanate heated together at 140—150° produce an orange-red mass with deflagration. The mass contains carbon, nitrogen, and sulphur, and when heated on platinum foil burns with a violet flame, leaving a small residue of carbon. The orange-red colour may be used as a test for chlorates by adding 1 c.c. of 0.5*N*-ammonium thiocyanate to 1 c.c. of a solution of a chlorate and evaporating to dryness. The orange-red coloration is given even with 0.00025 g. of potassium chlorate. G. W. R.

A Method for the Simultaneous Estimation of Sulphur and Halogen in Organic Compounds. CLIFFORD S. LEONARD (*J. Amer. Chem. Soc.*, 1923, 45, 255—257).—A detailed account of Klason's method for the combined estimation of sulphur and halogens in an organic substance (*A.*, 1886, 918). The material to be analysed is placed in a porcelain boat at one end of a combustion tube which contains in sequence a platinum spiral, a boat filled with fuming nitric acid, and a second platinum spiral. The first end of the tube has attached to it a bubbling flask of fuming nitric acid, and the other end is drawn out so as to dip into water or silver nitrate solution. The combustion is thus carried out in an atmosphere of nitrous fumes, and air or oxygen may be slowly passed through the tube. At the end of the combustion, the tube and its contents are rinsed with distilled water, the rinsings being added to the liquid in the receiving flask. In this liquid, the halogens and sulphur may then be estimated as is done after a Carius combustion. W. G.

Micro-estimation of Sulphuric Acid and Sulphur in Organic Substances by the Benzidine Method. G. ZIMMERLUND and O. SVANBERG (*Svensk. Kem. Tidskr.*, 1922, 34, 139—146; from *Chem. Zentr.*, 1922, iv, 1094).—The solution containing sulphuric acid is exactly neutralised and precipitated with a solution of benzidine hydrochloride. The precipitate is centrifuged

and the total filtrate titrated with 0.05*N*-sodium hydroxide and phenolphthalein according to Bang's method (*Mikrobestimmung von Blutbestandteilen*, 1922). The sulphuric acid content is derived from the difference between the titre thus obtained and the titre of the acid benzidine solution. Directions are given for the preparation of the benzidine hydrochloride solution. G. W. R.

Volumetric Estimation of Sulphates in Sea-water. JOSÉ GIRAL PEREIRA (*Anal. Fis. Quím.*, 1922, 20, 577—585).—The method consists in boiling the solution containing an alkali sulphate with excess of a solution of barium chromate in 0.1*N*-hydrochloric acid. Excess of calcium carbonate is added and after filtering, 5 c.c. of fuming hydrochloric acid are added for each 100 c.c. of filtrate, followed by excess of solid potassium iodide. By the action on the alkali chromate (equivalent to the original sulphate), iodine is liberated and may be titrated in the usual way with thiosulphate. G. W. R.

Refractive Indices of Selenic and Selenious Acid. HOSMER W. STONE (*J. Amer. Chem. Soc.*, 1923, 45, 29—36).—The refractive indices of solutions of selenic and selenious acid in water have been determined for concentrations varying between 0.00% and 98.98% for selenic acid and 0.00% and 79.14% for selenious acid, using an Abbé refractometer and sodium light at 20°. Tables have been constructed giving the refractive indices of solutions of the two acids for every percentage value over the whole range measured. Using this method, the two acids may be rapidly and accurately estimated in solution. Selenic acid may be estimated gravimetrically as follows. The sample, 0.2—0.5 g., is treated with 50 c.c. of concentrated hydrochloric acid and diluted to 75—100 c.c. with water. The solution is heated to boiling and 30 c.c. of saturated aqueous sulphur dioxide solution are added. The solution is maintained at 90° until the red precipitate first formed turns black and further additions of sulphur dioxide gave no red precipitate. After the reaction mixture had been kept four to five hours at 80—90°, the precipitate was collected on a Gooch crucible, and dried at 105—110°. J. F. S.

Estimation of Nitric Oxide. A. KOEHLER and M. MARQUEYROL (*Mém. Poudres*, 1922, 19, 359—361).—Excess of oxygen is added to the gaseous mixture in the presence of a liquid secondary amine, such as ethylaniline, which absorbs the nitrous anhydride formed. The excess of oxygen is removed with alkaline pyrogallol and the contraction of volume gives the volume of nitric oxide. Under atmospheric pressure, ethylaniline dissolves its own volume of carbon dioxide, so that if this gas is present considerable excess of oxygen should be added so as to keep the partial pressure of the carbon dioxide low. A high degree of accuracy is attainable. H. C. R.

Detection of Nitrites in Water. RODILLON (*J. Pharm. Chim.*, 1923, [vii], 27, 64—65).—The author concedes priority to Denigès

(*Bull. Sci. Pharmacol.*, 1914) for the use of resorcinol in sulphuric acid solution as a reagent for nitrites. G. F. M.

The Detection of Nitric Acid by Ferrous Sulphate. CARL FAURHOLT (*Ber.*, 1923, 56, [B], 337—341).—The customary browning test for nitric acid occasionally gives very erratic results. These are traced to insufficient rapidity in the reduction of nitric acid. The defect can be most readily remedied by the addition of hydrochloric acid, a drop of which (4*N*) is introduced previously to the addition of sulphuric acid. The brown coloration is produced immediately. The presence of 0.5 mg. of potassium nitrate in 2 c.c. of solution can be detected with certainty. The limit of applicability of the method lies at about 0.2 mg. if control solutions are used to obviate the disturbance caused by the formation of yellow solutions of ferric chloride.

The oxidation of ferrous sulphate in solutions containing nitric and hydrochloric acids appears to proceed in such a manner that the acids first react with one another and that the chlorine and nitrosyl chloride thus produced convert the ferrous into the ferric salt. The oxidation of ferrous sulphate by nitric acid which occurs at high concentrations of nitric and sulphuric acids or at elevated temperature in the absence of hydrochloric acid does not occur to an appreciable extent under the experimental conditions.

H. W.

Estimation of Nitrogen in Nitrates, Cellulose Nitrates, and Glyceryl Nitrates by Devarda's Method. A. KOEHLER, M. MARQUEYROL, and P. JOVINET (*Mém. des Poudres*, 1922, 19, 348—350; 351—355; 356—358).—If any ammonia is present, it is estimated by distilling into acid in the usual way. The contents of the flask are then cooled and a volume of water is added equal to that which has been distilled over. Twenty-five g. of finely pulverised Devarda's alloy (Al=45%, Cu=50%, Zn=5%) are added and the flask is connected to a Kjeldahl distillation apparatus and hydrogen allowed to come off for fifteen to twenty minutes, after which it is gently boiled for ten minutes, and the ammonia formed is distilled into acid and estimated in the usual way, methyl-red being used as indicator. A blank determination must be carried out with the reagents used. In the case of cellulose nitrate, the ester is first hydrolysed with aqueous potassium hydroxide and hydrogen peroxide. The temperature must not exceed 60° until all the cellulose nitrate is dissolved, but the liquid is afterwards boiled until oxygen ceases to be given off and then cooled to the ordinary temperature. The nitrate is then reduced with Devarda's alloy as described above. The method can be applied to glyceryl nitrate, but to obtain accurate results the hydrolysis must be carried out below 40°. This is only possible with the aid of violent agitation. A form of glass agitator suitable for use in a conical flask for this purpose is illustrated. It is provided with two bulbs blown on the stem so as nearly to close up the mouth of the flask and so prevent loss of the contents through splashing. After

forty minutes' treatment, the glyceryl nitrate is completely dissolved and the temperature increased to 70° for a few moments. The estimation is then carried out as described above. This method gives more accurate results than the nitron method.

H. C. R.

Separation of Arsenic from other Elements. N. TARUGI (*Gazzetta*, 1922, 52, ii, 323—332).—The quantitative separation of arsenic from antimony, tin, copper, lead, mercury, and iron may be effected as follows: the arsenate solution is heated for thirty minutes with hydrazine sulphate and sufficient sodium hydroxide to correspond with about one-half of the hydrazine. The liquid is then cooled and distilled for one and a half hours with concentrated hydrochloric acid, the distillate, which is found to contain the whole of the arsenic, being collected in a flask connected with a Péligré tube. The arsenic may then be estimated, either gravimetrically as sulphide, or after the distillate has been rendered alkaline to methyl-orange by means of sodium hydroxide, and then treated with excess of solid sodium hydrogen carbonate, by titration with iodine solution.

T. H. P.

[Estimation of] Silicon in Aluminium. R. GUERIN (*Ann. Chim. Analyt.*, 1923, 5, 4—8).—The official French method for estimating iron, silicon, and aluminium oxide in metallic aluminium is described and the composition and nature of silicon-aluminium alloys are discussed. A method is also given for the estimation of combined silicon (as aluminium silicide) and of graphitoidal silicon in the alloys depending on the insolubility of the latter form in aqua regia and its solubility in a mixture of hydrofluoric and nitric acids (cf. *J.S.C.I.*, 1923, 186A).

A. R. P.

Use of Malic, Maleic, and Fumaric Acids in Volumetric Analysis. N. A. LANGE and HARRY KLINE (*J. Amer. Chem. Soc.*, 1922, 44, 2709—2711).—The suitability of malic, maleic, and fumaric acids for use as standards in the titration of alkalis and potassium permanganate has been investigated. It is shown that the three acids, suitably purified, give accurate and trustworthy results when used to standardise sodium hydroxide or potassium hydroxide. The commercial products must, however, always be purified before use for the above-named purpose. In the case of maleic acid, the purification is effected by a single crystallisation from water containing four drops of nitric acid for every 200 c.c. of solution; after air drying, the crystals are dried to constant weight over sulphuric acid or in an oven at 90°. Phenolphthalein is the best indicator for this acid. Fumaric acid is purified and used in the same way as maleic acid, but in this case, owing to the smaller solubility of the acid, the titration must be effected at a higher temperature. Malic acid is purified by dissolving in hot acetone, filtering, adding carbon tetrachloride to the hot solution, and allowing to crystallise. The crystals are air-dried for twenty-four hours, then for an equal time over sulphuric acid or for two hours at 90—120°. Although maleic and fumaric acids

may be used as standards for potassium permanganate solutions, they are neither as accurate nor as convenient as sodium oxalate for this purpose. Succinic, malic, maleic, and fumaric acids cannot be used as standards for ammonium hydroxide solutions, and the two last-named acids cannot be used for iodine titrations.

J. F. S.

The Estimation of Potassium as Alum. (MILLE) DE LE PAULLE (*Compt. rend.*, 1923, 176, 105—107).—The method is for use in estimating small quantities of potassium in rocks. It is based on the comparative insolubility of potash alum in 30% (by volume) aqueous ethyl alcohol. In alcohol of such a strength aluminium sulphate is readily soluble. The mineral is digested with sulphuric and hydrofluoric acids; the solution is evaporated to dryness, and the residue ignited at a dull red heat. A weighed portion of the residual sulphates is dissolved in water and the solution cooled, and sufficient alcohol is added to bring it to 30%. After the whole of the potash alum has separated, it is collected, washed with the dilute alcohol, dried, and weighed. W. G.

Estimation of Potassium Salts with Sodium Cobaltinitrite. E. CLERFEYT (*Bull. Soc. chim. Belg.*, 1922, 31, 417—420).—The perchlorate method of estimating potassium salts is said to be unsatisfactory, but it is claimed that accurate results are obtained by the use of sodium cobaltinitrite, numerous analyses showing an agreement within 0.1 to 0.2% of the results obtained by precipitation with platinic chloride. The reagent is made up in two solutions: I. 28.6 g. of cobalt nitrate and 50 c.c. of glacial acetic acid are made up to 500 c.c. with water. II. A solution of 180 g. of sodium nitrite in 500 c.c. of water. The two solutions should be kept separately, and for use I is slowly added to II twenty-four hours before the estimation to permit of the precipitation within that period of any potassium in the technical sodium nitrite, in which case the solution must be filtered before use. An excess of the reagent is added gradually with mechanical stirring to as concentrated as possible a solution of the potassium salt, slightly acidified with acetic acid. Forty c.c. are required for 0.25 g. of potassium chloride in 25 c.c. of solution, and in any case not less than 10 c.c. of reagent are used. Stirring is continued for half an hour, and the beaker set aside until next day, when its contents are filtered on a tared filter, the precipitate washed with 10% acetic acid until the washings are colourless, and then once with 95% alcohol, and dried at 120°. The dried precipitate has the formula $K_2NaCo(NO_2)_6 \cdot H_2O$, and contains 20.74% K_2O . P. M.

Estimation of Potassium by Przibylla's Sodium Hydrogen Tartrate Method and its Application to the Analysis of Potassium Salts of the Alsatian Basin. PAUL HUBERT (*Ann. Chim. Analyt.*, 1923, 5, 9—14).—The method of Przibylla (*Kali*, 1908, No. 18) as modified by Bokemuller (*ibid.*, 1918, No. 15) has been further modified and adapted to the estimation of potassium in Alsatian sylvinites of very varying richness. The method

consists essentially in adding a slight excess of sodium hydrogen tartrate to the solution containing a definite weight of the sample, filtering an aliquot part of the liquid, and titrating with sodium hydroxide free from carbonate. According to the richness of the sample, the quantities of reagents used are altered so that the percentage of potassium can be calculated directly from the amount of sodium hydroxide used (cf. *J.S.C.I.*, 1923, 181A). A. R. P.

Separation and Estimation of Sodium and Lithium by Precipitation from Alcoholic Perchlorate Solution. H. H. WILLARD and G. FREDERICK SMITH (*J. Amer. Chem. Soc.*, 1922, 44, 2816—2824).—A method for the quantitative separation of sodium and lithium is described. The method depends on the precipitation of sodium chloride from a mixture of the perchlorates by means of a butyl alcohol solution of hydrogen chloride, and is carried out as follows. The mixture of sodium and lithium salts must be converted into chlorides by any suitable method and must contain no trace of sulphate. The mixed chlorides are evaporated to dryness with an excess of perchloric acid. If potassium is present it is first separated by the usual perchlorate separation, and the filtrate after the addition of water is evaporated to dryness. The mixed perchlorates of sodium and lithium free from perchloric acid are dissolved in *n*-butyl alcohol, using at least 18·5 c.c. for each 0·1 g. of sodium chloride likely to be formed later. The mixture dissolves readily if the alcohol is boiled. Then 0·1 c.c. of 70% perchloric acid is added and the solution cooled to -15° , and 1·0—1·5 c.c. of 20% hydrogen chloride in *n*-butyl alcohol are added slowly from a burette with continuous stirring, after which sufficient of the hydrogen chloride solution is rapidly added to form a 6% solution. The solution is then heated to boiling for a few minutes, allowed to cool, and the sodium chloride filtered on a Gooch crucible, washed eight to ten times with a 6—7% solution of hydrogen chloride in *n*-butyl alcohol, dried for one hour at 250° , and ignited at 600° for five to eight minutes in a muffle furnace, cooled, and weighed. A correction of 0·6 mg. must be made for the sodium chloride remaining in each hundred c.c. of filtrate. The filtrate and washings, diluted with one-third of their volume of water, are evaporated to dryness. If the residue is brown, it must be heated on a gauze until fumes of perchloric acid are evolved, and if insufficient of this acid is present to effect the complete oxidation of the organic matter a little should be added. The colourless residue is treated with 0·5 c.c. of concentrated sulphuric acid and heated until the whole of the acid has been expelled. The beaker is cooled, 5—10 c.c. of water are added, and the lithium sulphate is transferred to a platinum crucible, evaporated to dryness, ignited to drive off all free acid, and finally heated at 600° in a muffle furnace for five to ten minutes. A correction of 0·7 mg. per 100 c.c. of filtrate and washings should be subtracted from the weight of lithium sulphate. The results given by the procedure are uniformly good. The solubilities of sodium perchlorate, lithium perchlorate, sodium chloride, and lithium chloride in

n-butyl alcohol at 25° have been determined along with the densities of the saturated solutions, and the following values are recorded: lithium perchlorate, 44.23; $d_4^{25}=1.1341$; sodium perchlorate, 1.83; $d_4^{25}=0.8167$; lithium chloride, 11.49; $d_4^{25}=0.8713$; sodium chloride, 0.014; $d_4^{25}=0.8060$. The solubilities are given in g. per 100 g. of solution. The densities, d_4^{25} , of solutions of hydrogen chloride in *n*-butyl alcohol have also been determined and the following recorded: 0%, 0.8060; 1%, 0.8130; 2%, 0.8195; 3%, 0.8255; 4%, 0.8315; 5%, 0.8370; 6%, 0.8425; 7%, 0.8485; 8%, 0.8540; 9%, 0.8590; 10%, 0.8635; 11%, 0.8685; 12%, 0.8730; 13%, 0.8770; 14%, 0.8810; 15%, 0.8850; 16%, 0.8895; 17%, 0.8935; 18%, 0.8960; 19%, 0.9010, and 20%, 0.9050. J. F. S.

Oxidimetric Estimation of Calcium, and its Employment in Technical Work. J. GROSSFELD (*Chem. Weekblad*, 1923, 20, 39—41).—In the method of estimating calcium by adding excess of ammonium oxalate, filtering, and titrating an aliquot part of the filtrate with permanganate, the solution should contain a considerable quantity of a weak acid; phosphoric acid is most suitable, but the amount used must be carefully regulated. The procedure of Vürtheim and van Bers (A., 1922, ii, 869) is tedious, requiring two hours' heating on the water-bath. A simplified method, which may be carried out in a beaker, consists in dissolving the substance (containing not more than 0.140 g. CaO) in the cold in 20 c.c. 4*N*-phosphoric acid, adding with stirring exactly 20 c.c. of the oxalate solution (20 g. per litre), and finally 30 c.c. of 2.5*N*-sodium hydroxide; the solution is filtered through a fine-pored filter, and 50 c.c. are titrated with *N*/10-permanganate.

The method can be employed for fertilisers, foodstuffs, waters, and for estimating very small quantities of calcium. If reducing substances are present, the material may be ignited. S. I. L.

The Approximate Estimation of Magnesium in a Single Drop of Sea-water. G. DENIGÈS (*Compt. rend.*, 1922, 175, 1206—1208).—The author describes the conditions under which the brown precipitate produced by the action of potassium hypiodite on a solution containing magnesium-ions may be employed as a method for the colorimetric estimation of magnesium. Full experimental details are given (cf. *J.S.C.I.*, 1923, 207A). It is claimed that the method is rapid and sufficiently accurate for most purposes; moreover, a single drop only of the solution to be analysed for magnesium is required. H. J. E.

The Acidimetric Titration of Magnesium in its Salts. I. M. KOLTHOFF (*Rec. trav. chim.*, 1922, 41, 787—794).—The potentiometric titration of solutions of magnesium salts by means of alkalis is tedious and can only be carried out in solutions of a concentration greater than 0.5*N*; even under the most favourable conditions the error lies between 1% and 2%. No greater accuracy is attained by titrating a magnesium solution of concentration 0.5*N* or greater with normal sodium hydroxide, using nitramine

as indicator. The method recommended is based on the addition of excess of alkali to the solution containing magnesium, which is then made up to a definite volume, shaken, and allowed to remain. An aliquot portion of the clear solution is then titrated for excess of alkali, which should not be present to a greater extent than 0.01*N*. The presence of calcium is not disadvantageous.

H. J. E.

A New Method of Estimating Cadmium. R. CERNATESCO (*Bull. Acad. Sci. Roumaine*, 1922, 8, 43—46).—The cadmium is precipitated as sulphide by means of hydrogen sulphide and excess of the gas boiled off. A known volume of silver nitrate is added to the solution together with the precipitate, and the latter is blackened immediately, owing to the formation of silver sulphide. The whole is heated so as to complete the transformation, and the excess of silver nitrate determined by titration (cf. Mann, A., 1879, 1054). If chlorine is present, the precipitated cadmium sulphide must be separated by filtration through asbestos before the silver nitrate is added.

H. J. E.

The Titration of the Mercuric-ion with the Chlorine-ion, and its Application to the Analysis of Cinnabar and Organic Derivatives of Mercury. ĚMIL VOTOČEK and LADISLAV KASÁREK (*Bull. Soc. chim.*, 1923, [iv], 33, 110—122).—The method previously described for the mercurimetric estimation of chlorides may, conversely, be used for the estimation of mercury (cf. A., 1918, ii, 238, 272). The metal in the form of a mercuric salt of an oxygenated mineral acid is titrated in the cold with standard sodium chloride solution in presence of 0.06 g. of sodium nitroprusside per 200 c.c. volume of liquid. The titration is continued until the cloudiness due to mercuric nitroprusside just disappears, and under these conditions 1 c.c. of *N*/10-sodium chloride is equivalent to 0.010124 g. of mercury. For the estimation of mercury in mercuric sulphide or in cinnabar, about 0.3 g. of substance is digested with 50 c.c. of an oxidising mixture of 1 vol. of nitric acid with 2 vols. of sulphuric acid, and diluted to 1000 c.c. after complete decolorisation, 200 c.c. of the diluted solution being used for a titration. For the estimation of mercury in organic derivatives, the same treatment was successful in the aliphatic series, but in the aromatic and heterocyclic series nitric acid and powdered potassium permanganate were required to effect the destruction of the organic matter. Oxides of manganese in the reaction product were dissolved by the addition of sodium nitrite solution, excess of nitrous acid was eliminated by permanganate and sulphuric acid, followed by a few drops of oxalic acid to produce a colourless solution, which was then titrated with sodium chloride as above. When halogens are present it is, of course, necessary to precipitate the mercury as sulphide and redissolve the precipitate in the nitric-sulphuric acid mixture before proceeding to the titration. The direct titration is not disturbed by the presence of metals of which the nitroprussides are soluble in water, and mercury can accordingly be estimated

by this method in presence of alkali or alkaline-earth metals, of lead, zinc, aluminium, chromium, ferric iron, or manganese.

G. F. M.

Estimation of Iron in Ores and Silicate Rocks. F. R. ENNOS and R. SUTCLIFFE (*Summary of Progress Geol. Survey*, 1921, 174—176).—In the case of samples containing iron, aluminium, titanium, and phosphate, the weighed oxides of the aluminium group are fused with pyrosulphate and the titanium is estimated colorimetrically in the solution resulting from this fusion. The solution is then evaporated to a volume of about 100 c.c., the excess of hydrogen peroxide is destroyed by treating the hot solution with the required quantity of sulphurous acid, and the solution at 90° is saturated with hydrogen sulphide. The precipitate of sulphur and platinum sulphide (the platinum is derived from the crucible in which the fusion was made) is separated by filtration and washed with very dilute sulphuric acid. The filtrate is cooled, oxidised with dilute potassium permanganate solution, 10 c.c. of concentrated hydrochloric acid and 5 c.c. of 20% ammonium thiocyanate solution are added, and the iron is titrated with standardised titanium trichloride solution.

W. P. S.

The Separation of Iron and Zinc by Means of Bases. K. SCHERINGA (*Pharm. Weekblad*, 1923, 60, 39—43).—Addition of sodium hydroxide to a solution containing both zinc and ferric salts precipitates the two metals together, the weight of zinc oxide carried down varying with the amount of iron present, although not directly. Even if the zinc salt be added after the sodium hydroxide, the results are the same, nor could complete separation be effected in any way with this base. Precipitation with cold concentrated ammonia (25%) effects complete separation, if ammonia of the same strength be used to wash the precipitate.

S. I. L.

Successive Electrometric Titration of Iron, Uranium, and Vanadium. R. G. GUSTAVSON and C. M. KNUDSON (*J. Amer. Chem. Soc.*, 1922, 44, 2756—2761).—Analyses of salts of iron, vanadium, and uranium have been investigated by the electrometric method, individually and in all possible combinations, and a number of curves plotted indicating the results. Iron, vanadium, and uranium may each be titrated electrometrically after reduction with zinc and sulphuric acid, but in the case of vanadium the titration must be carried out in an indifferent atmosphere, such as carbon dioxide. A high concentration of acid favours sharp inflection points at all three end-points in the vanadium titration. Mixtures of salts of iron and uranium may be titrated with permanganate solution after reduction with zinc and sulphuric acid by the electrometric method, provided the acidity is kept low, the optimum concentration being about 5 c.c. of concentrated sulphuric acid to 250 c.c. of solution. Iron and vanadium in mixtures may be estimated by a similar method, using 10 c.c. of acid to 250 c.c. of solution, but in this case the titration must be made in an atmosphere of carbon dioxide to obtain trustworthy

results. The volume representing the vanadium is obtained directly from the final step in the curve, whilst that representing iron can be obtained by subtracting this value from the first step in the same curve. The estimation of vanadium and uranium in mixtures when 5—10 c.c. of sulphuric acid are present may be made by titrating the mixture in a non-oxidising atmosphere. The vanadium is obtained directly as before, and the uranium by difference. When all three elements, iron, vanadium, and uranium, are present, the estimation may be made similarly. It is best to use 4 c.c. of sulphuric acid to 250 c.c. of solution for the first part of the titration, and then, after the second inflection is obtained, a like quantity of acid is added and the titration continued. The vanadium and iron are represented by the last and the next to the last steps, respectively, whilst the uranium is again found by subtracting the value found for vanadium from the value indicated in the portion of the curve between the first and second inflections.

J. F. S.

Gravimetric and Volumetric Methods for the Estimation of Tin in Alloys. ANTONÍN JÍLEK (*Chem. Listy*, 1923, **17**, 7—11).—Two methods for the estimation of tin in alloys are examined, namely, the gravimetric method of Czerwek (*Z. anal. Chem.*, 1876, **15**, 505) and an iodometric method. Czerwek's method and its modifications for the analysis of bearing metals are closely studied. The following observations are made. The stanniphosphate precipitate should be washed with a mixture of acids similar to that used to dissolve the alloy, but with the addition of phosphoric acid, and not with nitric acid alone, as Czerwek recommends, otherwise antimonious acid, which is insoluble in nitric acid, would remain adsorbed on the precipitate. The solution of this precipitate in alkali sulphide should not be boiled very long, as a gelatinous precipitate containing stannous oxide and phosphoric oxide tends to separate with increase in hydroxyl-ion concentration. In the conversion of the stannous sulphide into stannous oxide, the sulphide should be moistened before the addition of nitric acid, as otherwise the violence of the reaction would lead to spattering of the contents of the crucible. A series of analyses of pure tin was carried out, reducing progressively the quantity of tin, but keeping the quantities of the reagents constant. As a result, it was found that with the quantities of the latter used [6 g. of acetic acid, 15 c.c. of nitric acid (*d* 1.4), 30 drops of 45% phosphoric acid, and 15 c.c. of water, followed by dilution with 300 c.c. of boiling water] the best results are obtained using 0.1 g. of tin. Should more be used, the results are high, whilst with less, precipitation of tin is slow and incomplete, so that using 0.0022 g. of tin, only 43% was found by this method. The stanniphosphate precipitate was examined, and its composition found to be roughly $2\text{SnO}_2 : \text{P}_2\text{O}_5$. This varies with the quantity of phosphoric acid used, and can contain adsorbed lead, copper, and antimony salts. For this reason, the tin cannot be estimated by weighing the stanniphosphate precipitate.

R. T.

New Method for the Electrometric Titration of Vanadium in the Presence of Iron and Chromium. H. H. WILLARD and FLORENCE FENWICK (*J. Amer. Chem. Soc.*, 1923, 45, 84—92).—The electrometric titration of vanadium by means of ferrous sulphate solution and potassium permanganate solution has been investigated. It is shown that a polarised bimetallic electrode system affords a more sensitive means of determining the end-point in the reduction of vanadic acid by ferrous sulphate than the usual monometallic electrode. In acetic acid solution, the reduction of chromic acid by hydrogen peroxide in the presence of vanadic acid may be made selective and gives an excellent means of estimating the latter element in all alloy steels. Results may be obtained which agree to 0.005% when 5 g. samples are used; one advantage over the method involving selective oxidation of vanadium with nitric acid lies in the reduced period of boiling required. Traces of vanadium may be titrated directly in the presence of large quantities of phosphotungstate and phosphomolybdate. For the analysis of vanadium steels, the following procedure is recommended. *Chromium and chromium vanadium steel.* A sample requiring about 10 c.c. of 0.02*N*-ferrous sulphate is placed in a 600 c.c. beaker, 20–30 c.c. of water are added and the calculated quantity of concentrated sulphuric acid is added from a burette. Each gram of steel requires 1.0 c.c. of this acid and a 4.0 c.c. excess to effect rapid solution. The beaker is heated gently until the sample is dissolved and salts commence to separate. The solution is then diluted with 20 c.c. of hot water and warmed until clear, when 4–5 c.c. of concentrated nitric acid are added cautiously and the solution is boiled. The oxidation of the iron and vanadium is completed with a slight excess of a solution of potassium permanganate. Sufficient sodium acetate is added to combine with the sulphuric acid in excess over that required for solution of the steel (1 c.c. concentrated sulphuric acid \equiv 4.8 g. of sodium acetate trihydrate) and 40–50 c.c. of glacial acetic acid. Then 0.5 g. of neutral sodium perborate is added, the solution diluted to 200 c.c., and boiled for twenty minutes. The solution is cooled to the ordinary temperature, 25–30 c.c. of concentrated hydrochloric acid are added and titrated with 0.02*N*-ferrous sulphate solution, using a bimetallic system to ascertain the end-point (this vol., ii, 33). *Chromium vanadium molybdenum steels* are treated in exactly the same way. *Chromium vanadium tungsten steels.* The sample is treated with 40 c.c. of hydrochloric acid (3:1), and heated until action ceases. Then 8–10 c.c. of concentrated nitric acid are added drop-wise, and when the first violent action has ceased the solution is evaporated to 20 c.c. It is then diluted with hot water and boiled to dissolve soluble salts, filtered, and the residue washed with 2% hydrochloric acid. The filtrate is oxidised with potassium permanganate and the free acid neutralised by a sufficient excess of sodium acetate (1 g. of hydrochloric acid \equiv 3.73 g. of sodium acetate trihydrate). From this point the analysis is as described above. A small quantity of vanadium is occluded by the tungstic acid; to estimate this,

the tungstic acid is dissolved in sodium carbonate solution and boiled for ten minutes with about 0.5 g. of perborate. It is then acidified with 3—5 c.c. of phosphoric acid and 25—40 c.c. of sulphuric acid (3:1) and titrated electrometrically to the permanent drop in potential.

J. F. S.

Detection of Antimony and Tin in Qualitative Analysis.

E. RUFF (*Ber. Deut. pharm. Ges.*, 1922, **34**, 334—335).—A modification of the usual test for antimony in presence of tin (by means of platinum foil and granulated zinc) is described in which the platinum foil is replaced by a very small piece of platinum wire. Details are also given of a method in which the platinum is entirely dispensed with, being replaced by a piece of iron wire, by which it is claimed that 0.08 mg. of antimony can be detected with certainty.

P. M.

Interferometric Analysis of Liquid Mixtures of Organic Substances.

ERNST COHEN and H. R. BRUINS (*Z. physikal. Chem.*, 1923, **103**, 337—348).—The authors have investigated the difficulties which arise when the Rayleigh-Löwe water interferometer is used for the analysis of solutions of organic liquids. It is shown that when using this instrument with organic liquids the upper interference band undergoes a lateral displacement and becomes diffuse, whilst the bands are oblique and bent and continuously change their form. These changes are due to the influence of temperature on the refractive index of the solvent, the vaporisation of the liquid and condensation on the cover glass, the absorption of water from the air during the placing of the liquid in the observation vessels, and the index of refraction of the bath liquid. Each point has been subjected to careful experiment and precautions for eliminating the disturbance in each case are indicated. When all these precautions are taken, the water interferometer gives results which are as sharp and as exact as those obtained with aqueous solutions.

J. F. S.

Estimation of Thymol in Thyme Oil.

HUGO MASTBAUM (*Anal. Fis. Quim.*, 1922, **20**, 501—504).—Phenols are extracted from thyme oil by repeated shaking with sodium hydroxide solution. On addition of strong hydrochloric acid to an aliquot portion of the extract, the phenols separate. The thymol is obtained by crystallisation and weighed after collection and drying.

G. W. R.

Colorimetric Estimation of Pyrogallol, Gallotannin, and Gallic Acid.

C. AINSWORTH MITCHELL (*Analyst*, 1923, **48**, 2—15).—The method is based on the fact that a solution containing 0.1% of ferrous sulphate and 0.5% of sodium potassium tartrate reacts immediately with gallotannin to form a soluble compound which, unlike the ink formed with ferrous sulphate alone, is fairly stable. The coloration ranges from reddish- to bluish-violet, it is apparently specific for the pyrogallol grouping,

and its intensity is proportional to the amount of this tinctogenic group in gallic acid and the various tannins. Thus the colour factor for gallic acid referred to pyrogallol is identical with the ratio of their molecular weights, namely 1:1.5 for crystalline gallic acid, and 1:1.36 for the anhydrous acid. Owing to its greater stability, it is preferable to use solutions of gallic acid rather than of pyrogallol as the standard for comparison, and in the estimation of the natural gallotannins the gallic acid equivalent is determined colorimetrically and this must then be multiplied by a suitable factor to obtain the absolute amount of gallotannin. Owing to the uncertainty of the constitution of these substances, this factor can only be obtained empirically, and it varies with different varieties; for Aleppo galls, for example, the factor 1.85 was found suitable, whilst for the tannin in Chinese galls the factor 2.1 is appropriate. For the estimation of the tinctorial value of a tannin it is, however, unnecessary to use these factors at all, the pyrogallol equivalent expressing all that is required. Based on the hypothesis that the colour intensity is always a measure of the pyrogallol groups present, it is suggested that the average "pure" gallotannin is a mixture of different glucosides, but mainly of di-digalloyl glucose, with a digallic anhydride of the type described by Nierenstein (*J. Soc. Chem. Ind.*, 1922, 29T). Such a mixture would yield the required proportion of dextrose and contain the necessary pyrogallol groups to give the observed coloration with the ferrous tartrate reagent. Most natural gallotannins contain a proportion of gallic acid, and each can be colorimetrically estimated by estimating the two substances together first in terms of gallic acid, then precipitating the gallotannin by means of quinine hydrochloride, and finally estimating the gallic acid in the filtrate, the difference between the two results multiplied by the appropriate factor giving the amount of gallotannin. The results of the estimation of gallic acid and gallotannin in numerous commercial varieties of nut galls, including white and roasted galls, and also in myrobalans and various other materials containing tannin such as tea, are given. G. F. M.

Estimation of the Admixed Arachidic and Lignoceric Acids in Peanut Oil by means of Magnesium Soaps. ARTHUR W. THOMAS and CHAI-LAN YU (*J. Amer. Chem. Soc.*, 1923, 45, 113—128).—The authors have made a systematic and quantitative study of the behaviour of a number of pure soaps in various solvents, and in particular the solubilities of the magnesium soaps of various fatty acids in 90% (by volume) ethyl alcohol have been measured. At 25°, 100 g. of the alcohol dissolve 0.007 g. of magnesium stearate, or 0.006 g. of magnesium lignocerate, but 8.60 g. of magnesium oleate. The results indicate that an excellent separation of magnesium stearate, arachidate, and lignocerate from magnesium oleate, linolate, and linolenate is possible by means of this solvent. Under the same conditions, 100 g. of 94.3% (by volume) alcohol dissolve 0.633 g. of potassium stearate, 0.153 g. of potassium lignocerate, or 41.1 g. of potassium oleate. The

solubilities of stearic and lignoceric acids in three strengths of alcohol have been determined and the results show that a quantitative separation of arachidic and lignoceric acids from other saturated acids can best be accomplished with 90% (by volume) alcohol after remaining for one night at 20° or 25°.

A new method for the estimation of peanut oil based on the above separation of the magnesium soaps of saturated and unsaturated acids is outlined as follows: 10 g. of the oil are saponified by boiling with a mixture of 50 c.c. of 5% alcoholic potassium hydroxide and 50 c.c. of 95% alcohol for half an hour. The soap solution, while still warm, is neutralised with 20% alcoholic acetic acid and then made just alkaline with the alcoholic potassium hydroxide, using phenolphthalein as indicator. To this solution, 25 c.c. of alcoholic magnesium acetate (50 g. of magnesium acetate dissolved in 100 c.c. of water, heated to boiling, and filtered and the filtrate diluted with three volumes of 95% alcohol) are added and the mixture is heated to boiling and left over-night at 10°. The insoluble soaps are collected and washed with 30 c.c. of 90% alcohol. These insoluble soaps are then hydrolysed by boiling with 100 c.c. of 5*N*-hydrochloric acid for five minutes. Cold water is added to precipitate the solid acids, which are collected and washed free from magnesium and chlorine. The solid acids are extracted with three successive portions of 20 c.c. of warm 90% alcohol and the solution left over-night at 20° or 25°. The crystals which form are separated and washed twice with 10 c.c. of 90% alcohol and then with 70% alcohol until the washings give no turbidity with water. The filtrate and washings are collected and measured. The solids are washed with alcohol into a weighed beaker; the solvent is evaporated and the residue dried at 80° and weighed. This weight is corrected for the weight of lignoceric and arachidic acids which remain dissolved in the filtrate and washings of 90% alcohol. In estimations of known mixtures of peanut oil with olive oil or cotton-seed oil, the error did not exceed 5% of the value found for the peanut oil. The percentage of arachidic and lignoceric acids in peanut oil are taken as 5% on an average.

Time and work may be saved by using the solution left after the ordinary determination of the saponification number, for the above procedure, if a high order of accuracy is not required.

The proposed method is not intended for the separation of saturated acids from all unsaturated acids in all fatty oils, as magnesium erucate and an unsaturated magnesium soap from tung oil (probably eleomargarate) were found to be insoluble in 90% alcohol (cf. following abstract). W. G.

New Qualitative Tests for Rape and Tung Oils. ARTHUR W. THOMAS and CHAI-LAN YU (*J. Amer. Chem. Soc.*, 1923, **45**, 129—130).—Rapeseed oil is subjected to the method of analysis outlined for peanut oil (cf. preceding abstract), and the acid cake left after hydrolysis of the magnesium soaps is dissolved in 60 c.c. of 90% alcohol and the solution is left over-night at 20° or 15°.

Any crystals which may have formed are filtered off and discarded and the filtrate and washings evaporated to dryness and the m. p. or acid number, or preferably the iodine number, of the residue is determined. Two samples of genuine rapeseed oil, thus treated, yielded about 25% of the final acid product having m. p. 35° (erucic acid has m. p. 32°), iodine number 70—72 (erucic acid has 74.99).

In the case of tung oil, the insoluble magnesium soaps are collected while hot, washed with 90% alcohol, and decomposed with dilute hydrochloric acid in the absence of air. The liberated acid has a strong odour characteristic of tung oil. It is soluble in cold 90% alcohol and melts at about 44°. After one or two days' contact with air it absorbs oxygen and gradually changes to a dark brown, resinous mass. The yield of this acid (eleomargaric) obtained from one sample of tung oil tested was about 20%. W. G.

The Estimation of Chloral Hydrate. I. M. KOLTHOFF (*Pharm. Weekblad*, 1923, 60, 2—8).—In the ordinary method, in which the chloral is converted by excess of sodium hydroxide into chloroform and sodium formate, and the excess of alkali titrated with standard acid, the results are always high; this has been attributed to action of the excess of alkali on the chloroform produced. The error is in fact due to absorption of carbon dioxide from the air by the alkali during the time required for the reaction, and if decinormal sodium hydroxide is used, the mixture may be allowed to remain at 40° for twenty minutes without decomposition of the chloroform. Accurate results are obtained by allowing 30 c.c. of *N*/10-sodium hydroxide to act on 25 c.c. of 0.1 molar chloral hydrate solution for fifteen minutes in a closed flask, and then titrating the excess, using phenolphthalein; the alkali must be standardised by carrying out the same procedure.

The iodine method of Rupp (A., 1903, ii, 699), in which the aldehyde is oxidised to trichloroacetic acid by excess of iodine, the latter being titrated back in the usual way, gives poor results if sodium hydroxide is used, as proposed by Rupp. Good results are obtained by adding 2 c.c. of *N*-sodium carbonate and 10 c.c. of 0.1 molar chloral hydrate to 25 c.c. of *N*/10-iodine solution, leaving one hour in a closed vessel, adding hydrochloric acid, and titrating with thiosulphate.

The chloral hydrate for the work was standardised by Wallis's method (A., 1906, ii, 255) as modified by van Rossum (A., 1908, i, 501), *i.e.*, complete hydrolysis to sodium chloride and sodium formate by heating with sodium hydroxide in a sealed tube, and gravimetric estimation of the chloride.

Bromine in acid solution will not oxidise chloral, which therefore must have a much greater reducing power in alkaline than in acid solutions. S. I. L.

A New Test for Acraldehyde and Its Bearing on Rancidity in Fats. WILMER C. POWICK (*J. Ind. Eng. Chem.*, 1923, 15, 66).—To a few drops of dilute acraldehyde solution in a test-tube, a drop of 3% hydrogen peroxide is added, and after about one

minute 5 c.c. of concentrated hydrochloric acid are added, and the test-tube is shaken. On shaking with 5 c.c. of a 1% ethereal solution of phloroglucinol, a deep red colour is imparted to the aqueous layer, showing a fairly narrow absorption band in the yellow-green. The red colour is not obtained in the absence of hydrogen peroxide, whilst if there be an excess of acraldehyde a purple precipitate is obtained. This test differs from the Kreis test for rancidity in fats by the addition of the hydrogen peroxide, and under these conditions no coloration is given by the saturated aldehydes or by crotonaldehyde. The spectrum given by the substance formed in the Kreis test is identical with that obtained as above, and it therefore seems that the substance responsible for this test in rancid fats is identical with that produced by the action of hydrogen peroxide on acraldehyde. P. M.

Use of Schiff's Reagent for the Estimation of Acraldehyde.

CHARLES MOUREU and ÉTIENNE BOISMENU (*J. Pharm. Chim.*, 1923, [vii], 27, 49—54, 89—97).—Acraldehyde can be accurately estimated colorimetrically by means of Schiff's reagent by adopting the following procedure: a standard solution of acraldehyde containing 0.5 g. per litre is prepared from the freshly distilled substance by collecting in an ampoule, sealing, and weighing, and then breaking in the requisite quantity of water to give a solution of the required strength. One arm of each of two inverted Y-tubes is filled respectively with 10 c.c. of this standard solution, and 10 c.c. of the unknown acraldehyde solution, diluted to contain slightly less than 0.05% of acraldehyde. The other arms are then filled with 5 c.c. of Schiff's reagent, the tubes are closed with glass stoppers and simultaneously inverted, thereby mixing the reagent with the two solutions at the same moment. For the attainment of the maximum intensity of coloration twenty-five minutes are allowed before examining the tints in the colorimeter. The height of the standard solution having the same intensity of coloration as 25 mm. of the solution under test is measured, and the acraldehyde content of the latter may be read off directly from the curve provided, which may be reconstructed from the following figures: where I is the height of standard solution in mm. and II the concentration of acraldehyde in mg. per litre in unknown solution.

I.	25	22	20.6	18.8	15.5	12.8	10.3
II.	500.0	476.2	454.5	434.8	400.0	370.4	333.3

It will be seen from these figures that on diluting a solution of acraldehyde the intensity of coloration is lowered more rapidly than the acraldehyde content. The whole of the above procedure must be carried out with cold solutions, as at higher temperatures the colours obtained are never comparable, but consist of a mixture of colours tending towards green with varying velocities with solutions of varying concentrations. The presence of stabilisers, such as pyrogallol, pyrocatechol, quinol, or gallic acid, does not interfere with the colorimetric estimation. G. F. M.

The Estimation of Acetone in Methyl Alcohol and the Purification of Methyl Alcohol by Sodium Hypiodite.

HENRY HUTCHINSON BATES, JOHN MYLNE MULLALLY, and HAROLD HARTLEY (T., 1923, 123, 401—404).

Estimation of Acetone in Methyl Alcohol. ELLA SÖDERLUND (*Svensk. Kem. Tidskr.*, 34, 152—157; from *Chem. Zentr.*, 1922, iv, 1074—1075).—A modification of the method of Messinger (A., 1889, 313). Ten c.c. of methyl alcohol are diluted to 100 c.c.; 10 c.c. of this solution are treated in a stoppered flask with 25 c.c. of sodium hydroxide solution. A large excess of 0.1*N*-iodine solution is added, and after keeping in darkness for ten minutes 26 c.c. of *N*-sulphuric acid are added. The excess of iodine is estimated by titration with thiosulphate. G. W. R.

Rapid Volumetric Method of Estimating Acetone. M. MARQUEYROL and P. LORLETTE (*Mém. des Poudres*, 1922, 19, 362—367).—The method depends on the action of sodium hypiodite on acetone in alkaline solution whereby iodoform and sodium acetate are produced. The hypiodite is formed by the interaction of potassium iodide and sodium hypochlorite. Commercial eau de Javel is used, and is standardised against pure acetone, 10 c.c. of which are dissolved in water and made up to 1 litre. Ten c.c. of this solution are diluted with 90 c.c. of water and 10 g. of potassium iodide and 20 c.c. of sodium hydroxide (*d* 1.325) added. The hypochlorite is run in from a burette with constant agitation, and the solution tested with an outside indicator consisting of 1 g. of starch, 10 g. of sodium hydrogen carbonate and 100 c.c. of water. The end-point is very sharp and is heralded by the precipitation of flocks of iodoform. In estimations of acetone, the acetone is distilled into a 500 c.c. measuring flask, and 100 c.c. are taken for the estimation, which is carried out as described above. The presence of alcohol, aldehyde, diphenylamine, or ammonia does not affect the titration. Substituted carbamides, however, give traces of iodoform, which can usually be neglected. H. C. R.

Estimation of Reducing Sugars by Means of Fehling's Solution with Methylene-blue as Internal Indicator. J.

HENRY LANE and LEWIS EYNON (*J. Soc. Chem. Ind.*, 1923, 42, 32—37T).—In the volumetric estimation of sugars by means of Fehling's solution the disadvantages attending the use of an external indicator can be altogether avoided by using a 1% solution of methylene-blue as internal indicator. So long as any copper remains unreduced, the indicator retains its colour, but it is immediately decolorised by the sugar the moment all the copper is reduced. The action is reversible. To attain the maximum of accuracy, consistent procedure is necessary, in combination with conversion tables based on the same method of operation. The following standard method of titration is recommended: 10 c.c. or 25 c.c. of Soxhlet's modification of Fehling's solution are measured into a 300 c.c. flask and treated cold with almost the whole of the sugar solution (determined by a preliminary trial) required to effect

reduction of all the copper. The liquid is then heated to boiling, kept in moderate ebullition for two minutes, and then, without removing the flame, 3—5 drops of the indicator are added and the titration is completed in one minute further so that the liquid is boiled in all three minutes. The end-point can be determined generally to within 1 drop of the sugar solution. Based on this method of procedure tables have been drawn up giving the weight in mg. of sugar required to reduce the volume of Fehling's solution employed. This factor varies appreciably with the concentration of the sugar solution, and values are given for volumes of 15—50 c.c. Tables are given for invert-sugar, both in presence and absence of sucrose, for dextrose, lævulose, maltose, and lactose. G. F. M.

Estimation of Dextrose in Cerebrospinal Fluid. J. LANZA (*Anal. Fis. Quím.*, 1922, 20, 400—402).—The method is based on the reaction whereby picric acid and dextrose in alkaline solution give picramic acid, $\text{OH}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_2\cdot\text{NH}_2$, which is distinguished by its red colour. To 2 or 3 c.c. of the cerebrospinal fluid, picric acid in the proportion of 0.05 g. for each c.c. of liquid used is added. After warming, the liquid is rapidly cooled and centrifuged. Dextrose is then estimated colorimetrically by comparison with a standard dextrose solution in a Duboscq colorimeter.

G. W. R.

The Tryptophan-Aldehyde Reaction. ERNST KOMM and EBERHARD BÖHRINGER (*Z. physiol. Chem.*, 1923, 124, 287—294).—A new modification of the aldehyde test for tryptophan is described. One c.c. of the solution of tryptophan is added to a 15% solution of hydrochloric acid containing, in 500 c.c., 6 c.c. of a 0.1% solution of formaldehyde. To the mixture are added 10 c.c. of concentrated sulphuric acid. The whole is shaken and allowed to cool. The colour produced is stable, and proportional to the tryptophan present, for the colorimetric estimation of which the reaction may be applied. It is sensitive to a solution of tryptophan containing 1 part in 175,000 parts.

W. O. K.

Modification of the Moreigne Ureometer. J. LANZA (*Anal. Fis. Quím.*, 1922, 20, 403—405).—A modification of Moreigne's apparatus for the estimation of urea by the hypobromite method is described.

G. W. R.

The Hydrocyanic Acid Question. XI. The Detection of Hydrocyanic Acid in Plants. L. ROSENTHALER (*Schweiz. Apoth. Ztg.*, 1922, 60, 477—481; from *Chem. Zentr.*, 1922, iv, 1124—1125; cf. A., 1922, i, 614—615).—Hydrocyanic acid in plants may be detected by its decolorisation of blue starch-iodide solution. In the presence of essential oils which contribute iodine the plant material should first be extracted with ether. Where only traces of hydrocyanic acid are to be expected, it may be removed from the material by long passage of a stream of air and collected in mercuric chloride solution. By addition of potassium iodide to the mercuric chloride solution with subsequent passage of carbon dioxide or warming with sodium hydrogen carbonate,

the hydrocyanic acid is again liberated. For the detection of hydrocyanic acid in plant sections, the starch-iodide method is suitable.

G. W. R.

Analysis of the Products of Hydrolysis of Cyanamide by Acids. A. GRAMMONT (*Bull. Soc. chim.*, 1923, [iv], 33, 123—128).—A satisfactory evaluation of fertilisers derived from cyanamide requires, not only an estimation of organic and ammoniacal nitrogen, but also that the former should be differentiated into carbamide nitrogen, dicyanodiamide nitrogen, and dicyanodiamidine nitrogen, as these substances have widely different values as fertilisers, and some are even toxic. Such discrimination between the forms of combination of the nitrogen present is obtained by the following method of assay: Total nitrogen is estimated by Kjeldahl's method; ammonia by converting the ammonium salts present in solution of the material, neutralised to phenolphthalein with dilute sodium hydroxide, into hexamethylenetetramine by the addition of formaldehyde, and titrating the liberated acid with standard alkali hydroxide; carbamide by precipitation by the Fosse method with xanthydrol as dioxanthylcarbamide, and weighing as such; dicyanodiamidine by precipitation as its nickel compound, $\text{Ni}(\text{C}_2\text{H}_4\text{ON}_4)_2 \cdot \text{H}_2\text{O}$, by the method of Dafert and Miklomb, washing the precipitate with 2% ammonia, drying at 100° and weighing; and finally arriving at the amount of dicyanodiamide by difference, as cyanamide itself is always absent. If the fertiliser contains phosphoric acid or soluble phosphates they must first be removed by adding sodium hydroxide solution to the material after digesting for one hour in water until neutral to phenolphthalein, whereby soluble phosphates are precipitated as calcium phosphate. The above estimations are then carried out on the filtrate. G. F. M.

The Interconvertibility of Creatine and Creatinine. III. The Estimation of Creatinine and Creatine in Blood-serum. AMANDUS HAHN and GEORG MEYER (*Z. Biol.*, 1922, 76, 247—256; cf. A., 1921, i, 517).—In the estimation of creatine in blood-serum, trichloroacetic acid is very suitable for precipitating the proteins. Fifty c.c. of serum are diluted with 25 c.c. of water, and 50 c.c. of a freshly prepared 10% solution of trichloroacetic acid are added. The creatine in the filtrate is then estimated by conversion into creatinine by treatment at $60\text{--}65^\circ$ with hydrochloric acid, and estimated along with the preformed creatinine as previously described (*loc. cit.*). In the estimation of the preformed creatinine, colloidal ferric hydroxide may be conveniently used as a protein precipitant.

W. O. K.

Purification of Picric Acid for Creatinine Estimations. STANLEY R. BENEDICT (*J. Biol. Chem.*, 1922, 54, 239—241).—Recrystallisation from benzene is recommended. Folin and Doisy's method (A., 1917, ii, 159) is unsuitable.

E. S.

Colorimetric Estimation of Cystine in Urine. JOSEPH M. LOONEY (*J. Biol. Chem.*, 1922, 54, 171—175).—Folin and Looney's method (A., 1922, ii, 539) for the estimation of cystine is applied

directly to urine. The coloration due to the presence of uric acid and other reducing substances is corrected for by making an estimation without the addition of sodium sulphite to the urine and subtracting the resulting value from that obtained in the presence of sodium sulphite. A cystine standard is used in each case. The readings must be made not later than eight minutes after the addition of the phosphotungstic acid reagent. E. S.

Colorimetric Method for the Estimation of Cystine. EUGEN HERZFELD (*Schweiz. med. Woch.*, 52, 411—412; from *Chem. Zentr.*, 1922, iv, 1076).—The method consists in precipitating the sulphur from an alkaline solution of cystine by addition of copper sulphate solution. After freeing the precipitated copper sulphide from copper oxide by treatment with dilute sulphuric acid, it is dissolved in nitric acid and by addition of ammonia converted into a solution suitable for colorimetric estimation. For comparison, a solution is prepared from a known weight of pure cystine. Experimental details of the method are given. G. W. R.

Estimation of Morphine. JOHN RALPH NICHOLLS (*Analyst*, 1922, 47, 506—510).—A general method for the extraction of morphine is described. One volume of the morphine solution is mixed with 1 volume of alcohol, the mixture is rendered ammoniacal and shaken with 1 volume of chloroform. The chloroform layer is drawn off, and the mixture is again shaken with the addition of 0.5 volume of alcohol and 1 volume of chloroform. This process of extraction is made three or four times, the combined extracts are then evaporated, the residue is dissolved in a definite volume of standardised acid, the solution diluted to a known volume, and the morphine is then estimated volumetrically, colorimetrically, or polarimetrically. W. P. S.

System of Blood Analysis. Supt. IV. Revision of the Method for Estimating Uric Acid. OTTO FOLIN (*J. Biol. Chem.*, 1922, 54, 153—170).—The various recent methods for the estimation of uric acid in blood are reviewed, and the author's method (A., 1919, ii, 308) is modified. The procedure now adopted is, in its essentials, similar to that of Benedict (A., 1922, ii, 403) except that the uric acid reagent of Folin and Denis is retained. The original precipitation method is retained in a modified form as a check on the direct method. Contrary to Pucher's statement (A., 1922, ii, 668), 90—100% of added uric acid can be recovered from the tungstic acid filtrate; the heat process recommended by this author gives irregular results and should be avoided. E. S.

Estimation of Uric Acid. STANLEY R. BENEDICT (*J. Biol. Chem.*, 1922, 54, 233—238).—Mainly a reply to Folin (cf. preceding abstract). E. S.

General and Physical Chemistry.

Variation of the Refractive Index of Oxygen with Pressure, and the Absorption of Light by Oxygen at High Pressures. (MISS) H. I. EADIE and JOHN SATTERLY (*Trans. Roy. Soc. Canada*, 1922, 16, III, 63—73).—Gladstone and Dale's law for the relation of refractive index to density has been confirmed in the case of oxygen for pressures ranging from 2.1 to 140 kg. per sq. cm. Evidence for the existence of absorption in oxygen at pressures up to 100 atmospheres, in the regions $\lambda\lambda$ 6285, 5800, and 5350 Å. was not conclusive. J. S. G. T.

Variation of the Index of Refraction of Water, Ethyl Alcohol, and Carbon Disulphide with the Temperature. ELMER E. HALL and ARTHUR R. PAYNE (*Physical Rev.*, 1922, 20, 249—258).—Measurements were made with a precision spectrometer, the construction and use of which are described. The two prisms used were of gold-plated brass, and optical glass sides, and had an angle of 60° and 75°, respectively; the temperature of the bath could be maintained indefinitely within 0.1° of any desired point. From tables showing the index of refraction of water relative to air, and the absolute index of refraction of water (both for sodium light), respectively, the following values are abstracted: 15°, 1.33341, 1.33377; 20°, 1.33299, 1.33327; 100°, 1.31783, 1.31819 (all ± 0.00002). When reduced to a vacuum, the experimental values for pure water are well represented by the empirical formula $n = 1.33401 - 10^{-7}(66t + 26.2t^2 - 0.1817t^3 + 0.000755t^4)$. The temperature coefficient, dn/dt , at the temperatures mentioned has the values -0.00008 , -0.00009 , and -0.00030 .

Corresponding values of the index of refraction, relative to air, and of the temperature coefficient, dn/dt , of ethyl alcohol (Kahlbaum's, 99.8% absolute) are abstracted as follows: 14°, 1.36290, (15°) -0.00040 ; 24°, 1.35885, (25°) -0.00041 ; 76°, 1.33626, (75°) -0.00046 . For carbon disulphide, 15°, 1.62935, -0.00077 ; 20°, 1.62546, (25°) -0.00081 ; 45°, 1.60499, -0.00083 . Although the absolute values obtained differ somewhat from those given by others for pure samples, the temperature coefficients are probably not affected by the slight amount of impurity present. For ethyl alcohol between 15° and 70°, the results correspond with the empirical equations $dn/dt = -10^{-6}[404 + 0.44(t-15) + 0.0075(t-15)^2]$; for carbon disulphide between 15° and 45° $dn/dt = -10^{-6}[766 + 5.12(t-15) - 0.105(t-15)^2]$. A. A. E.

The Secondary Spectrum of Hydrogen. E. GEHRCKE and E. LAU (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1922, 32, 453—458).—The secondary spectrum of hydrogen has been obtained almost free from the Balmer series by using a discharge tube silvered on the inside. The bands in the red-yellow and the yellow-green portion of the spectrum consist of a number of lines arranged

symmetrically about a middle point, but the middle line about which the other lines are grouped is missing. The distances between the principal line and its α - and β -companions stand in the relationship 1 : 2; the δ line divides up the distance between the principal line and α in the proportion 2 : 3. The distance between the principal lines of the successive bands shows that the series approximates to a system of $\Delta\lambda$ -bands, and, in this respect, they are similar to the resonance spectrum of sodium. In the bands in the blue-green region, the companions of the principal lines show a 3 : 2 relationship in their distances. The lines lying in the regions between the bands form symmetrical groups, and repetition of similar groups frequently occurs.

By the introduction of a spark gap into the discharge tube, the relative intensities of the hydrogen lines are very much altered. The change is in many respects similar to that observed by Merton when helium is mixed with hydrogen. The lines in the secondary spectrum are much sharper than the H_α line in the Balmer series. From the thickness of the lines it is deduced that the secondary spectrum owes its origin to molecular hydrogen (H_2 , H_3 , and H_4). The thickness of the lines increases with increase in the diameter of the tube owing to the higher temperature in the narrower tubes.

From the absence of the secondary spectrum in the light from the stars, it is concluded that the hydrogen giving rise to the Balmer series is always contaminated with other gases, and it is possible that it exists in the state of dissociated water vapour.

W. E. G.

Band Spectrum in the Arc Spectrum of Silicon. C. PORLEZZA (*Atti R. Accad. Lincei*, 1922, [v], 31, ii, 513—517).—The author's examination of the arc spectrum of silicon gives results differing little from those of Gramont and Watteville (A., 1908, ii, 909), but showing a band spectrum not previously observed.

T. H. P.

Relative Intensities of the Stark Effect Components in the Helium Spectrum. JOHN STUART FOSTER (*Physical Rev.*, 1922, 20, 214—220).—By the use of a discharge tube of the type first employed by Lo Surdo, the relative intensities of Stark effect components have been measured by means of a neutral wedge. Spectrograms were taken of the p and s components in turn, using a five-prism spectrograph; energy distribution curves were then calculated from the contour of the images and the corresponding wedge densities, and the relative intensities obtained by integration. The results for the main p components are : λ 4388, 8.2 (isolated), 4.1, 19.2, 28.0; λ 4472, 168, 694; λ 4922, 9.7, 31.6. Corresponding results for the s components are : λ 4388, 1.0 (isolated), 3.0, 11.3, 9.5; λ 4472, 76, 464; λ 4922, 6.2, 21.4.

A. A. E.

The Band Spectrum Associated with Helium. YUTAKA TAKAHASHI (*Proc. Phys. Math. Soc. Japan*, 1922, 4, 187—193).—The band spectrum of helium consists of two double-headed bands, the lines of which form series for which Fowler has derived formulæ

of the Hicks type. Band spectra are usually attributed to molecules and not to atoms. It is possible, however, to assume that under certain conditions unstable helium molecules may exist from which the observed band spectrum may originate. A mathematical analysis shows that the form of a helium molecule is such that two nuclei, each accompanied by one electron about it, are connected by means of an electron and form something like a nucleus around which the remaining electron describes its orbit.

CHEMICAL ABSTRACTS.

Arc, Spark, and Absorption Spectra of Argon. W. W. SHAVER (*Trans. Roy. Soc. Canada*, 1922, 16, III, 135—144).—The radiation produced in argon by electronic bombardment with an accelerating potential of 10.1 volts has been detected photographically and shown to consist of wave-lengths 4335.4, 4300.2, 4259.8, 4198.4, 4158.7, and 4055.9 Å. With accelerating fields ranging from 16 to 30 volts, the lines in the arc spectrum corresponded with those of the red argon spark spectrum. At 31 volts, the blue or enhanced spectrum began to appear, and at 54 volts, all the enhanced lines predicted by Bohr's theory were found. No new lines appeared when the potential was increased to 240 volts. No evidence of absorption was detected in the spectrum of ionised argon at pressures of 155, 5, and 2 mm. of mercury between wave-lengths 7000 Å. and 2150 Å., or in the spectrum of argon at 102.4 atmospheres pressure in the same region. J. S. G. T.

The Arc Spectra of Metals in Different Media and in a Vacuum. ST. PROCOPIU (*Compt. rend.*, 1923, 176, 385—388).—In continuation of the work on mercury (A., 1922, ii, 600), the author has studied the arc spectra of copper, gold, zinc, cadmium, magnesium, calcium, aluminium, and carbon in air, hydrogen, coal gas, nitrogen, under water, and in a vacuum. As in the case of mercury, in the arc spectra of the metals under water, in coal gas, and in hydrogen the rays of the arc series become much broadened, and those of the higher order are weakened or disappear. In addition, spark rays appear. In nitrogen, the arc is stable with all the metals, and the rays appear to be greater in number than in air. Certain rays previously only found in a vacuum appear. The radiated energy is displaced towards the last terms of the arc series. Numerous rays are inverted. The spark rays are weakened. In a vacuum, the arc is stable in all cases. The last terms are more intense than in the other media. The energy radiated is displaced towards the ultra-violet. Numerous rays, particularly the cathodic rays, are inverted, and the rays are broadened. The arc in a vacuum shows enhanced rays, and for the most part they are spontaneously inverted. W. G.

Series Regularities in the Arc Spectrum of Chromium. C. C. KIESS and HARRIET KNUDSEN KIESS (*Science*, 1922, 56, 666).—The arc spectrum of chromium contains at least three sets of series of which the members are triplets, two sets being composed of wide triplets, and one of narrow triplets. A constant difference

exists between the wave-numbers of homologous members of the wide-triplet series. Each component of the first member of the diffuse series is itself a narrow triplet. The principal, sharp, and diffuse series of the two parallel systems give values for $\Delta\nu$ of 112·44, 81·38; 112·45, 81·35; 112·78, 81·29; and 115·10, 91·42; 115·2, 91·3; 115·16, 91·54, respectively, whilst the narrow triplets are characterised by the frequency differences $\Delta\nu_1=8\cdot80$ and $\Delta\nu_2=5\cdot65$. A. A. E.

The Optical Spectrum of Hafnium. H. M. HANSEN and S. WERNER (*Nature*, 1923, **111**, 322; cf. A., 1922, ii, 463).—The optical spectrum of a large number of preparations containing hafnium has been examined and compared with that of a specimen of very pure zirconium prepared by Coster and Hevesy from commercial zirconium by removing the hafnium content. A table gives the wave-lengths and intensities of a number of lines, some of which have been observed by earlier investigators and ascribed to zirconium. There was, however, not the slightest trace of any of the lines ascribed by Urbain to an element, celtium, belonging to the family of rare earths, although this element has recently been assumed to possess the atomic number 72. A. A. E.

The K Absorption Spectrum of the Element 72 (Celtium). M. DE BROGLIE and J. CABRERA (*Compt. rend.*, 1923, **176**, 433—434).—Dauvillier has described in a preparation of celtium the presence in the spectrum of several feeble lines undoubtedly belonging to the element of atomic number 72, the presence of which has recently been recorded in several zirconium minerals by Coster and Hevesy. The absorption spectra of X-rays is an excellent means of revealing an element by its discontinuity K , and this method when applied to some minerals has shown the presence of the new element of atomic number 72. W. G.

The High Frequency Spectrum of Celtium. A. DAUVILLIER (*Compt. rend.*, 1923, **176**, 676—679).—A reply to Coster and von Hevesy's criticism (this vol., ii, 80, 171) of the author's attribution to celtium of the lines 1319·4 and 1561·8 X observed in a preparation of ytterbium oxides (A., 1922, ii, 463). It is contended that the difference between the observed wave-lengths and the theoretically calculated values is not outside the limits of possible error, that the lines cannot belong to higher orders of other elements, and that the line β_1 of celtium, lying between the two intense lines 1366·7 of lutecium and 1377·7 of copper, would not be expected to be visible on the photographic plate. G. F. M.

L-Series of Tungsten and Platinum. J. S. ROGERS (*Proc. Camb. Phil. Soc.*, 1923, **21**, 430—433).—The values of the wave-lengths obtained for the L -series of tungsten and platinum are in good agreement with those given by Dauvillier and Coster, although there are discrepancies for some of the fainter lines. A number of new lines have been discovered, and ascribed to definite electron passages within the atom. In the tungsten spectrum, the line 1·4503 has been called α_3 , and the line 1·2489, β_2' , and the former

is ascribed to the passage $M_1 L_1$, and the latter to $N_3 L_1$. Other faint new lines have been observed. In the platinum spectrum, line 1·0660 has been called β_{10} , the line 1·0803 appears to be due to the passage from an O to a L_1 orbit, and the line 1·0375 may be due to the passage $M_1 L_3$. Calculations have been made of the energies of these lines, and good agreement is found with the calculated values. The lines fall on the Moseley graphs.

W. E. G.

Ultra-violet Absorption Spectra of the Cresols. F. W. KLINGSTEDT (*Compt. rend.*, 1923, 176, 674—676).—*o*-Cresol and *m*-cresol have almost the same absorption spectra, having two broad bands occupying approximately the same position as those of phenol at $\lambda=2780$ and 2716 for the former and at $\lambda=2796$ and 2720 for the latter. The coefficients of molecular absorption $\epsilon=1810$ and 1770 . Compared with toluene, the bands are considerably displaced towards the red, and their intensity is about nine times as great. *p*-Cresol has seven bands between $\lambda=2858$ and 2644 . Compared with the *o*- and *m*-cresols, the spectrum of *p*-cresol is displaced 70 \AA . towards the red, the intensity of absorption is greater, and, like other para-derivatives, there are numerous narrow bands instead of two wide bands, this distinction being so characteristic as definitely to identify a para-compound. The seven bands of *p*-cresol can be distributed into three groups, the difference in the frequencies of each group being constant, whilst the intensity of absorption decreases. The mean fundamental period, $\Delta_\lambda^1 = 1217 \text{ \AA}$.

G. F. M.

The Ethylene Chromophor. H. LEY and F. RINKE (*Ber.*, 1923, 56, [B], 771—776; cf. Ley, A., 1917, i, 261; 1919, ii, 40).—A continuation of previous work.

The introduction of a methyl group into stilbene in the α -position causes a diminution of the selective absorption and a displacement of the continuous absorption towards the region of shorter wavelengths. The presence of a second methyl group increases the effect to such an extent that only a trace of selective absorption is observed with 7 : 7'-dimethylstilbene. A methyl radicle attached to the nucleus in the para-position has a normal influence. The spectroscopic analogy between stilbene and cinnamic acid is preserved in the methyl and dimethyl derivatives which contain the substituents in the aliphatic portion of the molecule.

The presence of a chlorine atom in the α -position of styrene has a weak, hypsochromic influence, whereas in the β -position it displaces the absorption towards greater wave-lengths. The absorption curve of 7-chlorostilbene is similar to that of the parent substance, with the exception that the band is sharper and somewhat displaced towards the ultra-violet; nuclear chlorine has a distinct bathochromic effect.

Comparison of the absorption curves of stilbene, 7-phenylstilbene, and 7 : 7'-diphenylstilbene shows that in the region of greater thicknesses or higher concentrations the absorption is progressively

displaced towards the red end, in the region of least transparency the absorption is diminished; with increase in the number of phenyl groups, the extinction coefficients become smaller, and the head of the bands is displaced slightly towards greater wave-lengths.

The additive compound of 7 : 7'-dimethylstilbene and 1 : 3 : 5-trinitrobenzene is markedly less coloured than the corresponding compound from 7-methylstilbene; similarly, in the phenylstilbene group the colour diminishes with increasing number of substituents.

β -Diphenyl-*n*-butane, m. p. 123–124°, is prepared by the action of magnesium on an ethereal solution of α -bromoethylbenzene; an isomeride, b. p. 162–164°/25 mm., appears to be produced simultaneously. Tetraphenylethylene, m. p. 221°, obtained from benzophenone chloride and sodium iodide in the presence of acetone, is reduced by sodium and boiling amyl alcohol to tetraphenylethane, m. p. 209°. α -Chlorostyrene has b. p. 83°/23 mm., 85–85.5°/22.5 mm., 73–74°/15 mm., d_4^{20} 1.0975, and 1.0916 for two different specimens. H. W.

Determination of Constitution by Spectrochemical Methods. The so-called Triphenylvinyl Alcohol. Enolic Salts. H. LEY and W. MANECKE (*Ber.*, 1923, 56, [B], 777–783).—As a result of purely chemical investigation, Meyer and Gottlieb-Billroth (*A.*, 1921, i, 422) have been drawn to the conclusion that the so-called triphenylvinyl alcohol, $\text{CPh}_2\text{:CPh}\cdot\text{OH}$, is actually a ketone, $\text{CHPh}_2\cdot\text{COPh}$. Spectrochemical investigation leads the authors to the same conclusion.

The optical behaviour of “triphenylvinyl alcohol” is completely different from that of triphenylvinyl acetate, $\text{CPh}_2\text{:CPh}\cdot\text{OAc}$, in which the enolic form is fixed. According to previous observations, it is to be expected that the optical properties of triphenylvinyl alcohol would not differ greatly from those of the parent hydrocarbon, 7-phenylstilbene; it is observed, however, that the absorption spectra of the hydrocarbon and triphenylvinyl acetate are closely similar, and differ entirely from that of triphenylvinyl alcohol. The enolic constitution of the latter compound is therefore regarded as impossible. Its ketonic nature is demonstrated by a comparison of its optical properties with those of acetophenone, deoxybenzoin, and β -benzpinacolin, $\text{COPh}\cdot\text{CPh}_3$. Further, the colour of the additive product of “triphenylvinyl alcohol” and 1 : 3 : 5-trinitrobenzene shows that it is not a derivative of stilbene.

The optical behaviour of 9-benzoylfluorene, $\begin{matrix} \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 \end{matrix} > \text{CHBz}$, has been examined in connexion with that of triphenylethanone. The parent hydrocarbon, 9-benzylidenefluorene, is closely analogous to 7-phenylstilbene, but the analogy between triphenylethanone and 9-benzoylfluorene is not at first sight so marked, probably by reason of the increased absorption attributable to the fluorenone ring. The absorption of the sodio-derivative of the enolic form of 9-benzoylfluorene has also been measured as well as that of the free enol (the apparatus required for the latter purpose is described in detail).

The enols, which have been generally investigated spectroscopically, contain a carbonyl group, and it has been assumed that in their salts the metal is also united to this group by a subsidiary valency, whereby an internal complex salt is produced. The authors consider this hypothesis untenable, and prefer to attribute the behaviour of the salts to the presence in them of readily altered, conjugated systems.

H. W.

Mode of Absorption of Triphenylmethane Colouring Matters. E. ADINOLFI (*Atti R. Accad. Lincei*, 1922, [v], 31, ii, 551—554).—Consideration of the various theories advanced to establish chemico-physical connexions between constitution and absorption, together with the results previously obtained (A., 1922, ii, 601), shows that triphenylmethane colouring matters, in solution in water or in methyl, ethyl, isobutyl, or amyl alcohol, give rise to absorption spectra of similar type, and with maxima which undergo increasing displacement as the molecular weight of the solvent increases. To this rule, rhodamine-B and uranine form exceptions, probably owing to re-emission resulting from fluorescence. The two characteristic absorption bands of these colouring matters are due to two distinct vibrators, which in some cases diffuse with unequal velocities, and in others disappear alternately in acid or alkaline solutions, and undergo displacements to different extents in different solvents.

T. H. P.

Infra-red Spectroscopy. V. P. LUBOVICH and (MISS) E. M. PEAREN (*Trans. Roy. Soc. Canada*, 1922, 16, III, 195—212).—The absorption of infra-red radiation by dilute alcoholic solutions of dicyanin, dicyanin-A, pinacyanol, nigrosin-SS, alizarin-blue-S, and Eastman red sensitiser No. 700 has been investigated. The results indicate that photography of the infra-red spectrum can be readily extended to λ 20,000 Å. Nigrosin and alizarin-blue are more suitable for the photography of certain regions of the spectrum than dicyanin or dicyanin-A. The infra-red spectra of tin, lead, bismuth, zinc, and antimony have been investigated from λ 8000 Å. to λ 11,000 Å. Particulars are given of the application of the "thalofide cell" to determine wave-lengths in infra-red spectra.

J. S. G. T.

A Simple Appliance for Detecting Traces of Fluorescent Substances. ED. MOREAU (*J. Pharm. Chim.*, 1923, [vii], 27, 184—187).—A box lined with black paper measuring about 8 cm. cube has a narrow observation slit in the middle of one side and a hole in the top opposite to the slit just large enough to take the test-tube containing the solution to be examined. This is illuminated from above by an electric lamp which is shaded from the observer by means of a cylinder fixed to the top of the box. By means of this appliance the least traces of fluorescence can with certainty be detected, and minute quantities of urobilin in biological work, fluorescein for detecting infiltrations in sanitary investigations, etc., can with certainty be found.

G. F. M.

Destruction of the Fluorescence of Dilute Solutions by Ultra-violet Light. (MISS) F. M. CALE (*Trans. Roy. Soc. Canada*, 1922, 16, III, 257—263).—Determinations have been made of the decrease of fluorescence of a dilute aqueous solution of *æsculin* by exposure to ultra-violet light. After the solution was once exposed, its fluorescence continued to decay even when the solution was kept in absolute darkness. On subsequent exposure of the solution to ultra-violet light, the rate of decay decreased very rapidly at first, then steadily. On further exposure, after an interval of several hours, the rate of decay was greater than before the interval. Ozone bubbled through the solution caused a very rapid decay of the fluorescence, the solution finally possessing the same colour and absorption spectrum as that transformed by ultra-violet light.

J. S. G. T.

Tesla-luminescence Spectra. I. The Form of Apparatus and the Spectrum of Benzene. WILLIAM HAMILTON McVICKER, JOSEPH KENNETH MARSH, and ALFRED WALTER STEWART (*T.*, 1923, 123, 642—654).

Luminescence of Compounds formed by the Action of Magnesium on *p*-Dibromobenzene and Related Compounds. W. V. EVANS and R. T. DUFFORD (*J. Amer. Chem. Soc.*, 1923, 45, 278—285).—Solutions of magnesium *p*-bromophenyl bromide in ether are strongly chemi-luminescent, so much so that if it is dropped from a rod through air the luminescence is visible in daylight; stirring the solution in air gives a strong luminescence, and when poured from a tube it glows with a greenish-blue light which suggests molten metal. The luminescence of this substance has been compared with that of other aromatic halogen compounds, when the substances are exposed to air or oxygen. No luminescence results from the action of other gases, such as carbon dioxide, hydrogen sulphide, sulphur dioxide, and nitrogen on Grignard compounds. The spectrum of the chemi-luminescence of magnesium *p*-bromophenyl bromide has been investigated by the use of light filters, and its lower and upper limits have been found to lie within the region λ 5200— λ 3500. This spectrum is found to be distinct from that of the associated fluorescence spectrum. Photographs of two kinds of fluorescence have been obtained from the oxidation products, one giving a single-banded spectrum, the other an entirely different multiple-banded spectrum.

J. F. S.

Spectral Study of the Triboluminescence of certain Substances. HENRI LONGCHAMON (*Compt. rend.*, 1923, 176, 691—693; cf. A., 1922, ii, 603).—A spectral study was made of the triboluminescence of tartaric acid, cadmium sulphate, uranium nitrate, and calcium fluoride. In spite of their widely different chemical constitution and crystalline form, the spectrum of the triboluminescence was in all cases the line spectrum of nitrogen. In the case of the uranium salt, however, and it would probably be so with other fluorescent substances such as the platinocyanides, etc., the triboluminescence was masked by the secondary pheno-

menon of fluorescence. Nevertheless, by the spectrographic method after an exposure of six hours, the presence of four other lines, coincident with the four most intense nitrogen lines, was revealed.

G. F. M.

Investigations on the Dependence of Rotatory Power on Chemical Constitution. XIX. The Rotatory and Refractive Dispersions and the Absorption Spectrum of *d*- γ -Nonyl Nitrite. ROBERT HOWSON PICKARD and HAROLD HUNTER (T., 1923, 123, 434—444).

Rotatory Dispersion of the Esters of Lactic Acid. I. Normal Esters. CHARLES EDMUND WOOD, JOHN EDWARD SUCH, and FRANK SCARF (T., 1923, 123, 600—616).

Magnetic Rotatory Dispersion in Gases. T. H. HAVELOCK (*Phil. Mag.*, 1923, [vi], 45, 560—576).—A comparison is made between the ordinary dispersion of certain gases and the dispersion of magnetic rotation in regions free from absorption. The formulæ derived from a simple static molecule with one type of vibrator are sufficient for both dispersions in the visible spectrum for gases like hydrogen and nitrogen. In the case of oxygen, it is necessary to include the magnetic properties of the molecule before a complete theory can be formed. Omitting paramagnetic effects, expressions for the rotatory dispersion are obtained for the anisotropic static molecule, such as have been used for the ordinary dispersion of hydrogen. The Bohr molecule of hydrogen is studied numerically. In order that the adjustable constants of the ordinary dispersion formulæ may be known more accurately, it is desirable that parallel sets of observations on ordinary rotatory dispersion be made on the same gas under similar conditions.

W. E. G.

The Mechanism of Photochemical Processes. II. The Behaviour of a Dry Mixture of Oxygen and Hydrogen. ALFRED COEHN and HEINRICH TRAMM (*Ber.*, 1923, 56, [B], 455—458).—A repetition of Baker's work (T., 1902, 81, 4000) has confirmed the observation that mixtures of hydrogen and oxygen which have been desiccated by prolonged contact with phosphoric oxide can be heated to redness in Jena glass tubes without the occurrence of an explosion. On the other hand, the presence of moisture does not appear to exert an appreciable influence on the rate of combination of hydrogen and oxygen when exposed to the ultra-violet light of the Heraeus lamp. Similar observations have been made previously (A., 1921, ii, 476) with mixtures of carbon monoxide and oxygen.

H. W.

The Mechanism of Photochemical Processes. III. The Effect of Desiccation on the Combination of Hydrogen and Chlorine. ALFRED COEHN and HEINRICH TRAMM (*Ber.*, 1923, 56, [B], 458—462).—The chlorine is dried and purified by fractional distillation at the temperature of liquid air. The hydrogen is prepared electrolytically, passed over heated palladised asbestos, and thence at increasing pressure through a series of U-tubes, in

each of which it is subjected to protracted cooling by liquid air. The moist and dry mixtures are exposed in quartz tubes to the light of a 100 candle-power Osram lamp; the gases are subsequently treated with neutral potassium iodide solution, and the liberated iodine and the hydrogen chloride estimated. Under identical conditions, the union of hydrogen with chlorine in the presence of moisture occurs quantitatively within twelve minutes, whereas in the dry mixture there is no sign of combination after two hours.

It has been shown previously (Coehn and Wassiljewa, A., 1909, ii, 846; Coehn and Stackardt, A., 1917, ii, 5) that hydrogen chloride, bromide, and iodide are decomposed to some extent by exposure to ultra-violet light. The presence of moisture is found to be without influence on the rate of decomposition of hydrogen bromide or iodide, whereas in the case of hydrogen chloride decomposition of the completely dry gas is not observed.

The velocity of combination of carbon monoxide with chlorine can be greatly reduced by thorough desiccation of the gases, but the process invariably takes place at an appreciable rate. Reaction in the case of sulphur dioxide and chlorine is completely inhibited by protracted drying of the gases. H. W.

The Mechanism of Photochemical Processes. IV. The Behaviour of Dry Mixtures of Hydrogen and Chlorine in Ultra-violet Light. ALFRED COEHN and GERHARD JUNG (*Ber.*, 1923, 56, [B], 696—698).—It has been shown recently (preceding abstract) that dry hydrogen and chlorine do not combine with one another when exposed to visible light. Under similar conditions, union is quantitative within twelve minutes under the influence of ultra-violet light; the wave-length of the active rays is less than $254\ \mu$. H. W.

Spectrophoto-electrical Sensitivity of Bournonite and Pyrrargyrite. W. W. COBLENTZ and J. F. ECKFORD (*U.S. Bureau of Standards Sci. Paper No. 451*, 1922).—A study of the effect of chemical constitution on spectrophoto-electrical sensitivity. The minerals were tested in the spectral region from $0.3\ \mu$ in the ultra-violet to $2\ \mu$ in the infra-red. Bournonite, $3(\text{Cu}_2\text{Pb})\text{S}_3\text{Sb}_2\text{S}_3$, has a high spectrophoto-electrical sensitivity from the extreme violet to $1\ \mu$ in the ultra-red with two wide, ill-defined maxima in the region of $0.55\ \mu$ and $0.95\ \mu$, its reaction being entirely different from that of the constituent sulphides. The intrinsic intensity is greatly increased with fall of temperature, the maxima shifting towards the short wave-lengths. The spectrophoto-electrical reaction of pyrrargyrite, Ag_3SbS_3 , consists at 22° of a wide, unsymmetrical maximum in the ultra-violet with a weak, ill-defined maximum in the region of $0.63\ \mu$. It also differs from that of the constituent sulphides, but resembles that of proustite (silver arsenic sulphide). At -165° , pyrrargyrite reacts electrically to all wave-lengths from the extreme ultra-violet to $1.5\ \mu$, but the greatest reaction is localised in the band at $0.63\ \mu$. On increasing the intensity of the radiation stimulus, there is a more rapid increase

of the response of bournonite and pyrargyrite in the long wave-lengths than the short. In a general way, the properties of photo-electrical reaction spectra and absorption spectra are affected analogously by chemical constitution, indicating that the two phenomena may have a common source within the molecule.

T. H. B.

The Distribution of the Length of α -Rays. (MLLE) IRÈNE CURIE (*Compt. rend.*, 1923, 176, 434—437).—A study of the distribution of the length of rays by photographing the trajectories obtained in an apparatus similar to that described by Wilson (A., 1913, ii, 92). On account of the difficulty of knowing in a precise manner the density of the gas in the chamber at the moment when the rays are emitted, the measurements are essentially a comparison of the length of the rays emitted at the same instant in an exposure. The rays used were those of polonium. For each exposure two curves are traced, namely, the number, n , of rays the lengths of which are comprised between $x-\Delta x$ and $x+\Delta x$, and the number, N , of rays of length superior to x in function of x . The first curve shows the existence of the most probable trajectory, l , of the rays. The second curve, the fall of which resembles that of Bragg's curve, shows that it is possible to define an extrapolated trajectory, p , in the same manner as Henderson defines it for the ionisation curve (A., 1921, ii, 617). Several hundred rays were photographed and curves are given for the results of 142 rays. The ratio of $p' : p$ for the rays of polonium and radium-*C* is exactly equal to that given by Geiger from the ionisation curve, namely, $6.971 : 3.925 = 1.775$ (*Z. Physik*, 1922, 45). Except for the very short rays the results as plotted correspond exactly with a law of probability of the form Ke^{-kx} . About 90% of the rays have a length between $l-1$ and $l+1$ mm. The second curve shows that $p=l+0.7$ mm., and taking for p the value 3.92 mm. as given by Geiger (*loc. cit.*) the most probable length of the trajectory will be 3.85 mm. in air at 15° and 760 mm. As a corollary, it is necessary to admit that the ionising power of an α -ray along its trajectory commences by increasing, passes a maximum 4—3 mm. from its end and then decreases rapidly during the last millimetres.

W. G.

Extension of the X-Ray into the Ultra-violet Spectrum. OTTO STUHLMAN, jun. (*Science*, 1922, 56, 344).—When thermions liberated from a tungsten filament are accelerated and allowed to impinge on a metal grid maintained at a variable positive potential, secondary electrons are emitted from the grid, the number being measured by means of a galvanometer in series with the grid and a plate maintained at a constant positive saturation potential. When the secondary current is plotted as a function of the accelerating voltage, a sudden change in the slope of the curve occurs at critical potentials, the equivalent wave-lengths being calculated from the energy-quantum relation $V(\text{volts})L(\text{\AA.})=12320$. Preliminary measurements are given in the case of tungsten and iron.

A. A. E.

The Increase of the Dispersion in the Photo-electric Spectra of X-Rays. RENÉ LEDRUS (*Compt. rend.*, 1923, 176, 383—385).—The dispersion is best increased by exciting the electronic emission by means of an X-radiation, the frequency of which is slightly superior to the frequencies of the layers to be studied, and by adjusting the magnetic field so as to bring the regions studied towards the edge of the photographic plate which corresponds with high values of the radius of trajectory of the electron. These conditions have been fulfilled in a study of the spectrum of velocities of electrons emitted by a radiation of gold excited by the radiation from a molybdenum anti-cathode. Seven rays were observed and the results obtained agree closely with those calculated. W. G.

The Colson-Russell Effect, Photochic, Radiation from Metals, Photoactivity, and Other Similar Radiation Phenomena. E. RUMPF (*Jahrb. Radioaktiv. Elektronik*, 1923, 19, 214—222).—A historical survey is given of the literature on this subject. The activity of a zinc surface has been investigated with a view to testing if the darkening of a photographic film is due to radiation or to the emission of corpuscles. Contrary to the observations of Blaas and Czermak (*Physikal. Z.*, 1904, 5, 363), the colour of the gelatin film is without effect. The action on the photographic film is not stopped by 16 sheets of aluminium foil. Since the foil is pierced by numbers of small holes, the possibility of diffusion of gases from the zinc plate to the film has not been eliminated. A powerful stream of air over the surface of the zinc was effective, however, in preventing any darkening of the film, and by maintaining a potential difference of 150 volts between the film and the zinc plate, it was shown that the effect cannot be due to electrically charged corpuscles. The only explanation of the phenomenon would thus appear to lie in some chemical influence, such as that suggested by Russell, who ascribed the action to hydrogen peroxide formed during the oxidation of the zinc plate in the presence of water vapour. W. E. G.

Positive Rays in Simple Gases. J. J. MCHENRY (*Phil. Mag.*, 1923, [vi], 45, 433—443).—A study of the proportion of atomic and molecular positive rays of the simple gases under varying conditions of pressure in the discharge tube. The presence of mercury vapour in oxygen gas causes most of the positive rays to become atomic, and its removal always brings into prominence the molecular positive rays. Mercury seems to exert no effect on the nitrogen positive rays. The slower positive rays are mostly atomic, whilst those of greater energy are mostly molecular. Since the energy of a positive ray depends on the potential difference through which it falls to the cathode, those of small energy must be produced near the cathode. In this region ionisation by the cathode rays is at a minimum, and ionisation by positive rays at a maximum, so it would appear that the positive rays tend to give atomic ions, and cathode rays molecular ions. This view is in agreement with experiments made on the action of a magnetic field at varying distances from the cathode, in which it is shown

that the molecular positive rays are reduced in increasing measure as the distance from the cathode increases. The ratio of molecular to atomic positive rays is the greater the lower the pressure and the higher the voltage of the tube. In mixtures of one volume of hydrogen and two volumes of oxygen, the hydrogen positive rays are smaller in number than the atomic positive rays, but the ratios O_1/O_2 and H_1/H_2 are practically the same in the two cases. This regularity does not persist with other mixtures of hydrogen and oxygen. Carbon monoxide is more easily broken down into its atoms than oxygen, and the proportion of atomic positive rays is much greater in the former gas than in pure oxygen.

W. E. G.

The Radiation and Ionisation Potentials of the Rare Gases, and the Singlet and Enhanced Series of Argon. W. M. HICKS (*Phil. Mag.*, 1923, [vi], 45, 480—496).—The true radiation and ionisation potentials are defined as the potentials required to produce radiation or ionisation of the atom when this is in its radiating configuration. The observed ionisation potential should be the sum of the dissociation potential and the true ionisation potential. In hydrogen, both radiation and ionisation potentials are observed, on account of the long life of the hydrogen atom. In the rare gases, the observed potentials are too large to represent the true values, although these gases are already in the atomic state. It is suggested that the ordinary atom in these gases is not capable of ionisation, but requires preliminary work to change it into a configuration capable of emission. The nature of these prepared atoms is discussed, and the true radiation and ionisation potentials deduced from the spectral lines of these gases. Evidence is adduced from the work of Kammenstine (*Astrophys. J.*, 1922, 55, 343) as to the existence of prepared atoms of the rare gases with long life periods. The life of a prepared helium atom must be of the order $1/200$ of a second, since a frequency of 220 cycles per second is just sufficient to enable an arc to strike in helium at 4 volts. Helium gives two types of prepared atoms, the first requiring about 1 volt less than the second for their preparation and possessing the longer life. The two forms are represented by $\cdot \bullet - \bullet$, and $\bullet \bullet - \bullet$, where a large dot represents an electron, a small dot a potential level, and a dash the nucleus. The true radiation and ionisation potentials of helium are given as follows: radiation potentials, $He=1.14$; $He^+=7.4$; ionisation potentials, $He=4.75$; $He^+=13.5$ volts. The ionisation and radiation potentials of neon may be explained, if there are three kinds of prepared atoms for this gas. The work required to change the first prepared state to the second is 6.1 volts, and to change the latter into the third is 11.8 volts. A similar analysis is made for argon from the work of Horton and Davies on radiation and ionisation potentials of argon, and from its spectrum.

W. E. G.

Luminous Discharge in Iodine. Determination of the Ionisation Potential of Iodine. W. ALBERT NOYES, jun. (*J. Amer. Chem. Soc.*, 1923, 45, 337—342).—The theory of the luminous

discharge put forward by Gibson and Noyes (A., 1921, ii, 610; 1922, ii, 812) has been discussed with reference to its applicability to the luminous discharge in an electro-negative gas or vapour such as iodine vapour. The discharge potential in iodine vapour at various temperatures between -3° and 29° has been determined. From the experimental values the most probable value of the ionisation potential of iodine is found to be 10.0 ± 0.2 volts. This leads to the value 8.4 volts as the ionisation potential of the iodine atom which would correspond with a wave-length of 1472 Å. It is impossible to verify this from the spectrographic data now available.

J. F. S.

Liquid Chlorine as an Ionising Solvent. J. MENNIE and D. McINTOSH (*Trans. Roy. Soc. Canada*, 1922, 16, III, 301—305).—In agreement with the observations of Johnson and McIntosh (A., 1909, ii, 881), the authors find no evidence of ionisation when inorganic substances or ordinary organic compounds are dissolved in liquid chlorine. Ethyl ether, ethyl alcohol, acetone, and ethyl acetate dissolved in liquid chlorine yield conducting solutions when hydrochloric acid is added, and determinations are detailed of the variations of the conductivities of these solutions as the amount of acid is increased up to 2.5 molecular proportions. In the case of alcohol, the conduction is due to the ionisation of an oxonium acid compound by the acid. The results obtained with a solution of acetone in toluene, to which hydrochloric acid was added, resembled those for the corresponding liquid chlorine solution, but the actual conductivities were much smaller in the former case.

J. S. G. T.

Condition of Bismuth Salts in Aqueous Solutions and the Molecular Electrode Potential of Bismuth. DAVID F. SMITH (*J. Amer. Chem. Soc.*, 1923, 45, 360—370).—The electrical conductivity and solubility of bismuth nitrate have been determined in solutions of nitric acid containing various quantities of acid at 25° . The results indicate that bismuth nitrate exists in solutions containing a considerable excess of nitric acid mainly in the form of partly ionised normal salt. Conductivity measurements of solutions of bismuth perchlorate show that the very soluble basic salt, $\text{Bi}(\text{OH})_2\text{ClO}_4$, has the conductivity of a non-hydrolysed uni-univalent salt like potassium nitrate, and that it is converted into less basic salts such as $\text{Bi}(\text{OH})(\text{ClO}_4)_2$ and $\text{Bi}(\text{ClO}_4)_3$ only slowly on the addition of an excess of acid. Even when the ratio of perchlorate to bismuth is as much as 4:1, not more than 40—50% of the bismuth oxyperchlorate is converted into the hydroxy-salt, $\text{Bi}(\text{OH})(\text{ClO}_4)_2$. *E.M.F.* measurements of cells of the type $\text{H}_2|\text{HClO}_4||\text{HClO}_4+\text{BiOClO}_4|\text{Bi}$ have been made at 25° for various concentrations of perchloric acid and the bismuth salt. The results fully confirm the conclusions drawn from the conductivity values. The measurements lead to the following values for the molecular electrode potential of bismuth, which were calculated on the two assumptions that the bismuth in solution exists entirely as the ion BiO^+ and the ion $\text{Bi}(\text{OH})^{++}$, respectively: $\text{Bi}|\text{BiO}^++\text{H}^+$:

-0.314 volt, $\text{Bi}|\text{Bi}(\text{OH})^{++}+\text{H}^+ : -0.298$ volt. For comparative purposes, the electrical conductivity of solutions of nitric and perchloric acid have also been measured at 25° . J. F. S.

Electrode Potential of Bismuth determined by Equilibrium Measurements. ERNEST H. SWIFT (*J. Amer. Chem. Soc.*, 1923, 45, 371—377; cf. preceding abstract).—The position of the equilibrium between bismuth and copper perchlorates and metallic copper and bismuth has been determined at 25° by shaking together the metal and the perchlorate of the other metal and analysing the equilibrium mixture. The reaction is represented by the equation $3\text{Cu} + 2\text{Bi}(\text{ClO}_4)_3 \rightleftharpoons 2\text{Bi} + 3\text{Cu}(\text{ClO}_4)_2$, and from the composition of the equilibrium solution the value of the molecular electrode potential of bismuth has been calculated on the assumption that the bismuth exists in such solutions entirely as the ion BiO^+ and on the assumption that it exists solely as the ion $\text{Bi}(\text{OH})^{++}$ and that the free perchloric acid present is completely ionised. The following values, referred to the molecular hydrogen electrode, were obtained: $\text{Bi}|\text{BiO}^+ + \text{H}^+|| = -0.318$ volt, $\text{Bi}|\text{Bi}(\text{OH})^{++} + \text{H}^+|| = -0.310$ volt. If the copper salt is regarded as completely ionised, whereby the errors in the ionisation assumptions are partly compensated, there result values which differ by about 5 m.-volt from the above, namely -0.323 and -0.314 volt, respectively. These results are in fair agreement with the values -0.314 and -0.298 volt obtained by Smith (*loc. cit.*) from *E.M.F.* measurements. J. F. S.

Hydrogen-Chlorine Cell. F. FOERSTER [with A. NOBIS, and H. STÖTZER] (*Z. Elektrochem.*, 1923, 29, 64—79).—With the object of finding a method by which chlorine and hydrogen can be combined on the large scale to form hydrochloric acid, the authors have investigated the element $\text{Pt}, \text{H}_2|\text{HCl}|\text{Cl}_2, \text{Pt}$. The cell was built up in a U-tube which was divided at the bend by a porous diaphragm, platinised electrodes were inserted and chlorine was led into one side, hydrogen into the other. It is shown that with such an arrangement current is furnished without any great amount of polarisation up to 10^{-2} amperes/cm.² of platinum surface in the solution. The action consists in the combination of hydrogen and chlorine to form hydrogen chloride, and since the transport number of the hydrogen-ion is greater than that of the chloride-ion, the concentration of the hydrochloric acid in the chlorine side of the cell increases much more rapidly than in the hydrogen side. By increasing the temperature, the terminal voltage of the cell increases up to a definite maximum temperature which is higher the larger the current drawn from the cell. At 80° , however, the voltage falls when large currents are drawn from the cell, because the reduction in the gas concentration retards the electromotive action more than it would normally have been increased by the increase in temperature. The velocity of the electromotive action of the chlorine is very great and independent of the nature of the electrode, platinum or various forms of carbon being equally good. Hydrogen, however, requires the catalytic action of platinum black to give it a somewhat larger activity, and even when this is used the

reaction velocity of the hydrogen is not very large, so that a marked polarisation appears when considerable quantities of current are withdrawn. The electromotive activity of the hydrogen is restricted to the thin layer of the electrolyte covering the surface of the electrode which protrudes into the gas atmosphere. To increase the surface layer and to keep the concentration of hydrogen in it sufficiently high to furnish the necessary amount of current, it is essential that a very rapid stream of hydrogen should be passed into the solution. Platinised carbon will serve as electrode just as well as platinised platinum. The action is very slow if a bright platinum electrode is used, and it does not take place at all with carbon electrodes. In apparent connexion with this is the fact that the overvoltage of hydrogen on carbon electrodes is considerable. On paraffined carbon electrodes the overvoltage of hydrogen shows unexpectedly large variations with time. Combinations such as $H_2|carbon|HCl|carbon|Cl_2$ or $H_2|bright\ Pt|HCl|carbon|Cl_2$ give *E.M.F.* values which arise from concentration cells of the form Cl_2 (of small partial pressure) $|HCl|Cl_2$ ($p=1\ atm.$). If on a platinised electrode the process $H_2 \rightarrow 2H^+ + 2e^-$ is no longer sufficient to furnish the current, the electrode becomes polarised to $+0.8 - +0.9$ volt, and the current furnishing process is then $Pt \rightarrow Pt^{++} + 4e^-$, which continues as long as the platinum deposit lasts. The potential of the element $Pt|0.01M\ H_2PtCl_6\ in\ 2NHCl||$ has been measured and found to have the value $+0.74$ volt. Oxygen is capable, if but slowly, of displaying an electromotive activity on carbon electrodes, which appears to be brought about by a small quantity of a carbon oxide present on the electrode. By using comb-shaped electrodes, of which the one in the hydrogen part of the cell is platinised, cells of about 600 c.c. capacity can be constructed which will furnish a continuous current of $0.5 - 0.63$ ampere at 0.75 volt for many hours. To achieve this result, the hydrogen must be led in at $10 - 30$ litres per hour. In the chlorine part of the cell $10N$ -hydrochloric acid is produced with a 90% yield calculated on the chlorine led in, and a material yield on the hydrogen of $1 - 2\%$. In view of the necessity of using highly platinised electrodes and a very high rate of flow of hydrogen, it is shown that the process considered is impossible for the commercial manufacture of hydrochloric acid. The burning of hydrogen in chlorine is a more suitable and at the same time a simpler process for this purpose.

J. F. Š.

New Form of Electrical Resistance of Electrolytes.

MAURICE PHILIPPSON (*Bull. Acad. roy. Belg.*, 1922, [v], 8, 76-80).—Since an electrolytic ion possesses inertia, the magnitude of an alternating current passing through an electrolyte should decrease as the frequency of the current increases, the effect being analogous to that of electromagnetic self-induction. An electrolyte should, in fact, possess two kinds of resistance, frictional and kinetic. The author obtained evidence of the existence of the latter kind of resistance and succeeded in measuring the "self-inductance" and "kinetic reactance" of an electrolytic cell,

using a resonance method, "tuning" a circuit containing the cell to one in which induced alternating currents of known frequency were produced. For a cell of 20 ohms resistance, containing a normal solution of potassium chloride, the kinetic reactances corresponding with frequencies of 4×10^5 , 1.5×10^6 , and 3×10^6 , were found to be respectively 0.60, 13.09, and 7.35 ohms, a maximum figure also being obtained at frequency 1.5×10^6 when a cell of 100 ohms resistance was used, or when sodium lactate or acetate was substituted for potassium chloride. For frequencies of 1×10^6 to 3×10^6 , the kinetic reactance of a cell is roughly proportional to the volume of solution between the electrodes. E. E. T.

Anodic Behaviour of Metals in Non-aqueous Solutions.

III. Iron, Nickel, Cobalt, and Chromium in Ethyl-alcoholic Solutions of Nitrates. UMBERTO SBORGI and GINO CAPPON (*Nuovo Cim.*, 1922, [vi], 23, 303—331).—The authors have investigated the anodic behaviour of various metals in ethyl-alcoholic solutions of calcium and ammonium nitrates, the apparatus employed being similar to that previously used (A., 1921, ii, 572), but modified to render it applicable at higher temperatures and to allow of the separate collection of the anodic and cathodic gases.

Cobalt exhibits complete activity, dissolving as a bivalent metal at all current densities from 0.03 to 3 amps. per sq. cm., and at all temperatures (from -10° to 60°). The other three metals show passivity phenomena. Nickel is passive at all temperatures from -10° to 25° . At 60° , it is partly active if the current-density is high (0.3—3 amps. per sq. cm.); in the ammonium nitrate solution, at low current density (0.03), not only is there complete electrochemical activity, but superposed on this is chemical activity, nickel being attacked by alcoholic ammonium nitrate, particularly at high temperatures. With iron, there is complete passivity at all temperatures and current densities employed.

Chromium shows in the alcoholic solutions passivity phenomena similar to those observed in aqueous solutions, the attack being approximately (but somewhat less than) hexavalent; chromic, and not chromate, ions appear.

In the alcoholic calcium nitrate solutions, there is formed at the cathode a badly conducting layer composed, partly at least, of calcium ethoxide. In all cases in which partial or total passivity is observed at 25° , oxygen is liberated at the anode in amount corresponding with 7.5% of the total current, the remainder, allowing for the current expended in dissolving the metal, giving rise to acetaldehyde; the latter is formed almost quantitatively, only a trace of acetic acid being obtained. T. H. P.

Application of the Theory of Magnetism to the Calculation of Atomic Diameters. J. F. T. YOUNG (*Trans. Roy. Soc. Canada*, 1922, III, 16, 49—61).—Attention is directed to the periodic distribution of paramagnetic and diamagnetic properties among the elements arranged in the customary periodic table. A mathematical theory, applicable either to the dynamic or static atomic model, permitting atomic dimensions of an element to be calculated

from the value of the magnetic permeability is detailed, and the results are applied to calculate the atomic radii of 26 elements. The values obtained are of the correct order in all cases.

J. S. G. T.

The Specific Heat of Saturated Benzene Vapour, and the Adiabatic Curve of the Liquid-Vapour Mixture. G. BRUHAT and A. DELAYGUE (*J. Phys. Radium*, 1923, 4, 1—10).—From the experimental critical constants of benzene, its specific heat at low pressure, and its heat of evaporation, deductions have been made of the specific heat of the saturated vapour over a range of temperatures. At low temperatures, and in the neighbourhood of the critical temperature, this specific heat is negative, but at intermediate temperatures becomes positive. The values deduced for the two inversion points, 121° and 254° , are in good agreement with the experimental values 122° and 258° (cf. A., 1922, ii, 348). From the specific heats of the saturated vapour, the entropies of the vapour, the liquid, and mixtures of both have been deduced for temperatures ranging from ordinary temperatures up to the critical temperature. On a diagram, in which values of the entropy are plotted against temperature, the paths of the points for which an adiabatic expansion does not change the relative amounts of the two phases is indicated. By employing Young's tables, the usual volume-temperature and pressure-temperature diagrams may be constructed.

W. E. G.

The Specific Heats of Nitrous and Nitric Oxides. J. R. PARTINGTON and W. G. SHILLING (*Phil. Mag.*, 1923, [vi], 45, 416—430).—The specific heats of nitrous and nitric oxides are of special interest from the point of view of the Lewis-Langmuir theory, because of the similarity of the electronic configurations of nitrous oxide and carbon dioxide, and of nitric oxide, carbon monoxide, and nitrogen. Nearly all the previous work on nitrous oxide was vitiated by the use of impure gas, and results varying from $C_p/C_v=1.25$ — 1.32 are recorded in the literature. For nitric oxide, previous values range from 1.38 — 1.415 . The nitrous oxide in the present experiments was freed from oxygen and nitrogen by passing it through a tube immersed in liquid air. The ratio of the specific heats of the two gases was determined by measurement of the relative velocities of sound in these gases and in pure dry air. The effect of the tube on the velocity of sound was eliminated. It was shown that Wohl's equation of state has no advantage over that of Berthelot for the reduction of the results, and that of the latter is employed as the basis of the calculation of the specific heats. The values obtained were, for nitrous oxide, $C_p/C_v=1.302$, $C_p=8.799$ cal., $C_v=6.758$ cal.; for nitric oxide, $C_p/C_v=1.400$, $C_p=6.990$ cal., and $C_v=4.993$ cal.

W. E. G.

The Meaning of a and b in the Equation of State. ANGUS F. CORE (*Phil. Mag.*, 1923, 45, [vi], 622—624).—In the general virial equation, $pv=RT+B/v$, the term B/v does not naturally fall into two parts, one of which is proportional to the temperature,

RTb/v , and the other independent of the temperature a/v . It is necessary to define either a or b . Thus a/v may be defined as half the work necessary to abstract N molecules chosen at random from the interior of the gas to infinity outside the gas, the other molecules remaining fixed in position. Thus defined a/v corresponds most closely with the equation of van der Waals. The term RTb/v cannot be called the collision virial, for when the molecules contain a hard kernel it does not in general reduce to the collision virial of Reinganum. The effect of making RTb/v equal to the collision virial is critically discussed, and shown to lead to $a/v=0$ if the molecule is regarded as a hard sphere without external field.

W. E. G.

Freezing Points of Organic Substances. VII. JEAN TIMMERMANS (*Bull. Soc. chim. Belg.*, 1922, **31**, 389—397; cf. A., 1921, ii, 622).—The freezing points of a further 68 organic liquids are given in tabular form. The results confirm the author's previous conclusion that the alternation of melting points between the odd and even members of a homologous series is a general phenomenon, and allow this generalisation to be extended to include substances possessing two hydrocarbon chains linked by a central characteristic group (secondary amines, ethers, alkyl sulphides, etc.). Inverse alternation, in which the odd members of a series melt at a higher temperature than the adjacent even members, is shown to be frequent, even in series of symmetrical compounds. The melting points of the higher terms of all the homologous series considered tend towards a common value of 117° and, further, for the paraffins and most of their monosubstitution derivatives, it is found that the C_{30} member melts at about 65° , the C_{16} member at about 20° , and the C_8 member at about -45° . Compounds containing an amino- or a hydroxyl-group do not conform to this rule, their melting points being always higher than those quoted above. Amongst the lower members of a series there is often considerable and irregular variation in the melting points of successive members, but a minimum is usually observed at about the C_3 term. H. H.

Outer Jacket for Beckmann's Boiling-point Apparatus. JAMES FREDERICK SPENCER (*J. Soc. Chem. Ind.*, 1923, **42**, 126).—An outer jacket for the Beckmann boiling-point apparatus is described. The jacket is made on the same plan as the usual porcelain jackets, but is of copper. The mica windows are carried by light copper castings brazed to the inner and outer walls of the jacket. Only one side tube is attached to the jacket and this serves for putting the solvent and beads into the jacket and also for carrying the condenser. The boiling tube is supported by a ring of cork placed at the top of inside wall of the jacket. The jacket is superior to porcelain and glass jackets since it reduces the breakage and danger of fire with inflammable liquids to a minimum, and since it is less sensitive to draughts the equilibrium temperature is reached more rapidly and becomes steady much more quickly.

J. F. S.

Comparison of the Normal Boiling Temperatures of Undesiccated Sulphur as Measured by the Dynamic and Static Methods. ALAN W. C. MENZIES (*J. Amer. Chem. Soc.*, 1923, 45, 327—331).—Since the boiling point of sulphur is used as a standard in thermometry, the author has redetermined this value by both the static and dynamic methods with the object of ascertaining whether or no the equilibrium between liquid sulphur freshly condensed from recently generated sulphur vapour and sulphur vapour occurs at the same temperature as that between liquid sulphur and vapour of a greater age, at the same pressure near to 760 mm. The results show that the boiling point of undesiccated sulphur is the same whether the dynamic or the static method be used. The actual values are not given in the paper, but it is stated that the two values do not differ by more than 0.02° , an amount which is not outside the estimated error of the experiment. It is suggested that this similarity might not be found if the sulphur were accidentally or intentionally intensively desiccated. The statement that delay may occur before a new phase, freshly formed, reaches its equilibrium constitution and properties, has been examined for certain cases of liquids and vapours.

J. F. S.

A New Process of Microsublimation. RICHARD KEMPF (*Z. anal. Chem.*, 1923, 62, 284—291).—The substance to be sublimed is placed on a square brass plate, 12 cm. square and 1 cm. thick, heated by means of two resistors of nickel-chromium wire connected with an external resistance and regulator. The resistors are so arranged that they may be used separately or together, either in series or in parallel. The layer of substance is made as thin as possible and is covered, at a distance of 0.1 to 0.01 mm., with the microscope slide. In this arrangement the temperature of the plate can be kept constant over long periods and by suitable cooling of the slide, sublimates of most substances in characteristic forms may be obtained at comparatively low temperatures, *e.g.*, for mercuric chloride 17° , arsenic and sulphur 50° , stearic acid 38° , vanillin 53° , indigotin 95° , cocaine 36° , strychnine 103° . These temperatures are considerably lower than those at which the substances sublime in a vacuum. By this process characteristic crystalline deposits from evaporated human urine and blood may be obtained, even if present as stains on fabrics, so that the method may find application in forensic analyses.

A. R. P.

Heat of Oxidation of Glucinum. H. COPAUX and CH. PHILIPS (*Compt. rend.*, 1923, 176, 579—580).—A redetermination of the heat of oxidation of glucinum by measuring separately the heat of dissolution of the metal and its oxide in acids, and taking into account this time the variation from unity of the specific heat of the acid solutions used, gave a value of 131.3 Cal. The heat of oxidation of calcium determined in a similar way as a check on the correctness of the principles employed was 150 Cal., a value in close agreement with that obtained by Guntz by other methods.

G. F. M.

Heats of Combustion and Energy of Dissociation. III.
A. VON WEINBERG (*Ber.*, 1923, 56, [B], 463—466; cf. A., 1920, ii, 668—669).—A reply to Fajans (A., 1922, ii, 818) and to Hückel (A., 1922, ii, 818).
H. W.

Calorimetric Researches. III. Some Remarks on an Attempt of Swientoslawski to Calculate the Heat of Combustion of Benzoic Acid by a Semi-theoretical Method.
P. E. VERKADE (*Rec. trav. chim.*, 1923, 42, 105—111; cf. A., 1922, ii, 474, 740).—A critical survey of the conclusions drawn by Swientoslawski and Popov (A., 1915, ii, 315) and of the method of calculation adopted. The author stresses his criticism on the ground that benzoic acid is accepted as the calorimetric standard substance with a heat of combustion of 6324 cal.₁₅ per g.(air), which is about 2% greater than the value given by Swientoslawski from a consideration of various experimental results (A., 1918, ii, 32; 1921, ii, 679).
H. J. E.

The Calorific Value of Organic Substances. D. P. KONOVALOV (*J. Russ. Phys. Chem. Soc.*, 1918, 50, 81—105).—The heats of combustion of many naturally occurring fuels and of many organic substances are compared. These heats are calculated, not on unit weight of substance burned, but as calories per unit quantity of oxygen used in the combustion. A new factor, π , the oxygen potential of carbon compounds, is introduced. This is calculated from the equation $\pi = T/K$, where T , the calorific power, is the heat of combustion, Q , minus the heat of vaporisation of the water produced, and K , the oxygen coefficient, is the ratio of the weight of oxygen used, to the sum of the weight of substance and of the water produced. π is calculated for a number of different coals, for petrol, for animal fat, and for various types of saturated aliphatic compounds, including paraffins, alcohols, amines, ketones, aldehydes, and acids, and found to vary very little for these substances, the mean value being 3.05 Cal., and hence π for normal carbon compounds is very little different from that for pure carbon. In the case of compounds containing oxygen, it is incorrect to calculate the heat of formation or combustion on the basis that one oxygen atom may be balanced against two hydrogen atoms in the compound; the correct method is to balance one carbon against two oxygen atoms. A formula for the calculation of the heat of formation of oxygen-containing saturated aliphatic substances is given, and the results obtained from it are found to agree satisfactorily with those found experimentally for a number of substances. In the case of nitro-compounds, however, in which the oxygen is united to nitrogen and not to carbon, this formula cannot be applied, and in these cases the heat of formation may be calculated by assuming that the oxygen is present in the free state. In the case of homologous hydrocarbons, it is found that π gradually increases as the proportion of hydrogen falls. Formulæ for the calculation of π for unsaturated hydrocarbons are deduced, and found to agree satisfactorily with results obtained experimentally for ethylene, acetylene, and allylene, π in these cases increasing with the degree

of unsaturation. The same formula is applied to the calculation of π for carbon as C_2 , which is found to 4.704. From this result, the heat of vaporisation of C_2 is calculated to be 103.6 Cal. π for saturated cyclic compounds differs little from that for straight chains, whilst for aromatic compounds it increases with increasing unsaturation, varying between 3.1 for benzene and 3.138 for diphenylacetylene. For terpenes, this value is of the same order as for aromatic substances. For rings containing oxygen, however, a great increase is observable, π for ethylene oxide being 3.585, for furfuraldehyde 3.364, and for trioxymethylene 3.509. Esters, such as ethyl nitrite, glyceryl trinitrate, and mannitol hexanitrate, behave differently from ordinary nitro-compounds, liberating more energy on combustion. A formula is deduced for the calculation of the heat of combustion of such substances, and it is shown that results calculated from it agree well with experimental figures. For cyanogen, π is only slightly less than for C_2 , i.e., 4.097, whilst for hydrocyanic acid it is 3.847, both being very close to calculated values. Nitriles also give values for π above the normal, and a small increase is apparent for compounds in which every carbon atom has a hydroxyl group attached, such as glycerol. Acid amides and carbamide, on the other hand, have a value below normal, e.g., for carbamide $\pi = 2.914$, and for oxamide 2.739. Many organic acids, such as acetic, propionic, malonic, and succinic acids, have also low values. Carbohydrates have all values considerably above normal, the heat effect being on the average 7.5% greater than that of their carbon content alone. Lignite and peat have slightly higher values than the normal, 3.05, although lower than that of cellulose, 3.262, indicating that they are transition stages to coal.

R. T.

The Heats of Combustion and of Formation of certain Explosive Nitro-compounds from their Elements. P. P. RUBCOV and L. A. SEVERJANOV (*J. Russ. Phys. Chem. Soc.*, 1918, 50, 140—144).—The heats of combustion of various nitro-compounds are measured and their heats of formation hence calculated. These are, for 1 : 3 : 5-trinitrobenzene 3178 cal. and + 8.5 Cal., respectively, for 2 : 4 : 6-trinitro-1-methylnitroaminobenzene 3016.5 cal. and - 14.2 Cal., for 2 : 4 : 6-trinitrotoluene 3691 cal. and + 13.6 Cal., for 2 : 3 : 4 : 6-tetranitro-1-methylnitroaminobenzene 2551 cal. and - 29.9 Cal., for ammonium picrate 2890 cal. and + 78 Cal., for the ammonium salt of hexanitrodiphenylamine 3128 cal. and + 14 Cal., and for trinitroethane 1777 cal. and + 4.3 Cal.

R. T.

Nernst's Theorem. TH. DE DONDER (*Bull. Acad. roy. Belg.*, 1922, [v], 8, 461—465).—The author obtains various expressions for the heat of reaction at constant pressure, making use of Nernst's theorem.

E. E. T.

Heat of Coagulation of Ferric Oxide Hydrosol with Sodium Sulphate. FREDERICK L. BROWNE (*J. Amer. Chem. Soc.*, 1923, 45, 311—321).—The heat of coagulation of ferric oxide hydrosol,

of widely varying purity, by means of 0.2*N*-solution of sodium sulphate, has been investigated, using sols prepared by three dissimilar methods. The sols employed were prepared, by the oxidation of a solution of ferrous chloride with hydrogen peroxide followed by dialysis, by the peptisation of precipitated ferric hydroxide in ferric chloride solution, and by the addition of various amounts of hydrochloric acid to a sol of a high degree of purity prepared by the first-named method. The same value for the heat of coagulation at a given purity and total iron concentration is obtained with sols prepared by all three methods, indicating that ferric oxide hydrosols represent an equilibrium which is defined by the temperature, pressure, concentration, and purity. The change in the degree of dispersion of ferric oxide during coagulation does not involve a measurable heat effect. The heat effects observed during the coagulation of sols of low purity are due to the dilution of the ferric chloride and hydrochloric acid contained in the sols, to the mixing of these electrolytes with the added coagulating electrolyte, and to changes in the adsorption equilibria.

J. F. Š.

Interfacial Tension. JAMES ROBERT POUND (T., 1923, 123, 578—599).

Viscosity, Neutralisation, and Isomorphism. L. J. SIMON (*Compt. rend.*, 1923, 176, 437—440).—A study of the variation in viscosity of solutions of phosphoric acid and arsenic acid during their neutralisation by sodium hydroxide shows that the curves obtained for the two acids are superposable. The results indicate that, in aqueous solution, of the same molecular concentration, isomorphous substances modify the viscosity of water at a given temperature in the same manner. By isomorphous substances is meant those having similar chemical formulæ, the same crystalline form and showing syn-crystallisation. A study of the chlorides of sodium, potassium, rubidium, and ammonium shows that this holds good for the last three named, but that for sodium chloride there is a marked difference at all temperatures and all concentrations.

W. G.

Dissociation Pressures of certain Salt Hydrates by the Gas Current Saturation Method. WALTER C. SCHUMB (*J. Amer. Chem. Soc.*, 1923, 45, 342—354).—Measurements of the dissociation pressures of nine pairs of salt hydrates have been made by the gas current saturation method at 25°, and the results compared with those obtained by other investigators using the same or other methods. The pairs of hydrates examined were the mono- and di-hydrates of barium chloride, di- and hexahydrates of strontium chloride, tri- and penta-hydrates of copper sulphate, anhydrous sodium sulphate and the decahydrate, hexa- and hepta-hydrates of magnesium, zinc, ferrous, cobalt, and nickel sulphates. It is found, contrary to the experience of several who have previously used the method, in particular Menzies (A., 1920, ii, 738) and Baxter and Lansing (A., 1920, ii, 286), that when suitable precautions are taken perfectly trustworthy results are obtained.

The necessary precautions concern the size of the saturator containing the mixture of salt hydrates, the method of measuring the total internal pressure, the intimate mixing of the two solid phases, the rate of flow of the current of air passing through the apparatus, and the weighing of the water taken up by the air. It is shown that the objection raised to this method, namely, that insufficient time is given for the attainment of an equilibrium, is without foundation, since the equilibrium may be reached from both sides. No certain relationship has been found to hold between the composition of analogous salt hydrates and their dissociation pressures measured at a given temperature, although the influence of such factors as atomic volume and valency is admitted. Exception is taken to the generalisations of Clark and Buckner (A., 1922, ii, 300) connecting the composition of ammines and hydrates with their stability, in view of the numerous exceptions found in the literature. It is pointed out that much further work is necessary, both in the formation and examination of new molecular compounds and in showing that numerous assumed compounds have no real existence, before any definite relationships can be established. J. F. S.

Abnormal Osmosis through Collodion Membranes. G. PREUNER [with O. RÖDER] (*Z. Elektrochem.*, 1923, 29, 54—64).—A number of osmosis experiments with dilute solutions of various potassium salts are described together with measurements of the potential difference at the collodion walls used to separate the dilute from the more concentrated solutions. The osmosis is shown to reach a maximum value at concentrations between $N/256$ and $N/512$. It is shown that when a concentrated solution is separated from a dilute solution by a collodion membrane a fall of potential is brought about by the diffusion, and this drives the solvent from the dilute solution to the concentrated solution, and so brings about the abnormal osmosis. Since the diffusion potential between the walls of the membrane depends on the fall of concentration inside the walls of the membrane, it follows that the abnormal osmosis is different with rotating membranes than with fixed membranes. With fixed membranes and stationary solutions the concentration on the surface of the membrane contiguous with the dilute solution is much greater than that in other portions of this solution. The ratio of the concentration on the two walls of the membrane approaches a maximum with increasing concentration of the concentrated solution. The maximum is reached at a concentration such that with the same concentration on both sides of the collodion wall the electro-endosmosis and the electro-adsorption potential ζ also have their maximum value. This is explained if it be assumed that at this concentration the coefficient of diffusion is at its minimum. Such an assumption is in keeping with the fact that the diffusion potential difference is much greater with membranes than without. The electrolyte behaves in the membrane as though the migration velocity of the anion, v , is reduced, and the more reduced the greater the value of ζ . Since in the equation for the diffusion potential difference the value of $(u - v)/(u + v)$

and the ratio of the concentrations, for concentrations in the region where the more concentrated solution shows a maximum osmotic pressure, decrease in the same way as ζ , the maxima of the diffusion potential difference of the abnormal osmosis and the electro-endosmosis must lie close together. With rotating membranes, the concentrations on the surface of the membrane differ only slightly from the concentration in the interior of the solution, since there is only a fall of concentration over the very thin adhering layer of the solution on the outside of the membrane. The diffusion potential difference increases with increasing concentration of the concentrated solution up to a very high value of this concentration. For these reasons, and because of the increased pure osmotic action, no maximum of the transport of liquid occurs. The maximum of the abnormal osmosis with collodion membranes is due to a further cause, if, as is stated by Loeb, it is caused by the increase in the diffusion potential difference and the decrease in the charge on the membrane with increasing concentration of the more concentrated solution.

J. F. S.

Potential Difference occurring in a Donnan Equilibrium and the Theory of Colloidal Behaviour. A. V. HILL (*Proc. Roy. Soc.*, 1923, [A], 102, 705—710).—A theoretical paper in which the contention of Loeb (Proteins and the Theory of Colloidal Behaviour), that the Donnan membrane equilibrium (A., 1911, ii, 848) involving the presence of an ion which does not diffuse, is the basis of the colloidal properties of a protein solution, is discussed. Whilst the possibility of Loeb's conclusion is admitted, it is pointed out that one of the main arguments used in its favour by Loeb is incorrect. Loeb shows that the potential difference observed experimentally between a protein and a non-protein solution separated by a membrane agrees very exactly with that calculated from the difference in hydrogen-ion concentrations also observed experimentally, and concludes that this supports his hypothesis. As a matter of fact, this equality is a necessary and inevitable consequence of the manner in which the observations were made and of general thermodynamic principles, and its proof is independent of any hypothesis of the mechanism by which the potential difference is produced.

J. F. S.

Anomalous Osmosis of Solutions of Electrolytes with Colloidal Membranes. I. The Electrical Properties of the Membrane System. F. E. BARTELL and DWIGHT C. CARPENTER (*J. Physical Chem.*, 1923, 27, 101—116).—It is shown that in the measurement of osmosis in collodion bags as prepared by Loeb (A., 1919, ii, 399, 497) an increase in volume of 15% is brought about by small heads of solution which causes a considerable error in the pressure values obtained. To avoid this source of error, the authors have used collodion membranes prepared by Bigelow and Gemberling's method (A., 1907, ii, 933), which they find are uniform in thickness and permeability, and by regulating the conditions under which they are formed the permeability can be adjusted to any particular value. The membranes were mounted in a non-

leaking osmotic cell made of two T-shaped glass compartments of equal volume, held together by a brass coupling which holds the membrane firmly between the two compartments. The osmosis values of 1.0, 0.1, 0.01, and 0.001*M* solutions of hydrochloric acid and potassium hydroxide, chloride, sulphate, ferrocyanide, ferricyanide, carbonate, phosphate, acetate, oxalate, and tartrate, sodium chloride, calcium, magnesium, and aluminium chlorides have been determined and the maximum potential of each osmotic system has been measured at 25°. The sign of the membrane charge has been determined by cataphoresis experiments, using finely ground suspended membrane material. The data show that the initial rate of osmosis bears a definite relationship to the electrical properties of the membrane system for practically all the salts examined. The anomalous effects obtained with collodion are very similar to those obtained with membranes of porcelain, gold beater's skin, calf's bladder, and parchment paper. The maximal and minimal values obtained with these different membranes do not come at exactly the same concentrations, but when the results are considered in the light of the exact condition of the electrical orientations of the different membrane systems, they are found to be closely comparable. It is also shown that the anomalous effects are somewhat related to a time factor. For example, the data for the osmosis of potassium carbonate at the end of a two-hour period, when plotted against the logarithm of the concentration, did not give an *N*-shaped curve, whilst the *N*-shape is pronounced in the curve obtained at the end of a twelve-hour osmosis period. This makes it appear probable that the process of diffusion is in some way responsible for the repressing effects noted at the intermediate concentrations.

J. F. S.

Four Laws of the Mutual Influence of Salts on the Solubility.

P. P. VON WEIMARN (*Kolloid Z.*, 1923, 32, 145—149).—The author discusses four laws of mutual influence of salts on solubility and shows the importance of these to the behaviour of colloidal solutions. The four laws are: (1) Nernst's law. The solubility of a salt is decreased by the presence of a second salt which has a common ion with the first. (2) Noyes's law. The solubility of a salt increases in the presence of a second salt which has no ion in common with the first salt. (3) The solubility of a salt in the presence of a second salt with a common ion commences to increase from a definite concentration of the second salt. The definite concentration is determined by the nature of the two salts and the solvent, and is lower the smaller the power of the solvent to break up the complexes formed. (4) When two or more salts are dissolved in a given solvent, a competition for the solvent between the salts takes place, so that a decrease in the solubility of the salt which takes up least of the solvent follows. The existence of the third law demands a new statement of Nernst's law, which is therefore now written: The solubility of a salt in the presence of a second salt with a common ion decreases when the concentration of the second salt does not exceed a definite value.

J. F. S.

Relation between Molecular and Crystal Symmetry as shown by X-Ray Crystal Analysis. G. SHEAREB (*Proc. Physical Soc.*, 1923, 35, 81—100).—A theoretical paper, in which the methods of X-ray analysis, the nature of the elementary crystal lattice, and the meaning of axes and planes of symmetry in the lattice are discussed. It is shown that the methods of X-ray analysis enable the number of molecules associated with the unit cell to be determined. With the aid of this information an attempt is made to connect the symmetry properties of the crystal with this number and with the symmetry properties of the molecules from which the crystal is formed. The symmetry number for each of the thirty-two crystal classes is given, and is shown to mean the minimum number of asymmetric molecules necessary in the unit cell to satisfy the symmetry conditions. The relative orientations and positions of these molecules in the cell are discussed. It is suggested that this symmetry number is the actual number of molecules in the cell when the molecule is asymmetric; further that, if the molecule possesses symmetry, this symmetry appears also in the crystal, and the number of molecules in the unit cell is obtained by dividing the symmetry number of the crystal by the symmetry number of the molecule. Evidence is produced in support of these hypotheses, and examples are given of their application to inorganic and organic crystals. J. F. S.

Structure of Metal Crystals. Modification of the Powder Method of Determining the Structure of Metal Crystals. E. A. OWEN and G. D. PRESTON (*Proc. Physical Soc.*, 1923, 35, 101—108).—Plates of aluminium, iron, copper, lead, and magnesium have been examined by means of a Bragg X-ray spectrometer, employing radiation from a molybdenum anti-cathode. The maxima observed in the spectra are sufficiently intense to measure with accuracy, and the crystalline structure of the materials examined is readily determined. The following data have been obtained: aluminium has a face-centred cubic lattice, the length of the side of the unit cube of which is $a = 4.041 \text{ \AA}$, and the number of atoms associated with each elementary cube is $n = 3.98$; iron has a centred cubic lattice, $n = 2.015$ and $a = 2.869 \text{ \AA}$; copper has a face-centred cubic lattice, $a = 3.628 \text{ \AA}$, and $n = 4.06$; lead also has a face-centred cubic lattice, $a = 4.983 \text{ \AA}$, and $n = 4.11$, and magnesium has a hexagonal lattice, the side of the hexagon having a mean value $a = 3.17 \text{ \AA}$, and $n = 0.98$. J. F. S.

The Mesomorphic State of Matter. G. FRIEDEL (*Ann. Physique*, 1922, [ix], 18, 273—474).—A new classification of liquid crystals according to their structure. Matter is capable of existing in two forms, neither crystalline nor liquid, for which the new designation, the *mesomorphic state*, is proposed. The first form is called the smectic phase, after the soaps which occur in this class, and the second, the nematic phase, on account of the linear discontinuities which are its principal feature. A short historical account of liquid crystals, and a summary of the substances giving rise to either or both of the two types are given.

The smectic and nematic phases, when they occur together, are always separated by a discontinuity, and the former is the phase which is stable at the lower temperature. The smectic form is always optically positive, but the latter may be divided into two classes, nematic proper and cholesteric, according to the sign of the rotation. The smectic phase possesses high viscosity and is rigid except in the direction of the optical axis, and displacement is accompanied by a change of structure. On the other hand, the nematic type is fluid, often more fluid than the liquid, and accommodates itself to movements within the film, brownian or otherwise. When the smectic phase is not homogeneous, as when the temperature is raised, there appears a new structure showing groups of lines which are always in the form of focal conics. The conics form groups of two, an ellipse and a hyperbola, and the focal groups are often systematically arranged inside a polygonal structure. This structure is discussed in detail. On cooling from the liquid or nematic state, the smectic phase makes its appearance in short rods, ornamented by focal groups; the nematic type gives droplets in similar circumstances. A magnetic or electric field is without action on the smectic phase, whereas the structural lines in the nematic phase are oriented so that the optical axis becomes parallel, and normal, respectively, to the lines of force. Another point of difference between the two forms is the behaviour on transition from the crystalline to the mesomorphic state. In both types, the new structure is based on the old, but whereas the old surfaces of separation of the crystals show focal conics in the smectic phase, the division in the nematic type is always absolute. The two kinds of complex structure possessed by the latter type are based on threads with no characteristic geometric form, and on centres which give rise to a spherolytic structure. The cholesteric type, which is optically negative, is only a special form of the optically positive variety, for there is a gradual change from the optically negative class to the normal nematic type.

W. E. G.

The Cholesteric Type of Compounds. GEORGES FRIEDEL (*Compt. rend.*, 1923, 176, 475—478).—The addition of very small amounts of a cholesteric substance to a substance, such as azoxyanisole or azoxyphenetole, having a nematic phase, impresses on the latter the characteristic properties of the cholesteric type. If it is admitted that the rotatory power of the cholesteric phase is due to a very high torsion round the normal to the positive optical axis, then the rotatory power, measured in the normal region of the spectrum, should be greater the smaller the torsion. This is shown to be the case for mixtures of azoxyanisole and cholesteryl acetate.

From a consideration of the behaviour of mixtures of azoxyanisole or azoxyphenetole or of methylbenzylidenbenzidine with colophony, it is shown that the addition, to a nematic substance, of any substance having molecular rotatory power gives rise to a cholesteric substance in which the two typical structures of this form of matter are seen. If the amount of the asymmetric sub-

stance exceeds a certain, generally very small, amount the structure with planes shows a very strong rotatory power of the type of ordinary cholesterol compounds, but if the amount of the asymmetric substance tends towards zero, there is a gradual passage from the cholesteric to the nematic characteristics. W. G.

Dielectric Constants of Colloidal Solutions. II. J. ERRERA (*Kolloid Z.*, 1923, 32, 157—163).—A continuation of work previously published (A., 1922, ii, 694). The dielectric constant of a number of vanadium pentoxide sols has been determined under a variety of conditions. It is shown that the constant is increased by passing an alternating current through the solution, due to electric coagulation. Dilution of a sol causes an immediate decrease in the value of the dielectric constant, but, on keeping, the value increases with time; this is due to the partial solution of the disperse phase. Increasing temperature decreases the dielectric constant to an amount corresponding with the increase in the molecular motion and the degree of dispersion. The dielectric constant increases with increasing current strength and increasing wave-length in accordance with the increased directing force. Measurements of the electrical conductivity of the solutions show that the changes observed in the dielectric constant are real and not due to changes in the conductivity factor. The importance of the above results for the theory of electrical double refraction and anomalous dispersion is pointed out. J. F. S.

The Study of Soap Solutions. J. W. MCBAIN (*Rep. Brit. Assoc.*, 1922, 360—361).—A review of the evidence for the existence of the ionic micelle and the theories arising therefrom. E. H. R.

Lyotropic Action in Processes of Solution of Colloids. N. P. PESKOV (*Kolloid Z.*, 1923, 32, 163—166).—The action of the kations, ammonium, lithium, sodium, potassium, rubidium, and caesium on the rate solution of arsenic sulphide, gold, and cupric sulphide sols in alkaline media has been investigated. It is shown in all cases that the lyotropic action of these kations is in the order $\text{NH}_4^+ \cdot [\text{H}_2\text{O}] \cdot \text{Li}^+, \text{Na}^+, \text{K}^+, \text{Rb}^+, \text{Cs}^+$. The ammonium ion decreases the rate of solution very strongly, whilst the other ions increase it more the greater the atomic weight of the element. The effect of adding the chlorides of the alkali metals on the time required for the production of the blue colour in mixtures of sodium sulphite, sulphuric acid, and iodic acid has also been investigated, and found to have in all cases an accelerating action, the order of increasing acceleration being $\text{Li}^+, \text{Na}^+, \text{K}^+, \text{NH}_4^+, \text{Rb}^+, \text{Cs}^+$. With the exception of ammonium, the order is the same as that noted above. Similar experiments with coagulated arsenic sulphide and gold gave exactly the same order as was obtained with the uncoagulated sols, showing that the lyotropic action extends to macro-heterogeneous systems. A still coarser system, gold obtained by the reduction of gold chloride with hydrogen peroxide, furnished identical results, and finally gold powder dissolved more rapidly in the presence of rubidium chloride than in pure water. Hence it is shown that the

lyotropic action refers only to the solvent, and is manifested with all degrees of dispersion of the system. Adsorption only plays a part in so far as it may displace the action. J. F. S.

The Effect of Dissolved Substances on the Deposition of Colloidal Particles from a Solution by means of an Electric Current. RICHARD D. KLEEMAN (*Physical Rev.*, 1922, 20, 272—279).—The addition of 0.1—0.3% of sodium hydroxide, silicate, sulphate, phosphate, hydrogen phosphate or tartrate, potassium hydroxide, or tartaric acid to porcelain slip (a colloidal solution of clay, flint, and felspar in water) results in the formation of a solid instead of a semi-liquid deposit when it is subjected to an electric current. The increase in compactness of the deposit, obtained on the addition to the slip of one of the substances mentioned, was found to be intimately connected with the increase in fluidity of the slip produced by them. In explanation, it is assumed that the addition of a small amount of a substance to the slip decreases the radii of the spheres of action of the particles, or the spheres associated with the particles which do not penetrate into each other during their motion of translation. The fact that continued addition of the substance first precipitates some of the particles, mainly the flint and felspar, and then causes redissolution is explained in the same way. The equations of distribution of colloidal particles under the action of gravity are obtained. The experimental results indicate that the volume of the spheres of action of a particle in porcelain slip is about twice the actual volume of the particle. A. A. E.

Ultramicroscopic Method for the Measurement of the Velocity of Kataphoresis. H. R. KRUYT and A. E. VAN ARKEL (*Kolloid Z.*, 1923, 32, 91—95).—An apparatus is described whereby the velocity of kataphoresis of ultramicroscopic particles may be measured. From the measurements it is shown that the potential at the interface colloid-dispersion medium may be calculated. Using this apparatus, the velocity of kataphoresis of selenium sols has been determined at distances 0—900 mm. from the walls of the containing vessel. The potential at the interface is found to be 43 m.-volts. J. F. S.

Heterogeneous Equilibria between the Chlorides of Calcium, Magnesium, Potassium, and their Aqueous Solutions. I. WILLIAM BELL LEE and ALFRED CHARLES EGERTON (*T.*, 1923, 123, 706—716).

Equilibria between the Acido- and Aquo-iridium-pentammines. ARTHUR B. LAMB and LAWRENCE T. FAIRHALL (*J. Amer. Chem. Soc.*, 1923, 45, 378—395).—Slight modifications have been made in Palmaer's method of preparing iridium-pentamine salts; these modifications give purer products and are more convenient (*A.*, 1896, ii, 179). Chloropentammineiridium chloride has been shown to undergo no appreciable decomposition in aqueous solution at 100°. The velocity of transformation of chloro-, bromo-, iodo-, and nitrate-pentammines into the corresponding aquammines and *vice versa* has been measured at 95°, and in the case of the

bromo-ammines at 80°. All these transformations have been found to follow the course of a unimolecular reaction, and their velocity constants have been found to have the same relative magnitudes as the corresponding constants of the cobaltammines. The equilibria reached in these transformations have been investigated analytically. For this purpose, the method of McLean and Van Slyke (A., 1915, ii, 479) has been carefully studied and still further refined. The values for the equilibrium concentrations, thus found, are shown to be substantially in agreement with those calculated from the velocity measurements, and similar to those of corresponding equilibria among cobaltammines. They are all, however, markedly displaced from the aquo-side of the reaction, as compared with the corresponding cobaltammines. The values for the concentrations found in the bromo-bromide equilibrium have been shown to agree reasonably well with the requirements of an empirical equation similar to that found for the cobaltammines. This equation has the form $[C_R - C_{Cl}]^{0.46}/C_P = K_2$ where C_R and C_P represent the total concentration of aquo- and acido-salts, respectively. The conclusion has therefore been drawn that, whilst the exchange of the central cobalt atom for an iridium atom in the ammines considered has produced a general displacement in the velocity and equilibria constants, it has produced no relative displacements.

J. F. S.

Dynamics of the Formation of Nitriles from Acid Anhydrides and Amides. IV. Investigation of the Reaction between Acetamide and Benzoic Anhydride by Phase Rule Methods. ROBERT KREMAN, ALOIS AUER, VIKTOR OSWALD, and ALFRED ZOFF (*Monatsh.*, 1923, 43, 345—358).—The interaction of equimolecular quantities of acetamide and benzoic anhydride proceeds according to the simple equation: $\text{CH}_3\cdot\text{CO}\cdot\text{NH}_2 + (\text{C}_6\text{H}_5\cdot\text{CO})_2\text{O} \rightleftharpoons \text{CH}_3\cdot\text{CN} + 2\text{C}_6\text{H}_5\cdot\text{CO}_2\text{H}$, no side-reaction (to produce acetylbenzoylimide) occurring (cf. A., 1922, ii, 748). The reaction was followed by the method previously employed by the author. The formation of an equimolecular compound (cf. this vol., i, 336) between acetamide and benzoic anhydride, melting at a temperature (84°) at which these two substances interact rapidly, caused difficulty in obtaining accurately the first few points on the temperature-freezing point curve. Other difficulties arose from the volatility of acetonitrile. The reaction studied is reversible, equilibrium (at 98°) being reached at 69% conversion from left to right of the above equation. The formation of the compound between acetamide and benzoic anhydride is thought to explain the fact that, from the results of the present investigation, benzoic anhydride appears to be a less effective dehydrating agent than acetic anhydride, whereas other results point to the contrary conclusion (cf. following abstract).

E. E. T.

Dynamics of the Formation of Nitriles from Acid Amides and Anhydrides. V. The Study of the Reaction: 1 Benzoic Anhydride + 2 Acetic Acid \rightleftharpoons 2 Benzoic Acid + 1 Acetic Anhydride. ROBERT KREMAN and WILHELM RÖSLER (*Monatsh.*, 1923, 43, 359—365).—The reaction studied proceeds from left to

right (at 77.5°) to the extent of about 65%, giving a reaction constant $K=6.4$. The reaction was studied by the usual method (freezing-point determinations at intervals, with subsequent reference to a freezing-point curve obtained from known mixtures, etc.), and it is shown that although, undoubtedly, two side reactions, producing the mixed anhydride, occur, these do not affect, to any extent, the figures given above for the main reaction.

E. E. T.

The Conditions of Reaction of Hydrogen with Sulphur. I. Direct Union. RONALD GEORGE WREYFORD NORRISH and ERIC KEIGHTLEY RIDEAL (T., 1923, 123, 696—705).

The Propagation of Flame in Complex Gaseous Mixtures. V. The Interpretation of the Law of Speeds. WILLIAM PAYMAN (T., 1923, 123, 412—420).

The Rate of Detonation in Complex Gaseous Mixtures. WILLIAM PAYMAN and NOEL STANLEY WALLS (T., 1923, 123, 420—426).

The Effect of Pressure on the Limits of Inflammability of Mixtures of the Paraffin Hydrocarbons with Air. WILLIAM PAYMAN and RICHARD VERNON WHEELER (T., 1923, 123, 426—434).

A Simple Form of Apparatus for Observing the Rate of Reaction between Gases and Liquids, and its Use for Determining the Rate of Solution of Oxygen by Water under Different Conditions of Mixing. H. G. BECKER (*Phil. Mag.*, 1923, [vi], 45, 581—592).—The principle on which the apparatus is based depends on the changes in pressure which occur when a liquid is placed in contact with a closed volume of gas. The measurements of the absorption of oxygen were made with a suspension of ferrous hydroxide in water. Five different rates of stirring of the water were employed, ranging from zero to 1000 revolutions per minute. The process of adsorption followed a linear law showing that the deoxygenation of the water was complete in a few seconds. The rate of solution per unit area increases rapidly with increase in the rate of stirring, and tends to a maximum as the higher rates are reached. Gentle stirring of the under layers of the water increases the rate of solution as much as twenty-fold compared with stationary water. When in the quiescent state, the rate of solution of a gas by a liquid is liable to sudden unaccountable changes. The maximum rate of solution attained in these experiments was 0.0016 c.c. per min., which was about half that obtained by another method, previously reported (cf. A., 1919, ii, 510).

W. E. G.

The Velocity of the Absorption of Carbon Dioxide by Ammoniacal Solutions. PAUL RIOU (*Compt. rend.*, 1923, 176, 581—583).—The influence of varying amounts of sodium and ammonium chlorides and sodium hydrogen carbonate on the

absorption of carbon dioxide by ammonium carbonate solutions was studied, and the results obtained are expressed by curves showing the c.c. of gas absorbed per second per sq. cm. of surface by ammonium carbonate solutions containing 0.04 g. mol. per 100 c.c. in presence of varying concentrations of the other salts. Sodium and ammonium hydrogen carbonates have the greatest retarding influence on the absorption, and ammonium chloride the least at 20°. The influence of temperature on the absorption in presence of ammonium and sodium chloride at different concentrations is also shown. With decreasing concentrations the maximum absorption velocity is displaced slightly on the temperature axis, being at about 20° with 0.5 g. mol. NH_4Cl per 100 c.c. and 35° with 0.1 g. mol. per 100 c.c. The maximum with sodium chloride solutions lies at about 50°.

G. F. M.

The Antagonistic Action of Ions. H. WASTL (*Biochem. Z.*, 1922, 134, 131—138).—The influence of the anions of various potassium salts on the time which elapses before the blue colour of starch iodide appears in the reaction between iodic acid and sulphurous acid (Landolt's reaction) has been studied. The results confirm Berczeller's observations that the reaction is accelerated by the anions in the order $\text{I} > \text{Br} > \text{Cl} > \text{NO}_3 > \text{SO}_4$. Sulphate is antagonistic to chloride, bromide, or iodide, the latter accelerating the reaction, the former retarding it.

H. K.

The Velocity with which Carbon Monoxide Displaces Oxygen from Combination with Hæmoglobin. I. H. HART-
RIDGE and F. J. W. ROUGHTON (*Proc. Roy. Soc.*, 1923, [B], 94, ([B], 662), 336—367).—The reaction $\text{CO} + \text{O}_2\text{Hb} \rightleftharpoons \text{O}_2 + \text{COHb}$ is a reversible one, and the equilibrium constant has a value in light different from that in darkness. On this circumstance are based two methods for measuring the velocity constant of the reaction, a determination difficult to carry out directly as equilibrium is attained very quickly. In the first method, hæmoglobin solution containing oxygen and carbon monoxide flows through two glass tubes in series, one illuminated and the other in darkness. Measurements are made of the percentage of oxyhæmoglobin and carboxy-hæmoglobin at various points in the illuminated tube by means of the reversion spectroscope (Hartridge, this vol., ii, 105). If the rate of flow is known, the time taken to reach the various points at which measurements have been made can be calculated, and hence the velocity constant of the reaction found. The second method consists in interrupting the illumination of the hæmoglobin contained in a trough, and measuring accurately the time taken for the change towards the new equilibrium to proceed a certain distance, as indicated by analysis by the reversion spectroscope. The values of k , the equilibrium constant, obtained by the two methods at 16° are 0.55 and 0.42, respectively, the difference being within the experimental error. The mean temperature coefficient as obtained by the two methods is 2.5, and $\log k$ is approximately inversely proportional to the temperature.

W. O. K.

The Decomposition of Formic Acid by Sulphuric Acid.

ERNEST R. SCHIERZ (*J. Amer. Chem. Soc.*, 1923, 45, 447—455).—A study of the velocity of decomposition of formic acid by sulphuric acid, of different concentrations, at temperature intervals of 10° from 15° to 45°. The reaction is unimolecular and probably one of dehydration. The addition of small amounts of water to the reaction mixture markedly decreases the velocity of the reaction which, however, increases rapidly with rise in temperature. There is a marked irregularity in the temperature coefficients of the reaction for 91.8% sulphuric acid. The presence of copper, silver, potassium, sodium, or mercurous sulphates causes only a slight retardation of the reaction. Acetone and acetic acid act as inert diluents but hydrochloric acid increases the velocity of the reaction considerably.

W. G.

Hydrolysis of Methyl *o*-Nitrobenzoate in Acid Solution.

GERALD E. K. BRANCH and DONALD S. MCKITTRICK (*J. Amer. Chem. Soc.*, 1923, 45, 321—327).—The rate of hydrolysis of methyl benzoate and methyl *o*-nitrobenzoate, the rate of esterification of *o*-nitrobenzoic acid, and the position of the equilibrium in each case has been determined under the same conditions. The reaction mixtures contained 60% of methyl alcohol, 40% of water, 0.25*N*-sulphuric acid, and 0.1104 g.-mols. per litre of organic acid or ester. It is found that the equilibrium for the unsubstituted and the substituted compound lies at practically the same point. The esterification is found to be of a higher order than the corresponding hydrolysis. The rate of hydrolysis of methyl benzoate is found to be twenty times as great as that of methyl *o*-nitrobenzoate. This result is at variance with the results obtained by Kellas (*A.*, 1898, i, 96) for alkaline solutions. The discrepancy is explained by assuming the reactions to be preceded by complex formation between the ester and the hydrogen- or hydroxyl-ion. As is to be expected, the nitro-group favours the formation of the complex with the hydroxyl-ion and the dissociation of that with the hydrogen-ion, and consequently accelerates the reactions in alkaline solution but retards those in acid solution.

J. F. S.

Enzymatic Hydrolysis of Alkyl Glucosides. Determination of some Molecular Weights. H. COLIN and (MLLE) A. CHAUDUN (*Compt. rend.*, 1923, 176, 440—442).—When to a given weight of a glucoside increasing amounts of a preparation of emulsin are added the weight of dextrose liberated in twenty-four hours gradually increases to a maximum beyond which any further addition of the enzyme does not cause any increase in the amount of dextrose liberated. In the cases of methyl, propyl, isopropyl, butyl, and isobutyl glucosides it is shown that the volume of the given enzyme preparation required to give the maximum hydrolysis in twenty-four hours is, within the limits of error of the experiment, inversely proportional to the molecular weight of the glucoside.

W. G.

Dependence of the Velocity of Coagulation of Suspensoids on the Temperature. W. W. LEPESCHKIN (*Kolloid Z.*, 1923, 32, 166—167).—The temperature coefficient of the rate of coagulation of denatured albumin, arsenic trisulphide, and lecithin in the presence of alkali salts has been determined. The value of the coefficient in the case of arsenic sulphide is the smallest and is the same as that of the salt diffusion. Lecithin has a somewhat greater coefficient whilst that of albumin is greatest and has a value approximating to that of a chemical reaction. J. F. S.

Mechanism of the Catalysis of Hydrogenation by Nickel. MATTLAND C. BOSWELL (*Trans. Roy. Soc. Canada*, 1922, 16, III, 1—25).—By a quantitative study of the reduction of nickel oxide by hydrogen, and of the catalysis of the hydrogenation of ethylene by partially reduced nickel oxide, it is shown that oxygen necessarily present in a normal nickel catalyst exists partly in the form of nickel oxide in the interior of the catalyst particles and partly as negatively charged hydroxyl groups together with positively charged hydrogen on the surface nickel of the particles. Hydrogen absorbed during the reduction of nickel oxide, exists on the nickel surfaces with both positive and negative charges. The structure of the catalyst is represented by $(\text{NiO})_x.\text{Ni}(\overset{+}{\text{H}}\overset{-}{\text{O}}\overset{+}{\text{H}}\overset{-}{\text{O}}\text{H} \dots)$ and the catalysis of the hydrogenation of ethylene by the following:

$$(1) (\text{NiO})_x.\text{Ni}(\overset{+}{\text{H}}\overset{-}{\text{O}}\overset{+}{\text{H}}\overset{-}{\text{O}}\text{H} \dots) + \text{C}_2\text{H}_4(\overset{+}{\text{H}}\overset{-}{\text{H}}) \rightarrow (\text{NiO})_x.\text{Ni}(\overset{+}{\text{H}}\overset{-}{\text{O}}\text{H}) + \text{C}_2\text{H}_6 + \text{H}_2\text{O}.$$

$$(2) (\text{NiO})_x.\text{Ni}(\overset{+}{\text{H}}\overset{-}{\text{O}}\overset{+}{\text{H}}\overset{-}{\text{O}}\text{H}) + (\overset{+}{\text{H}}\overset{-}{\text{H}}) \rightarrow (\text{NiO})_x.\text{Ni}(\overset{+}{\text{H}}\overset{-}{\text{O}}\overset{+}{\text{H}}\text{H}) + \text{H}_2\text{O}.$$

$$(3) (\text{NiO})_x.\text{Ni}(\overset{+}{\text{H}}\overset{-}{\text{O}}\text{H}\text{H}) \rightarrow (\text{NiO})_{x-1}.\text{Ni}(\text{HOH}) + \text{H}_2\text{O}.$$

A fourth reaction representing the mechanism of hydrogen absorption also occurs, and involves the addition of positive and negative hydrogen-ions derived from neutral hydrogen molecules to the complex on the right-hand side of reaction (1) to form the complex on the left-hand side of reaction (3). Of these reactions, (1) is very fast and (2) and (3) are very slow. The latter pair also represents the reactions occurring on continued reduction of nickel oxide by hydrogen. Finally, by such reduction all hydroxyl groups on the surface are removed and only absorbed hydrogen with positive and negative charges remains.

J. S. G. T.

The Catalytic Decomposition of Formic Acid in Acetic Anhydride. ERNEST R. SCHIERZ (*J. Amer. Chem. Soc.*, 1923, 45, 455—468).—Sulphuric, nitric, hydrochloric, hydrofluoric, phosphoric, and oxalic acids act as catalysts in the decomposition of formic acid in acetic anhydride, but owing to side reactions it is not possible to obtain quantitative data. Tertiary bases cause a similar catalytic decomposition and the velocity of decomposition corresponds roughly with the basicity of the base. A weak base like caffeine does not cause decomposition. Velocity constants have been determined for a number of bases at 50°. The reaction

is one of the first order and the velocity increases with the concentration of the catalyst. The decomposition by pyridine proceeds with different velocities in different solvents such as benzene, toluene, acetone, carbon tetrachloride, nitrobenzene, ethyl, amyl and *isobutyl* alcohols, amyl acetate, and benzaldehyde. Acetic acid has an inhibitory effect on the catalysis by brucine, strychnine, and morphine, but not on the catalysis by pyridine. This inhibitory effect may be used as a quantitative method for estimating acetic acid in its anhydride. In two cases, the joint effect of two bases was the sum of their separate effects. The author suggests a possible mechanism for the reaction by the formation of an intermediate compound.

W. G.

The Constitution of the Atom. A. REYCHLER (*Bull. Soc. chim. Belg.*, 1922, **31**, 411—417; cf. A., 1922, ii, 279).—The author's previous formula for the calculation of atomic weights from atomic numbers, $A = 2N + \beta N^2$, is now derived from theoretical considerations, and it is shown that the atomic radii of the elements of the helium group deduced by extrapolation from Bragg's crystal measurements are proportional to the cube roots of their atomic numbers. From a consideration of the energy changes involved when an electron is transferred from one shell to another, the author is able to derive Moseley's frequency formula, $\nu = \text{const.}(1/m^2 - 1/n^2)(N - b)^2$.

H. H.

The Structure of the Atomic Nucleus. W. VAN DER BERG (*Chem. Weekblad*, 1923, **20**, 54—58).—A critical discussion of the results of Harkins (A., 1922, ii, 172). The packing effect of four protons in the helium nucleus corresponds with a loss of mass of 0.032 on the mass 4.032, or about 0.8%; a loss of mass is to be expected from the theory of relativity. The deductions of Lunn are criticised as being based on the assumption that Coulomb's law is valid within the nucleus, and as ignoring differences in mass due to the velocity of the nucleus.

The velocity required in an α -particle to disintegrate a helium nucleus is calculated as more than one-eighth the velocity of light; the fastest α -particle, that projected by radium C, has a velocity one-fifteenth that of light. The β -particle has a velocity approaching that of light, but its mass is insufficient; neither has any known electro-magnetic radiation a frequency high enough to effect the disintegration. Since there is no measurable loss of weight in the formation of carbon, oxygen, and heavier atoms from δ -particles, it should be possible to disintegrate these by bombardment.

From a consideration of the atoms of low atomic weight, up to calcium, it appears that where elements of uneven atomic number contain, in addition to α -particles, both external and internal (binding) electrons, the stable configuration is $n\alpha$ -particles with three protons and two external electrons. No stable configuration can be formed from two helium nuclei. It is clear that for the lighter elements, those having an even atomic number are much more stable than those having an odd atomic number, whilst the heavier elements are much less stable than the lighter. S. I. L.

The Number of Radiating Atoms of Various Dimensions within Gaseous Hydrogen, from the Point of View of Bohr's Atom Model. P. LASAREV (*Phil. Mag.*, 1923, [vi], 45, 430—432).—On the Rutherford-Bohr theory, the radius of an electronic orbit moving round a hydrogen atom is given by $a = \hbar^2 \tau / 4\pi^2 m e^2$. On account of the mutual influence of the electric fields of the atoms, τ cannot exceed 15, and thus the dimensions of the orbits will range between $2a = 1.1 \times 10^{-8}$ cm. ($\tau = 1$) to 247.5×10^{-8} cm. ($\tau = 15$). In star spectra, however, the existence of atoms with an electronic orbit of the order 33 is indicated. Calculations are made from the energy of definite spectral lines of the relative number of atoms of hydrogen gas possessing electron orbits of the different orders. Most of the electrons causing the radiation spring over from the third orbit to the second, and the quantity springing over from the fourth orbit to the second equals only 25% of the first quantity. Those from the fifth to the second orbit are only 17% of the number from the third to the second. Thus the quantity of springing electrons decreases with the distance of the electrons from the centre.

W. E. G.

Compressibility, Internal Pressure, and Atomic Magnitudes. THEODORE W. RICHARDS (*J. Amer. Chem. Soc.*, 1923, 45, 422—437).—A theoretical paper in which the respective bulks of the elements in combination have been evaluated from considerations of the compressibilities of the individual elements and the contraction which occurs during combination. With the help of Bridgman's accurately determined pressure volume curves for potassium and sodium (*Proc. Nat. Acad. Sci.*, 1922, 8, 361) and the author's own earlier results of the compressibilities of bromine and chlorine (*A.*, 1922, ii, 42), extrapolated by careful study of the nature of the curves [for which surprisingly concordant equations of the type $(p+P)(v-B)=K$ are derived], the values of the internal pressures existing in these salts, as well as the relative volumes of the components and the atomic diameters in combination, were calculated.

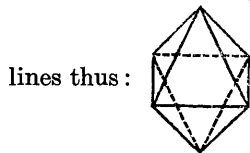
J. F. S.

The Influence of the Atomic Nucleus on Valency, Orientation, and the Induced Polarity of Atoms. HERBERT HENSTOCK (*Chem. News*, 1923, 126, 129—135).—A theoretical paper in which the alternate polarity of a chain of atoms is ascribed to a rotation of the nuclei and the inner electrons of the atoms. The nucleus of an atom is assumed to be a dipolar sphere, with the inner electrons situated at or near the poles, and according to the direction of the dipole within the atom, the valency bond will be either positive or negative. A strong outside influence may rotate the nucleus of a key atom, thus determining its polarity and inducing an opposite arrangement in a neighbouring atom. This in turn will determine the orientation of the next atom and so give rise to alternate polarity. The relationship between electrovalence and covalence is discussed.

W. E. G.

Method of Representing Co-ordinated Compounds. T. M. LOWRY (*Chemistry and Industry*, 1923, 42, 224—225).—The dis-

advantages of the conventional representation of the stereoisomerism of co-ordinated compounds, *e.g.*, potassium cobaltinitrite or cobalthexammine chloride, by a square pierced by an axis of fourfold symmetry, as suggested by Werner, or by the crystallographic projection of an octahedron, are briefly referred to. Alternatively the author suggests that such stereoisomerism should be graphically represented by the plane diagram of an octahedron obtained by drawing the customary hexagonal representation of the benzene ring, and joining the 2 : 4 : 6 positions by full straight lines, and, if desired, joining the 1 : 3 : 5 positions by dotted straight



lines thus :

The usefulness of this method of represent-

ation is illustrated by diagrams showing the enantiomorphism of the different types of compounds to which Werner attributed asymmetry. More especially it is pointed out that enantiomorphs exhibiting optical activity, and in which three identical bivalent radicles are associated with a single atom of metal, can be readily depicted by using the two variants of Kekulé's formula for benzene.

J. S. G. T.

Change of Water of Hydration into Adsorbed Water during the Mechanical Subdivision of Crystal Hydrates. T. HAGIWARA (*Kolloid Z.*, 1923, **32**, 154—156).—Weimarn has previously stated that the affinity of a substance for its water of crystallisation decreases as the size of the particles diminish. With the object of testing this statement, the author has determined the amount of water which the hydrate $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ will retain at various temperatures in ordinary circumstances, and how this amount is affected by grinding the alumina with four times its weight of quartz. The experimental results show that Weimarn's hypothesis is in keeping with the facts, for example after heating a specimen of $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ at 180° for five hours the material still retained 2.82 molecules of water, whilst heating the finely ground material at the same temperature for four hours removed all the water but 0.99 mol. per mol.

J. F. S.

Lecture Experiment Demonstrating Adsorption. H. G. TANNER (*J. Amer. Chem. Soc.*, 1923, **45**, 437—438).—A quantity of a solution of malachite green oxalate is poured into a clean beaker and immediately poured away. The beaker is then washed with large volumes of water. Then a few c.c. of water are poured into it, shaken round the walls, and poured into a test-tube. The solution is quite colourless. A few c.c. of glacial acetic acid are next added to the beaker, shaken round the walls, and poured into a test-tube. The solution in this case is distinctly green, due to malachite-green which has been adsorbed on the walls of the beaker and dissolved in the acetic acid.

J. F. S.

Inorganic Chemistry.

Preparation of Active Hydrogen. Y. VENKATARMAIAH (*J. Amer. Chem. Soc.*, 1923, 45, 261—264).—An active form of hydrogen, which will react with cold sulphur to produce hydrogen sulphide may be produced by the continuous burning of oxygen in hydrogen, by the surface combustion of hydrogen and oxygen on a platinum surface, and by a high tension arc in hydrogen between silver electrodes. When gold or platinum electrodes were used in place of silver electrodes in the last method, no active hydrogen, as tested by the non-formation of hydrogen sulphide, was obtained. The author considers that the failure in this case is due to the adsorption of the gas by the thin film of these metals which is deposited on the walls of the reaction vessel during the experiment. Success in all the experiments depends on the temperature being kept low. J. F. S.

Ethyl Alcohol as a Stabiliser for Hydrogen Peroxide. (MME) LISIEVICI-DRAGANESCU (*Bul. Soc. Chim. România*, 1922, 4, 65—68).—Ethyl alcohol is a satisfactory stabiliser for hydrogen peroxide. Added in the proportion of 10% to hydrogen peroxide of 10 vols. strength, a diminution of only about 0·3% was observed after four months with a sample stored in open glass bottles and exposed to sunlight, and only 0·1% in closed coloured glass bottles. To effect the same stabilisation with "perhydrol," the addition of 30% of ethyl alcohol was necessary. G. F. M.

The Magneto-chemical Effect. IV. A. N. SCHTSCHUKAREV (*J. Russ. Phys. Chem. Soc.*, 1918, 50, 109—122).—Chlorine, produced by the electrolysis of barium or caesium chlorides in a magnetic field, disintegrates, giving rise to positive particles, having a mass of about 0·013 that of a hydrogen atom, and to negative particles which are shown to be ordinary electrons. This decomposition is explained as being due to the effect of the magnetic field on the chlorine produced under conditions of changed valency. R. T.

Reaction between Silver Perchlorate and Iodine : Chlorine Tetra-oxide. M. GOMBERG (*J. Amer. Chem. Soc.*, 1923, 45, 398—421).—An investigation of the action of iodine and bromine on dry silver perchlorate in anhydrous solvents has been carried out with the object of ascertaining whether a substance of the formula $(\text{ClO}_4)_x$ could be prepared. The reaction $2\text{AgClO}_4 + \text{I}_2 = 2\text{AgI} + 2(\text{ClO}_4) \rightarrow (\text{ClO}_4)_x$ is found to take place in ethereal solution, but in this case there is a very small amount of a labile iodine compound also formed, which is assumed to be iodine tetra-oxide, produced according to the equation $\text{ClO}_4 + \text{I} \rightarrow \text{IO}_4 + \text{Cl}$. This iodine compound is very unstable and decomposes readily into iodine and oxygen, so that a solution of pure chlorine tetra-oxide in ether is readily obtained. It was found advisable in the preparation to use solutions not exceeding 0·1N. With solutions of this concentration, the properties of the new oxide have been

investigated. The substance is colourless, and is stable in ether solution. It does not volatilise in the ether vapour. It is probably bimolecular, $(\text{ClO}_4)_2$. The chemical activity of the substance would indicate that there is a considerable dissociation into single molecules, but this point has not been investigated. It is readily hydrolysed, yielding ultimately perchloric acid as the only product, but reasons are given for assuming that the primary course of the reaction with water is $2\text{ClO}_4 + \text{H}_2\text{O} = \text{HClO}_4 + \text{HO}\cdot\text{ClO}_4$. It liberates iodine from iodides, but not in equivalent amount. It reacts quantitatively with zinc and magnesium, forming perchlorates; with iron, tin, and copper, forming salts of the metal of lower and higher valency. It acts slowly and incompletely on cadmium, bismuth, and silver. Ethereal solutions of anhydrous perchloric acid and ethyl perchlorate have been submitted to the tests which are characteristic of chlorine tetra-oxide and found to respond to them in a manner entirely different from chlorine tetra-oxide.

J. F. S.

Atomic Weight of Selenium. P. BRUYLANTS and J. DONDENEYNE (*Bull. Acad. roy. Belg.*, 1922, [v], 8, 387—405).—A previous determination was made in 1912 (A., 1913, ii, 500) and gave the figure 79.18. The weight of a normal litre of hydrogen selenide has been determined at pressures of 1, 0.6, and 0.3 atmosphere, the three values being, respectively, 3.6721, 3.65732, and 3.64407 g. The atomic weight of selenium is calculated, making use, in connexion with the compressibility values, of the two methods recommended by Guye (A., 1919, ii, 318), and taking the weight of a normal litre of oxygen as 1.4289 (Moles and Gonsalez, A., 1921, ii, 546). The difference between the new value of the atomic weight, 79.37, and that previously obtained is due to three causes: (a) The divergence of the compressibility between 0 and 1 atmosphere A_0' is, by Guye's method, 0.01083, whilst the value of A_0' calculated from direct measurements of p_v at different pressures and using Berthelot's formula is 0.01302. Guye's method is preferable, owing to the high compressibility of hydrogen selenide. (b) The 1912 determinations of compressibility (from measurements of p_v) give A_0' 0.01191, the density figures giving A_0' 0.01083. (c) In 1912, the local value of g was not known, this difficulty being surmounted by actually determining the weight of a normal litre of oxygen.

These three causes of difference all act in the same direction. The above figure (79.37) will therefore be subject to further correction when new data (for compressibility and weight of normal litre of hydrogen selenide) are available.

The paper contains a very complete table of vapour pressure measurements from $t = -78.01^\circ$ (p 82.89 mm.) to $t = -20.77^\circ$ (p 1799.0 mm.). From these results, the following constants are obtained: b. p.— $-41.2^\circ/760$ mm.; triple point at p 203.3 mm., $t = -65.9^\circ$; molecular latent heat of vaporisation at -41.2° , L 4.76. The boiling points of hydrogen selenide and carbon disulphide give a constant T_1/T_2 ratio between pressures of 230 and 1550 mm. E. E. T.

Catalysis in Homogeneous Gas Reactions: (I) The Catalysis of Formation of Nitrosyl Chloride by means of Bromine. A. KISS (*Rec. trav. chim.*, 1923, 42, 112—144).—The preparation of nitrosyl chloride by combination of nitric oxide and chlorine in presence of bromine takes place with preliminary formation of nitrosyl bromide. Measurements of the velocity of reaction between nitrosyl bromide and chlorine were carried out at temperatures ranging from 0° to 100° and show the reaction to be a clean, rapid gas reaction of the third order. It is accelerated by the presence of water vapour, although water does not act as a catalyst in the reaction between nitric oxide and chlorine at 18°. The formation of nitrosyl chloride either directly or through the intermediate stage of nitrosyl bromide is not affected by light; the direct formation is stimulated by the catalytic effect of a rough surface. The reaction velocity is not affected by the presence of hydrogen chloride or carbon dioxide and if light is excluded both hydrogen and carbon monoxide are without effect. In the case of the reaction between nitrosyl bromide and chlorine, no alteration is brought about by carbon dioxide. H. J. E.

A Low Temperature Electrolyte. WORTH H. RODEBUSH and THEODORE O. YNTEMA (*J. Amer. Chem. Soc.*, 1923, 45, 332—337).—When nitric oxide and hydrogen chloride mixtures are submitted to the temperature of liquid air an intensely purple coloured solid is produced. This solid melts to a purple liquid, which between the temperatures 120° K. and 130° K. has a specific conductivity of more than 10^{-3} ohms, a value which is about the same as that of 0.01N-potassium chloride solution. Attempts to ascertain the composition of this substance were unsuccessful, but it is shown that the vapour pressure of nitric oxide from the purple solid is not appreciably less than that of pure liquid nitric oxide. This indicates that the complex is an exceptionally unstable one. The range over which it exists is small, being roughly between 120° K. and 130° K. It is suggested that the complex is of the form $[\text{NOH}]^+\text{Cl}^-$, and that it is one of the type of compounds containing an odd number of electrons and therefore, according to Lewis's hypothesis (A., 1916, ii, 310), is highly coloured. J. F. S.

Behaviour of Phosphoric Oxide towards Water. A Direct Method for the Preparation of Tetraphosphoric Acid. M. A. RAKUSIN and A. A. ARSENEEV (*Chem. Ztg.*, 1923, 47, 195).—After the violent reaction resulting from the addition of phosphoric oxide to water and formation of orthophosphoric acid has subsided, further quantities are gradually added until the amount reaches about 520% of the water present. After keeping for five days, crystals of tetraphosphoric acid, $\text{H}_6\text{P}_4\text{O}_{13}$, separate from the syrupy liquid. This acid has previously only been prepared in the form of its salts. It melts at 34°, and has d^{15}_4 1.8886. G. F. M.

The Solubility of Phosphoric Oxide in Ethyl and Methyl Alcohols. M. A. RAKUSIN and A. A. ARSENEEV (*Chem. Ztg.*, 1923, 47, 178). Phosphoric oxide dissolves readily to the extent

of 60% in ethyl and methyl alcohols with the development of heat. Considerably greater quantities of the oxide dissolve in the resulting liquids, on continued stirring and heating, up to 295 g. in the case of methyl alcohol giving a liquid of d^{15}_4 1.5437 and up to 258 g. in the case of ethyl alcohol giving a liquid of d^{15}_4 1.5894. These liquids react acid and do not boil on adding water, or give a precipitate with silver nitrate solution.

Phosphoric oxide causes phenol, menthol, and similar substances to dissolve in chloroform without apparently entering into any reaction with them. If the solutions are left for several days and the chloroform is then removed by a current of dry air, the phosphoric oxide and the phenol are recovered unchanged. A. R. P.

Studies in Hypophosphorous Acid. V. Its Reaction with Silver Nitrate. ALEC DUNCAN MITCHELL (T., 1923, 123, 629—635).

Reducing Action of Arsenious Acid. MORITZ KOHN (*Monatsh.*, 1923, 43, 367—371).—Silver nitrate is completely reduced to metallic silver in ammoniacal solution by arsenious acid, which is oxidised to arsenic acid. The reduction is not affected by the addition of neutral salts such as sodium nitrate or sulphate, but is hindered by ammonium sulphate, which causes a decrease in the concentration of hydroxyl-ions. The reduction of cupric sulphate by arsenious acid in presence of aqueous ammonia is not influenced by neutral salts such as potassium chloride or nitrate.

E. E. T.

Phosphorescent Boric Acid. ERICH TIEDE and ALFRED RAGOSS (*Ber.*, 1923, 56, [B], 655—666; cf. Tiede, A., 1921, ii, 75; Tiede and Wulff, A., 1922, ii, 245).—It has been shown previously that intense phosphorescence is produced by the presence of certain organic substances in partly dehydrated boric acid. It is now found that similar products can be derived from boric acid and from completely dehydrated boron trioxide. Products derived from boric acid are obtained by crystallising the acid from water or acetone containing a small amount of the desired organic substance, e.g., terephthalic acid, whereas those from boron trioxide are prepared by drying a mixture of hydrated boric acid and the required impurity over phosphoric oxide at 200°. Since boric acid readily becomes "infected" by the organic impurities present in the air, it is necessary to work under particular conditions which are described in detail in the original. Phosphorescence is excited by exposure to the light of a mercury lamp or iron-carbon arc; it does not generally persist during more than two minutes, the greatest diminution in intensity being observed during the first thirty seconds.

The activating effect of a large number of organic compounds has been examined. Aliphatic compounds do not exert an appreciable effect unless they have become decomposed to some extent. The presence of an aromatic nucleus or condensed system appears to be necessary. The colour of the emitted light depends almost

entirely on the nucleus which is present, with increasing complexity of which it is displaced towards the red. The presence of substituents greatly influences the intensity, but not the colour of the emitted light. Two substituents present simultaneously have their maximum action when in the para-position to one another, their minimum effect in the ortho-position. Saturated side chains, hydroxyl, and sulphonyl groups are feebly activating, the amino-group is inactive by reason of salt formation, and carboxyl greatly increases the brightness, particularly in the presence of a second carboxyl or of one of the feebly activating groups. Coloured substances seldom excite emission. Chlorinated compounds cause an extraordinary shortening of the period of phosphorescence. The presence of bromine, iodine, or the nitro-group inhibits phosphorescence.

Both physical and chemical examinations lead to the conclusion that the organic molecule is to be regarded as causative of the luminescence, and that the boric acid provides the necessary physical conditions. The presence of compounds derived from boric acid and the organic component is in many cases possible and probable, but these substances, *e.g.*, triphenyl borate and tri- β -naphthyl borate, are not in themselves phosphorescent.

The physical characteristics of boric acid phosphors have been described in detail by Tomaschek (A., 1922, ii, 763). It is however, pointed out that the absorption spectra of organic substances in boric acid are similar to those in alcohol, and that phosphorescence of the boric acid phosphors is excited by rays of the same length as those absorbed; the emission spectra in boric acid and in alcohol are compared.

H. W.

The Hydrates of Krypton and Argon. R. DE FORCRAND (*Compt. rend.*, 1923, 176, 355—358).—The dissociation pressures of the hydrate of krypton as measured at various temperatures are 14.5 atmos. at 0°, 23.5 atmos. at 4.8°, 38.7 atmos. at 10.3°, and 47.5 atmos. at 12.5°. At 13°, the hydrate could not be obtained even with a pressure of 100 atmos. The critical temperature of decomposition of the hydrate is thus between 12.5° and 13°. From the above data the formula of the hydrate is calculated as being $\text{Kr}_5\text{H}_2\text{O}$.

A redetermination of Villard's value of the dissociation pressure of argon hydrate (A., 1897, ii, 31) gives the value as 98.5 atmos. at 0.2°, Villard's value thus being too high. From this and the value 210 atmos. at 8° the formula for this hydrate is calculated as being $\text{Ar}_5\frac{1}{2}\text{H}_2\text{O}$.

W. G.

Perchlorates of the Alkali and Alkaline-earth Metals and Ammonium. Their Solubilities in Water and Other Solvents. H. H. WILLARD and G. FREDERICK SMITH (*J. Amer. Chem. Soc.*, 1923, 45, 286—297).—The perchlorates of calcium, strontium, barium, magnesium, lithium, sodium, potassium, rubidium, caesium, and ammonium have been prepared and investigated. The method of preparation in all cases but that of ammonium consists in evaporating the chloride or nitrate to dryness with an excess

of perchloric acid. The ammonium salt was prepared by leading ammonia into a dilute solution of perchloric acid. The solubility of the salts has been determined at 25° in water, methyl alcohol, ethyl alcohol, *n*-propyl alcohol, *n*-butyl alcohol, isobutyl alcohol, acetone, ethyl acetate, and ethyl ether. The density of the solvents and saturated solutions at 25°, and the solubility in each solvent, in grams per 100 c.c. and per 100 g. of solvent and solution and in g.-mols. per 100 c.c. and per 100 g. of solvent and solution are recorded in a number of tables.

J. F. S.

Inorganic Luminescence Phenomena. V. Preparation and Properties of Phosphorescent Sulphides of Sodium and Rubidium. ERICH TIEDE and HERBERT REINICKE (*Ber.*, 1923, 56, [B], 666—674).—In continuation of previous work (Tiede and Richter, A., 1922, ii, 215), the sodium and rubidium sulphide phosphors have been examined. As in the case of the phosphors of the sulphides of the alkaline-earth metals, the presence of a trace of a heavy metal appears necessary for the development of phosphorescence.

Attempts to prepare sodium sulphide by the direct union of sulphur vapour with sodium, by the use of carbon disulphide as in the case of magnesium sulphide (*loc. cit.*), from the azide or by the reduction of sodium sulphate with hydrogen, did not yield a sufficiently pure product. Success was, however, obtained by dissolving sodium hydroxide in absolute alcohol at the atmospheric temperature, dividing the filtered solution into two nearly equal portions, saturating the smaller portion with hydrogen sulphide, uniting it with the second portion, and crystallising sodium sulphide pentahydrate from the mixture as rapidly as possible. The product is dried in small portions over phosphoric oxide at 55°, and is subsequently heated at 600—650° in a graphite boat in a current of pure, dry nitrogen. The material prepared in this manner contains 95% of sodium sulphide, the remainder being composed of sodium hydroxide and a little sodium oxide, the presence of which is regarded as advantageous. When excited by the light of the mercury lamp it shows a faint, ill-defined phosphorescence, whereas specimens prepared from the technical sulphide are either non-phosphorescent or, more frequently, emit a relatively bright green light. The active agent in causing the sulphide to phosphoresce is iron which exerts its maximal action when present in traces much smaller than those generally necessary to produce similar effects; the introduction of suitable traces of the metal is effected by the addition of ferric chloride to the original sodium hydroxide solution. The induced phosphorescence is green, whereas that due to copper is pale yellow. The emission spectrum of sodium sulphide iron phosphor exhibits a narrow green band at 505—560 $\mu\mu$, whereas that of the corresponding copper phosphor has a broad band at 510—650 $\mu\mu$ with a maximum at about 550 $\mu\mu$.

It is remarkable that iron should be the excitant with sodium sulphide phosphors, since it has been found to be inactive with the sulphides of the second group at the concentrations examined

previously. New experiments on the action of much smaller amounts of iron on highly purified zinc sulphide indicate that the metal is active under these conditions.

Attempts to apply the method used in the preparation of sodium sulphide to that of the sulphides of lithium, potassium, or rubidium did not meet with success. Phosphorescent mixtures of rubidium sulphide and sulphate are prepared by the reduction of rubidium sulphate in a graphite boat by hydrogen at about 650° . The emitted light is bluish-red. The preparations decompose very readily. The amount of material available was insufficient to permit the certain identification of the exciting agent which appears to be effective at very small concentrations. H. W.

The Action of Alcohol on the Sulphates of Ammonium.
HORACE BARRATT DUNNICLIFF (T., 1923, 123, 476—484).

Reaction between Selenium and Silver Nitrate in Aqueous Solution. F. GARELLI and A. ANGELETTI (*Atti R. Accad. Lincei*, 1922, [v], 31, ii, 440—445).—The authors are unable to confirm Guyot's statement (this Journal, 1871, 660) that, from neutral or acid solutions of salts of the metals, selenium dissolved in carbon disulphide precipitates only silver as silver selenide. In aqueous solutions the silver may be precipitated completely if excess of selenium is used and the liquid is boiled, the reaction corresponding with the equation: $4\text{AgNO}_3 + 3\text{Se} + 3\text{H}_2\text{O} = 2\text{Ag}_2\text{Se} + \text{H}_2\text{SeO}_3 + 4\text{HNO}_3$ (cf. Senderens, A., 1887, 331). From a neutral solution containing silver, lead, and mercurous or mercuric nitrate, the silver may be precipitated completely in this way, the amount of selenium added being at least twice that of the silver in solution, and the liquid being boiled for fifteen minutes and filtered when cold. The precipitate is heated with nitric acid and the silver estimated as chloride.

Before precipitating selenium from a nitric-hydrochloric acid solution of selenious acid, Treadwell recommends that the liquid be evaporated to dryness to expel excess of nitric acid. This procedure, however, involves loss of selenium owing to the volatility of selenious acid. The addition of alkali chlorides, as suggested by Fresenius, does not entirely overcome this difficulty. If, however, oxidation is effected by nitric acid alone, this may be eliminated by evaporation and the residue then taken up in hydrochloric acid without appreciable loss of selenium. T. H. P.

Hydration of Anhydrite. G. WEISSENBARGER (*Kolloid Z.*, 1923, 32, 181—192).—The hydration of anhydrite has been investigated by following the hardening of the material in the presence of water. It is found that the rate of hydration is accelerated by the presence of ferrous sulphate and other catalysts. The rate of hydration also depends on the size of the particles. When the size of the particles is greater than a definite maximum value anhydrite is not hydrated, but when the particles are very small water is taken up readily. The following substances are shown to be definite compounds involved in the process of the

hydration of anhydrite : gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$; soluble anhydrite, CaSO_4 ; anhydrite, $(\text{CaSO}_4)_2$; and the hemihydrate, $2\text{CaSO}_4 \cdot \text{H}_2\text{O}$.

J. F. S.

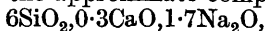
Suspensions of Particles of Barium Sulphate of Various Sizes Examined by Transmitted and Reflected Light. AAGE W. OWE (*Kolloid Z.*, 1923, 32, 73—77).—Suspensions of barium sulphate in glycerol, mixtures of alcohol and glycerol and water and glycerol have been examined by both reflected and transmitted light. It is shown that the degree of turbidity as determined nephelometrically and also by transmitted light is dependent not only on the size of the particles but also on the composition of the dispersion medium. This dependence is due chiefly to changes of the index of refraction of the solvent and to the changes in the form of the combined particles. The degree of turbidity, obtained nephelometrically in pure glycerol, reaches a maximum value with particles somewhat less than $200 \mu\mu$. In aqueous glycerol the maximum is probably displaced toward larger particles. The degree of turbidity, as obtained by means of transmitted light, increases steadily with increasing size of particles at least up to $1000 \mu\mu$. The maximum which must of necessity exist lies probably in the region of particles having a size of several thousand $\mu\mu$.

J. F. S.

[A Simple Method for the Preparation of Highly Phosphorescent Zinc Sulphide.] ERICH TIEDE and ARTHUR SCHLEEDE (*Ber.*, 1923, 56, [B], 674—675).—In a recent communication (this vol., ii, 75), Schmidt has described the preparation of highly phosphorescent zinc sulphide, and has been drawn to the conclusion that its phosphorescence is inhibited by the presence of metals which yield black sulphides. This observation is directly opposed to the observations of Tomaschek (*A.*, 1921, ii, 588). It is pointed out that Schmidt's procedure does not give any guarantee that the necessary amounts of copper are not introduced with the many salts employed and that it is therefore quite possible that subsequent additions of the element may cause its concentration to exceed the narrow limits required for optimal effect. A specific action in Schmidt's method cannot be attributed to the chlorides of the alkaline-earth metals and magnesium, since they can be replaced by the alkali chloride; the chloride is the important component.

H. W.

The Action of Water and Steam under Pressure on some Soda-Lime-Silicate Glasses. F. W. HODKIN and W. E. S. TURNER (*J. Soc. Glass Tech.*, 1922, 6, 291—308).—Four soda-lime-silicate glasses having the approximate compositions



$6\text{SiO}_2, 0.7\text{CaO}, 1.3\text{Na}_2\text{O}$, $6\text{SiO}_2, 0.8\text{CaO}, 1.2\text{Na}_2\text{O}$, and $6\text{SiO}_2, \text{CaO}, \text{Na}_2\text{O}$ were subjected to the action of water and steam at pressures varying from 2 to 25 atmospheres above normal. The action of steam on these glasses is considerable, being greater than that of water at the higher pressures in the case of the glass having the

lowest lime content. Corrosion diminishes as the amount of lime is increased and the amount of sodium oxide decreased. The glass with the highest lime content was unattacked by steam or water in three hours at 2 to 4 atmospheres. The incrustation formed as a result of corrosion was harder the greater the lime content; a gelatinous layer was formed beneath the incrustation on the glass containing only 0.3CaO at 15 atm. pressure. Since the loss in weight recorded was less than the total alkali found in the water, it is clear that the glass absorbs a considerable quantity of water. The character of the corrosion, which clearly brings out pouring and moulding lines, is influenced markedly by the condition of the surface. The autoclave test is considered too severe for soda-lime-silicate glasses which are only required to resist the action of boiling water.

E. H. R.

The Crystal Structure of the Alums. RALPH W. G. WYCKOFF (*Amer. J. Sci.*, 1923, 5, 209—217).—Studies of the Laue and spectrum photographs of potassium and ammonium aluminium alums were undertaken with a view to determine the space grouping of the alums. The hemihedral nature of the crystal structure is evident at once from the photographs, and from a study of the reflections from planes with one index zero, it is shown that the corresponding space group is T_h^6 , rather than T_h^2 . There are four molecules with the composition $\text{R}'\text{R}''(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ in the unit cell, and in this space group the four sulphate oxygen atoms cannot be exactly alike. Three of these atoms will be similarly placed, but the fourth will be different from the other three. The twelve water molecules fall in two groups of six each. The positions of the K or N and the Al and S atoms are given, but no attempt has been made to locate those atoms having variable parameters. The hydrogen atoms of the ammonium groups cannot be arranged in a chemically plausible radicle which will possess a symmetry in keeping with the rest of the crystal. The spectrographic observations show that unaided spectrometer measurements are insufficient for the determination of crystal structure.

W. E. G.

Some Properties of Manganese Dioxide. A. DE HEMPTINNE (*Bull. Acad. roy. Belg.*, 1922, [v], 8, 71—75).—Manganese dioxide is slowly reduced by hydrogen at room temperatures, to give a product which slowly re-oxidises in the air. The dioxide rapidly absorbs hydrogen sulphide from a mixture of this gas with hydrogen, manganese sulphides being formed. The absorption is much more rapid than with dry hydrogen sulphide alone, although in presence of moisture this gas is readily absorbed by manganese dioxide.

E. E. T.

Cementation by means of Boron. N. PARRAVANO and C. MAZZETTI (*Atti R. Accad. Lincei*, 1922, [v], 31, ii, 424—425).—When steel is heated at 900° in an atmosphere of boron chloride and hydrogen, it becomes coated with a layer of very hard alloy rich in boron and capable of cutting glass. Nickel also undergoes cementation under these conditions.

T. H. P.

The Constitutional Diagram of the Iron-Carbon-Tungsten System. SIGEAKI OZAWA (*Sci. Rep. Tôhoku Imp. Univ.*, 1922, **11**, 333—350).—There is only one compound in the iron-tungsten system, viz. Fe_2W . In the iron-carbon-tungsten system this compound and iron carbide are mutually soluble at certain concentrations and the resulting solution splits up with the simultaneous separation of tungsten carbide, WC. A ternary eutectic containing 15% W, 3.6% C, and 81.4% Fe is formed and melts at 1065° (cf. *J.S.C.I.*, 1923, April).
A. R. P.

Constitution of Ferric Oxide Hydrosol from Measurements of the Chlorine and Hydrogen Activities. FREDERICK L. BROWNE (*J. Amer. Chem. Soc.*, 1923, **45**, 297—311).—Using a calomel electrode as comparison electrode the chloride-ion activity has been measured in solutions of ferric chloride and in ferric oxide sols of various concentrations and widely varying purity. A method is described for using the hydrogen electrode in the presence of dilute solutions of ferric chloride, and this has been used for the measurement of the hydrogen-ion activity in ferric oxide sols. Ferric oxide sols having a total iron concentration of about 0.5 g. equiv. per litre and a purity of less than 14 (purity=g. equiv. Fe/g. equiv. Cl) contain ferric chloride and hydrochloric acid in the aqueous phase and the dispersed ferric oxide carries considerable amounts of adsorbed ferric chloride and hydrochloric acid. The adsorption of ferric ion and hydrogen-ion is greater than that of chloride-ion, thus giving the dispersed phase a positive charge. At higher purities, the adsorption of ferric-ion and hydrogen-ion is complete and the aqueous phase contains only chloride-ion, the “kations” for which are the dispersed particles. At lower concentration of total iron, ferric-ion and hydrogen-ion disappear from the aqueous phase at somewhat lower purity and at higher concentrations at high purity. The effect of dextrose on the freezing point of ferric oxide sol shows that practically all the water present in the sol acts as solvent for substances dissolved in the sol. Tables are given showing the concentrations of chloride-ion and its distribution between ferric chloride and hydrochloric acid in sols of widely varying purity and concentration, as well as the total chloride compounds adsorbed by the ferric oxide.
J. F. S.

The Higher Oxide of Nickel. OWEN RHYS HOWELL (*T.*, 1923, **123**, 669—676).

The System Chromium Trioxide-Nitric Acid-Water. STANLEY AUGUSTUS MUMFORD and LIONEL FELIX GILBERT (*T.*, 1923, **123**, 471—475).

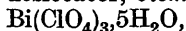
The Adsorption of Stannous Chloride by Stannic Acid. GEORGE ERNEST COLLINS and JOHN KERFOOT WOOD (*T.*, 1923, **123**, 452—456).

Constitution of Black Maketu Sand. C. J. SMITHELLS and F. S. GOUCHER (*Nature*, 1923, **111**, 397; cf. Scott, *T.*, 1923, **123**, 311).—Careful chemical and X-ray analysis of the black sand from

Maketu, N.Z., confirms Bohr's conclusion that no new element is present. A residue insoluble in sulphuric acid and fused sodium hydrogen sulphate was attacked by potassium hydrogen sulphate, and was found to contain iron and aluminium in equal parts (cf. Scott, T., 1923, 123, 881). A. A. E.

Studies on Metal Hydrides. The Electrolytic Formation of Stibine in Sulphuric Acid and in Sodium Hydroxide Solution. HENRY JULIUS SALOMON SAND, EDWARD JOSEPH WEEKS, and STANLEY WILSON WORRELL (T., 1923, 123, 456—470).

Perchlorates of Bismuth and Antimony. FR. FICHTER and ERNST JENNY (*Helv. Chim. Acta*, 1923, 6, 225—231).—The method described by Muir (this Journal, 1876, i, 878) for the preparation of a perchlorate of bismuth, which is reproduced in the text-books, is attended with serious danger of explosion, especially when bismuth powder is dissolved in 70% perchloric acid. By dissolving bismuth powder very carefully in 40% perchloric acid a solution was obtained similar to that obtained by dissolving bismuth oxide in 70% acid. When this solution is evaporated in a vacuum desiccator, *bismuth perchlorate*,



is obtained in small, hexagonal tables which rapidly change in moist air into a bismuthyl salt. When an aqueous solution of the normal perchlorate is evaporated slowly, *bismuthyl perchlorate trihydrate*, $\text{BiO} \cdot \text{ClO}_4 \cdot 3\text{H}_2\text{O}$, is obtained in aggregates of doubly refracting prismatic needles. It is very unstable and has a great tendency to change even in the mother-liquor into the *monohydrate*, $\text{BiO} \cdot \text{ClO}_4 \cdot \text{H}_2\text{O}$. This is the most stable salt and separates from all solutions not too concentrated with respect to perchloric acid. It forms very hygroscopic, rhombohedral crystals. The anhydrous salt, obtained by drying the monohydrate at 80—100°, is a white powder, differing from that described by Muir in being completely soluble in water. When concentrated perchloric acid is saturated with bismuth oxide, a mass of crystals separates, the composition of which approximates to $\text{OH} \cdot \text{Bi}(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$.

A perchlorate of antimony is obtained by dissolving antimony oxide in ten times its weight of 70% hot perchloric acid. Too high a temperature causes oxidation to antimonic acid. On cooling, antimonyl perchlorate separates in small needles having the composition $\text{SbO} \cdot \text{ClO}_4 \cdot 2\text{H}_2\text{O}$. Some preparations were anhydrous. E. H. R.

Formation of Colloidal Gold Solutions by Means of Electrical Spark Discharges. W. NAUMOV (*Kolloid Z.*, 1923, 32, 95—100).—During a repetition of Donau's experiments on the preparation of colloidal solutions of gold (A., 1915, ii, 352) it was found that two types of discharge have to be differentiated. In the first type, where the discharge occurs between two dry electrodes hydrosols are produced because new reducing gases are produced in the vapour above the solution; these gases dissolve

in the solution and reduce the gold chloride. In the second types, the discharge occurs between one dry electrode and the solution or between two moist electrodes, whereby hydrogen peroxide is produced in the solution which reduces the gold chloride. In the portion of the solution which serves as negative pole, coarse violet or blue sols or suspensions are produced whilst the positive portion of the solution contains more or less highly disperse red hydrosols. In both positive and negative parts of the solution acid hydrosols are produced. The polarity of the solution exercises a great influence on the amount of acid in these solutions, which in its turn is determinative of the character of the sol and of its properties. The addition of a solution containing nuclei to the gold chloride solution causes the formation of the sol to take place more easily, reduces the time required for reduction, and produces bright red sols.

J. F. S.

Mineralogical Chemistry.

Some New Derivatives of Bituminous Coal. ARCHIBALD R. PEARSON (*J. Soc. Chem. Ind.*, 1923, 42, 68—72T).—The term "ultrahumin" is suggested for the constituents of coal derived from humified vegetable proteins and celluloses as distinct from resins, waxes, etc. The preparation of α -(pyridine insoluble) and β -, and γ -(pyridine soluble) ultrahumins is described. Oxahumins, produced by oxidation of ultrahumins with fuming sulphuric acid, contain more than 90% of the nitrogen content of the ultrahumins, and, when brominated, take up about one-third of their weight of bromine, forming a series of compounds of approximately constant composition. The brominated products form negative sols in water or alcohol. It is concluded that ultrahumins contain a very stable molecular nucleus including the nitrogen in heterocyclic combination. The oxidised nucleus is retained, at least in part, in oxahumins brominated to saturation. J. S. G. T.

The Deposits of Potassium Chloride at Solikamsk. N. S. KURNAKOV, K. F. BELOGLAZOV, and M. K. SCHMATKO (*J. Russ. Phys. Chem. Soc.*, 1918, 50, 122—130).—Samples of rock salt and of sylvine from Solikamsk are described and analysed. The potassium chloride in the former is from 0.26% to 11.9%, and in the latter up to 63.2%. The sylvine is very similar in content and appearance to that found at Stasfurt or Kalusz. Varying small percentages of potassium chloride are found to be present in the mother-liquors from salt works in different parts of Russia. R. T.

Brugnatellite from Monte Ramazzo (Liguria). ETTORE ARTINI (*Atti R. Accad. Lincei*, 1922, [v], 31, ii, 491—496).—Analysis of brugnatellite from Monte Ramazzo gives the following results :

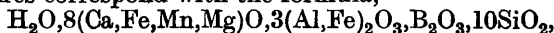
H ₂ O.	CO ₂ .	Fe ₂ O ₃ .	MnO.	CaO.	MgO.	Insol. residue.	Total
32.42	8.00	16.12	1.77	1.19	39.13	0.99	99.62

When corrected for the small proportion of extraneous calcium carbonate present, these numbers are in good agreement with those obtained for brugnatellite from Val Malenco (A., 1909, ii, 247) and with the formula proposed by the author, the slight excess of ferric oxide probably existing in the free state as a product of alteration. The results also render evident the distinction between this mineral and pyroaurite, this being borne out by physical differences (cf. Foshag, A., 1920, ii, 765). The brucite from which this brugnatellite is derived by epigenesis contains: H_2O , 30.37; FeO , 1.37; MnO , 0.38; MgO , 67.96; insoluble residue, 0.10; total, 100.18. If these numbers are corrected for the insoluble matter and the FeO and MnO are replaced by MgO , they correspond closely with the composition of $\text{Mg}(\text{OH})_2$. T. H. P.

Chemical and Optical Study of the Axinite of Prali (Valle della Germanasca). E. GRILL (*Atti R. Accad. Lincei*, 1922, [v], 31, ii, 521—524).—This axinite, d 3.314, occurring as a pale, violet-red vein in a mass of erratic gneiss, has the composition:

SiO_2 .	TiO_2 .	B_2O_3 .	Al_2O_3 .	Fe_2O_3 .	FeO .	MnO .	MgO .
41.26	nil	4.70	18.74	2.02	6.11	4.43	1.75
CaO .	H_2O (-110°).	H_2O ($+110^\circ$).		F .		Total .	
19.52	0.46	1.25		trace		100.24	

These figures correspond with the formula,



which contains 1 mol. of water less than that established by Whitfield (A., 1888, 347) and is not reducible to that of an orthosilicate (cf. Ford, A., 1903, ii, 436). T. H. P.

Analytical Chemistry.

Spectroscopic Methods of Analytical Chemistry. C. AUERWELSBACH (*Monatsh.*, 1923, 43, 387—403).—A survey of the actual experimental methods employed by the author in carrying out analyses with the aid of spark spectra. Photographs of the apparatus used and a chart showing the lines in the spark spectra of a large number of elements are appended. The effect of the presence of alkalis, zinc oxide, etc., on the spark spectrum of platinum is discussed.
E. E. T.

The Application of the Quinhydrone instead of the Hydrogen Electrode in the Potentiometric Measurement of Acidity. I. M. KOLTHOFF (*Rec. trav. chim.*, 1923, 42, 186—198; cf. Biilmann, A., 1921, ii, 372).—The quinhydrone electrode gives excellent results in the titration of acid solutions and may replace the hydrogen electrode for that purpose. It is, however, unsuitable for use in alkaline solution if air is not excluded owing to the oxidation of a portion of the quinhydrone to acid.
H. J. E.

Estimation of Blood Alkalinity. HANS GOLLWITZER (*Biochem. Z.*, 1923, **134**, 590—600).—The exact gas analysis method of Barcroft has been compared with the titration methods of Rohanyi (*Münch. med. Woch.*, 1920, **67**, 51), and of Van Slyke (*A.*, 1919, ii, 298). The Van Slyke method yields too high and the Rohanyi method too low results. The gas analysis method is much to be preferred to either of the other two. W. O. K.

The Stability of an 0·01N-Sodium Oxalate Solution. EDWARD S. HOPKINS (*Ind. Eng. Chem.*, 1923, **15**, 149).—The addition of 100 c.c. of 1:4-sulphuric acid per litre to sodium oxalate solution prevents its deterioration for at least two months, even when the solution is stored in clear glass bottles exposed to daylight. G. F. M.

The Colorimetric Estimation of Water in Absolute Alcohol. I. M. KOLTHOFF (*Pharm. Weekblad*, 1923, **60**, 227—231).—The sensitiveness of methyl-orange to acids is much less in alcohol solutions than in water solutions, diminishing to a minimum for alcohol of about 90% volume strength, and increasing again for alcohols between 90 and 100%. The sensitiveness is determined by the volume of alcoholic hydrogen chloride (*N*/10) required to produce a standard tint with 0·1 c.c. saturated methyl-orange solution in 25 c.c. of the alcohol under examination. A suitable standard is obtained by adding 0·4 c.c. of *N*/100-hydrochloric acid solution to 0·1 c.c. of saturated methyl-orange solution in 25 c.c. of water; a table is given showing for various alcohols between 95 and 99·7% by volume the sensitiveness expressed in quantities of acid required at 15° to produce the standard tint, compared with the quantity used in water, the figure rising from 5·2 for 99·7% alcohol to 126 for 95% alcohol, compared with 1 for water. The influence of temperature is important, a rise causing the colour to change to the alkaline side in water, but having the opposite effect in alcohol. Figures for temperature correction are given.

S. I. L.

Detection of Chlorine, Bromine, Iodine, and Silver in a Mixture of Silver Halides. H. SCHMALFUSS (*Z. anal. Chem.*, 1923, **62**, [6], 229—231).—Silver chloride is extracted from the mixture of silver halides by shaking with a 15% solution of ammonium hydrogen carbonate. The presence of the chloride is confirmed by reprecipitation as silver bromide with potassium bromide. The residue is shaken with hydrogen sulphide solution, and the silver precipitated as sulphide, collected, dissolved in nitric acid, and confirmed by precipitation as chloride with hydrochloric acid. Half the filtrate, after the removal of the silver sulphide, is treated with carbon disulphide and sodium nitrite, and concentrated nitric acid added drop by drop. A violet coloration in the carbon disulphide indicates iodine. The remaining half of the filtrate is treated with carbon disulphide and chlorine water; after the iodine has been oxidised to iodic acid, any bromine liberated produces a brown coloration in the carbon disulphide.

Alternatively, the liquor from the first half after the removal of the iodine may be decanted off, more carbon disulphide added, and the bromine liberated with chlorine water. J. B. F.

Apparatus for the Estimation of Halogens in Organic Compounds. K. RÜBKE (*Z. angew. Chem.*, 1923, 36, 156—158; cf. Voigt, A., 1923, ii, 34).—The halogen compound is dissolved in benzaldehyde or, in the case of liquids of high b. p. and of solids, in a mixture of benzaldehyde and alcohol, and the solution burnt in a lamp of about 20 c.c. capacity provided with an asbestos thread as wick. The lamp is surrounded by a glass chimney and the products of combustion pass through two U-tubes containing glass beads. In each U-tube 25 c.c. of *N*/50-potassium hydroxide are placed to absorb the halogen acid produced in the combustion; this is ultimately washed out through taps at the bottom and titrated with standard silver nitrate. Halogen-free air for the combustion, drawn from outside the laboratory by means of a water-pump, passes through a sulphuric acid drier and enters the combustion chimney through a glass tube in which the lamp is loosely held. The current of air should be about 1 litre per minute. In the case of chlorine compounds, the whole of the hydrogen chloride is absorbed in the first U-tube. Hydrogen bromide, however, is not so readily absorbed and part of it is found in the second U-tube. Whilst the method of Voigt (cf. above) is valuable for rapid routine analyses, the present variation is to be preferred where the time involved is of secondary importance. Further, oxy-hydrogen explosions, which can occur if due precautions are not taken in Voigt's method, are impossible in the above. Full working details and a sketch of the apparatus are given. W. T. K. B.

The Titration of Bleaching Powder. I. M. KOLTHOFF (*Pharm. Weekblad*, 1923, 60, 241—248).—Bunsen's iodine titration in acid solution gives higher results than other methods; this is not due to the presence of chlorate, but to chlorite formed when the solution or the damp solid is kept. Suitable conditions for the titration are given. Penot's direct titration with arsenite and Pontius's iodide method give accurate results for the hypochlorite content; the best conditions are given. In the latter, petrol is suggested as an indicator instead of starch, the first trace of free iodine forming a violet solution in the organic liquid on shaking.

S. I. L.

The Detection of Fluorine in Inorganic Fluorides. H. TER MEULEN (*Chem. Weekblad*, 1923, 20, 59).—In presence of borates, the etching test gives no result, owing to the formation of boron fluoride. If the gas is passed into water, a cloud is formed, which is seen under a lens to consist of fine crystals.

S. I. L.

Limit of Sensitiveness of the Acidification Reaction for Thiosulphates. O. HACKL (*Chem. Ztg.*, 1923, 47, 174).—The limit of sensitiveness of the reaction for the detection of thiosulphates by the precipitation of sulphur on acidification lies

between a content of 0.1 and 0.05 mg. of S_2O_3 per c.c. With the latter concentration, no cloudiness whatever appears, even on boiling or on long keeping, and even with the former concentration and up to 1 mg. of S_2O_3 per c.c. no immediate separation of sulphur occurs in the cold, and only after some minutes at the boiling temperature. G. F. M.

The Reaction of Silver Nitrate with Thiosulphate and its Sensitiveness. O. HACKL (*Chem. Ztg.*, 1923, 47, 210).—The production of a yellow to brown colour when very dilute solutions of a thiosulphate are treated with silver nitrate is a very delicate reaction, as 0.1 mg. of S_2O_3 can thereby be detected in 100 c.c. of water, whereas the acid test (formation of a white sulphur cloud on acidification) will detect 0.1 mg. in 1 c.c. only. A. R. P.

General Method for the Detection of Volatile Acids. G. KARAOGLANOV (*Z. anal. Chem.*, 1923, 62, 217—222).—The salt solution is mixed in a flask with 2*N*-acetic acid and a current of an indifferent gas such as air or hydrogen drawn through the solution. The gas is then led through tubes containing reagents sensitive to the acids concerned. The method is applicable to the following volatile acids: hydrogen cyanide, hydrogen sulphide, nitrous acid, sulphurous acid, hypochlorous acid, and carbonic acid, the detection reagents being silver nitrate, lead acetate, diphenylamine, dilute starch-iodide solution, indigo-solution, and barium hydroxide, respectively. Thiosulphuric acid is decomposed by concentrated acetic acid with the precipitation of sulphur, but in dilute acid no decomposition takes place. Ferro- and ferricyanic acids only decompose on long keeping. The remaining acids under these conditions are non-volatile. To detect sulphite in presence of thiosulphate, acetic acid is added of such a strength that no sulphur is precipitated, and the issuing gas passed through starch-iodide solution. To test for *thiosulphite*: To a portion of the clear solution from the flask, sulphuric acid is added; a precipitation of sulphur indicates thiosulphate. If sulphide is also present, the sulphide is precipitated from neutral solution by zinc chloride, the filtrate tested as above, and the precipitate tested separately. Nitrite in presence of nitrate and chlorate, hypochlorite in mixtures of hypochlorite, chlorate and perchlorate, cyanide in presence of chloride, bromide, ferro- and ferri-cyanides can be readily detected, since the remaining acids in each case are not volatile under the conditions of the experiment. To detect two or more volatile acids in the same mixture the gas is passed through the reagents in series. Thus (a) for cyanide and sulphite it is passed successively through (i) a nitric acid solution of silver nitrate, (ii) starch-iodide solution. (b) For sulphide and cyanide, through (i) an acetic acid solution of lead acetate, (ii) nitric acid solution of silver nitrate. (c) For sulphite, cyanide, and carbonate, through (i) a nitric acid solution of silver nitrate, (ii) a weak solution of starch-iodide to detect sulphite, (iii) concentrated iodine solution to retain sulphite, (iv) barium hydroxide solution. (d) For cyanide, sulphite, sulphide, thiosulphate, and carbonate, zinc chloride is added to a neutral solu-

tion and the sulphide, cyanide, and carbonate precipitated and filtered off. The filtrate and precipitate are then examined separately as above. As a preliminary experiment in order to determine whether any of the volatile acids are present the gas is passed separately through reagent tubes containing (i) a nitric acid solution of silver nitrate, (ii) barium hydroxide solution, (iii) starch-iodide solution. A turbidity indicates in (i) cyanide, sulphide, or hypochlorite, in (ii) sulphite or carbonate; a blue coloration in (iii) indicates hypochlorite or nitrite. The volatile acids included in this scheme form an analytical group.

J. B. F.

Detection of Nitrogen in Mineral and Organic Substances by Microchemical Methods. AL. IONESCU and C. HÂRȘOVESCU (*Bul. Soc. Chim. România*, 1922, 4, 61—65).—The formation of yellow crystals of ammonium picrate of characteristic appearance when even small traces of ammonia vapour are allowed to impinge on a drop of picromalonic reagent (a saturated solution of picric acid in ethyl malonate) or of an alcoholic solution of picric acid containing 5% of glycerol, on a microscope slide, may be used as a delicate specific test for ammonia nitrogen. With the picromalonic reagent tiny, quadratic crystals are formed, whilst with the alcoholic picric acid larger crystals in the form of more or less elongated yellow prisms are obtained. The latter reagent is the more sensitive owing to the evaporation of the alcohol. The ammonia is generated by heating the substance to be tested with sodium hydroxide solution if inorganic, or with soda-lime if organic. Volatile amines do not give the reaction.

G. F. M.

Estimation of Phosphorus. G. E. F. LUNDELL and J. I. HOFFMAN (*Ind. Eng. Chem.*, 1923, 15, 171—173).—Details are given of the application of the methods described in the first part of this paper (this vol., ii, 85) to the estimation of phosphorus in metallurgical products such as iron, plain carbon steel, alloy steel, and bronze. The reduction method is slightly more trustworthy with solutions which do not contain interfering elements than the alkalimetric method, but the advantage does not outweigh its inconvenience, and probably vanishes with phosphomolybdate obtained in the presence of such reducible substances as titanium, arsenic, or vanadium. The alkalimetric method yields under severe conditions values sufficiently accurate for technical purposes provided attention is paid to the temperature at which precipitation is effected. The direct precipitation of phosphorus as phosphomolybdate in bronze assays has not hitherto been recommended, but by following the method here described, provided a clear solution can be obtained in the amount of mixed nitric and hydrochloric acids specified, better recovery of the phosphorus has actually been obtained than by the widely-used Oettel method. 1—3 G. of the bronze are dissolved in a mixture of 15 c.c. of nitric acid and 5 c.c. of hydrochloric acid, 15 c.c. of water are added, and after digesting at 80° for ten minutes and diluting to 50 c.c., 100 c.c. of the molybdate reagent are added, and the mixture is kept for four to six hours. The precipitate is then collected, dissolved in 20 c.c. of ammonia

containing 2 g. of citric acid, and the ammoniacal solution treated as previously described (*loc. cit.*). Tungsten steel must also be dissolved in a nitro-hydrochloric acid mixture. G. F. M.

Estimation of Phosphorus in Vanadium Ores. F. W. KRIESEL (*Chem. Ztg.*, 1923, 47, 177—178).—Precipitation of phosphoric acid in the presence of relatively large amounts of vanadic acid by means of ammonium molybdate yields an orange-brown precipitate containing much vanadic acid. Treadwell's modification involving reduction of the vanadium to vanadyl sulphate also gives high results. Satisfactory results may be obtained by removing the vanadium as vanadyl ferrocyanide after first effecting a concentration and partial separation of the phosphoric acid by boiling the solution with nitric acid and tin. The precipitate contains all the phosphorus and some vanadium; it is fused with potassium cyanide to remove tin and arsenic and the solution of the fused mass is boiled with hydrochloric acid to expel hydrocyanic acid, then with potassium ferrocyanide to precipitate the remaining vanadium. The filtrate is treated with alum and ammonia to separate the phosphoric acid from chlorides and ferrocyanides, the precipitate is dissolved in nitric acid, and the solution treated with molybdate mixture in the usual way (cf. *J.S.C.I.*, 1923, April). A. R. P.

Valuation of Insoluble Phosphates by means of a Modified Citric Acid Test. G. S. ROBERTSON and F. DICKINSON (*J. Soc. Chem. Ind.*, 1923, 42, 59—62r).—The authors contend that the respective values of phosphatic fertilisers may be determined by a modification of the solubility test proposed by Wagner. For this purpose, they propose that the solubility be determined by shaking 1 g. of the phosphate (in place of 5 g. proposed by Wagner) with 500 c.c. of 2% citric acid solution for half an hour in a shaker making 30 revolutions per minute. Results of field tests are given in support of the contention. J. S. G. T.

Electrolytic Apparatus for the Estimation of Arsenic. G. W. MONIER-WILLIAMS (*Analyst*, 1923, 48, 112—114).—The apparatus is a modification of that described by Sand and Hackford (*T.*, 1904, 85, 1018), lead electrodes being used. The walls of the porous pot are little more than 1 mm. thick. The anode is a strip of lead foil and the cathode a disk of the same material about 2.5 cm. in diameter. The central glass vessel and the tap funnel are blown in one piece and the calcium chloride tube is connected by a ground glass joint. The hard glass tube for the reception of the arsenic mirror is 2 mm. in diameter and is connected with the apparatus by a short piece of caoutchouc tubing. A piece of metal gauze is wrapped round the part of the tube exposed to the flame and a sharper arsenic mirror is obtained by wrapping a small piece of filter-paper round the tube, with its end dipping into water. The current used is 5—6 amperes, the potential difference between the electrodes being 7—9 volts. Foodstuffs of the most varied character can be tested without preliminary treat-

ment. Large amounts of phosphoric acid or phosphates appear to inhibit the formation of arsine. Iron also acts as an inhibiting agent when no organic matter is present. The small quantities of phosphates and iron present in many foodstuffs do not appear to have any effect. The electrolytic method is sensitive to 0.001 mg. of arsenious oxide, and to a great extent eliminates the personal equation.

H. C. R.

Potentiometric Titration of Arsenic and Antimony.
EDUARD ZINTL and HERMANN WATTENBERG (*Ber.*, 1923, 56, [B], 472—480).—Tervalent arsenic and antimony can be readily estimated by titration with standard potassium bromate in hydrochloric acid solution, the end-point being determined potentiometrically (cf. Zintl and Wattenberg, A., 1922, ii, 871).

In the case of trivalent arsenic, the end-point indicated potentiometrically is identical with that given by methyl-orange if the concentration of hydrochloric acid is below 10%. The potentiometric method has, however, the advantage that the proximity to the end-point is much more distinctly indicated and the titration can therefore be more rapidly performed.

Tervalent antimony may be estimated in cold solution in the same manner as arsenic. [Test analyses indicate that the value, 120.2, usually adopted for the atomic weight of antimony is more than 1% low, but are in harmony with the datum, 121.77, of Willard and McAlpine (A., 1921, ii, 405).] The titration can be equally effected in hot solution if atmospheric oxidation is avoided by rapid manipulation.

Reduction of quinquivalent antimony is effected by the action of titanium trichloride solution in the presence of a little copper sulphate on the nearly boiling antimony solution, which must contain about 5% of hydrochloric acid. The end-point of the reduction is determined potentiometrically, after which the titration with bromate is effected as usual. Alternatively, the antimony solution, containing at least 5% of free hydrochloric acid, is heated nearly to boiling and treated with ten drops of phosphotungstic acid (10%). Titanium trichloride is added with constant shaking until a marked blue colour is developed which does not disappear after two minutes. Three drops of copper sulphate solution (1%) are added as catalyst, and the solution is shaken and exposed to air as much as possible, whereon the blue colour disappears within one to two minutes. The solution is immediately titrated with bromate in the presence of methyl-orange. The presence of stannic salts does not cause complications in this or the potentiometric estimation of antimony.

The reduction of quinquivalent arsenic is effected with great difficulty by stannous chloride, chromous chloride, or titanium trichloride. It is therefore readily possible to estimate antimony by titration in the presence of quinquivalent arsenic; in this case, the potentiometric method must be used, since the presence of phosphotungstic acid causes the reduction of arsenic acid.

If arsenic and antimony are present entirely in the trivalent

condition, they may be estimated in a single solution. Their sum is first estimated by titration with bromate solution, and subsequently the antimony is determined alone after reduction with titanium chloride under potentiometric control.

Preliminary experiments show that thallium, sulphurous acid, potassium ferrocyanide, and hydrazine can also be estimated potentiometrically. H. W.

The Estimation and Separation of Arsenic, Antimony, and Tin. K. K. JÄRVINEN (*Z. anal. Chem.*, 1923, 62, 184—204).—After describing experiments in which the accuracy of the bromate method for the titration of arsenious and antimonious chlorides is proved, it is shown that the completeness of the reduction of stannic chloride by iron depends on the complete exclusion of air from the apparatus until the solution is quite cold and on the use of sufficient iron, at least 6 g. of ferrum redactum per 100 c.c. of solution being required. The most satisfactory reducing and volatilising agents for use in the separation of arsenic from antimony and tin by distillation from a chloride solution were found to be potassium iodide and a mixture of potassium bromide and sodium sulphite. In the latter case, the distilling flask must be fitted with a 3-bulb Young's stillhead in order to avoid any antimony passing over towards the end of the distillation. The complete separation of antimony from tin by precipitation with metallic iron is extremely difficult, as the precipitate almost invariably contains tin and if an attempt to remove this by prolonged digestion of the precipitate in the solution is made a certain amount of antimony dissolves. However, addition of a further small quantity of iron and filtration of the solution before all the iron is dissolved yields a precipitate free from tin, but containing iron and not suitable for titration with bromate. It is rinsed back into the beaker, the residue on the paper dissolved in hydrochloric acid with a few mg. of potassium chlorate, and the solution treated with twice its bulk of hydrogen sulphide water. The precipitate is collected, washed, and dissolved in nitric and sulphuric acids. The solution, including the filter-paper, is heated in a Kjeldahl flask until colourless, 1 g. of sodium thiosulphate is added, and the heating continued until all the sulphur has disappeared. The mass is dissolved in water and titrated with potassium bromate. The filtrate from the first antimony precipitate is reduced with iron and titrated for tin as usual. A. R. P.

Apparatus for Use in the Combustion Analysis of Volatile Hygroscopic Liquids. JOHN BALDWIN SHOESMITH (*J. Soc. Chem. Ind.*, 1923, 42, 57—58t).—The apparatus consists of a capillary bulb tube which is connected by a capillary opening with a second and somewhat larger bulb; the latter serves as an air reservoir. After the sample has been introduced into the capillary bulb, the capillary is sealed and the end inserted into a short piece of glass tubing which is constricted at its middle. The whole is placed in the combustion tube and the capillary is broken against the constriction in the glass tubing by applying pressure to the

latter. The sample is expelled from the capillary bulb by the expansion of the air in the second bulb as this becomes heated.

W. P. S.

Estimation of Carbon Dioxide in Carbonates. K. K. JÄRVINEN and O. SUMELIUS (*Z. anal. Chem.*, 1923, 62, 222—229).—For carbonates associated with starch, as in baking powders, the substance containing 0.3—0.6 g. of carbon dioxide is introduced into a 200 c.c. flask, fitted with a dropping funnel, and connected to a ten-bulbed absorption tube containing 50 c.c. of *N*-sodium hydroxide, and this in turn connected to a guard tube also containing sodium hydroxide. The rate of evolution should be one to two bubbles per second. Then air free from carbon dioxide is slowly passed through the contents of the flask at the ordinary temperature for two hours to expel the last traces of carbon dioxide. The solution from the bulbs is treated with 50 c.c. of barium chloride solution, then titrated with *N*-hydrochloric acid with phenolphthalein as indicator. In cases in which the solution may be boiled, the substance, together with 100 c.c. of water, is placed in a 300—400 c.c. Kjeldahl flask, through the stopper of which passes a 40 cm. dropping funnel; the stem is filled with water and the funnel closed with a well-fitting stopper to prevent regurgitation by the back pressure due to boiling. By means of a 50 cm. tube, drawn out for 2 cm. at the lower end, the flask is connected to the bottom of an 80 cm. burette tube, the two tubes being inclined at about 30°. The top of the burette is fitted with a soda-lime tube. Fifty c.c. of *N*-sodium hydroxide are put into the burette, lacmoid and pumice added to the flask, and the contents boiled to expel all the air. Keeping a similar rate of boiling, 25 c.c. of 2*N*-hydrochloric acid are added at a rate of one to two drops per second, and when all the acid has been added, the liquid is boiled for two to three minutes. The contents of the burette are then treated with barium chloride, and titrated as already described. The operation takes half an hour and is very accurate.

J. B. F.

Rapid Estimation of Potassium in Acid-insoluble Silicates. MANUEL M. GREEN (*Ind. Eng. Chem.*, 1923, 15, 163).—The method depends on the assumption that all metals except potassium form perchlorates soluble in 97% alcohol; 0.15—0.35 g. of the sample is weighed out into a platinum crucible, 1.5 c.c. of 2*N*-perchloric acid and 3—4 c.c. of 48% hydrofluoric acid are added, and evaporated until fumes of perchloric acid are given off. The crucible is cooled and two-thirds filled with water, heated to boiling, filtered, and thoroughly washed with hot water, the filtrate and washings being run into a platinum dish. The liquid is evaporated until fumes of perchloric acid are evolved, cooled, and 25 c.c. of 97% alcohol are added. The residue is broken up and filtered on an untared Gooch crucible and thoroughly washed with the perchloric acid-alcohol mixture. The asbestos mat and precipitate are transferred to a filter, thoroughly washed with hot water, and filtered into a platinum dish. 0.5—1.0 C.c. of 2 *N*-perchloric

acid is added and the liquid evaporated until fumes appear, cooled, 25 c.c. of 97% alcohol are added, the precipitate is broken up and filtered on a tared Gooch crucible, washed with alcohol containing perchloric acid, and dried to constant weight at 110°. The method is accurate to $\pm 0.2\%$, and the estimation requires two to three hours.

H. C. R.

The Alkali Content of Blood and Cerebrospinal Fluid. A New Method for the Estimation of Sodium. M. RICHTER-QUITTNER (*Biochem. Z.*, 1922, 133, 417—432).—A method for the estimation of sodium in the blood is described, based on ultra-filtration followed by precipitation of the sodium by potassium pyroantimonate. Venous stasis, and likewise the removal of carbon dioxide has no influence on the sodium content. Under normal conditions, the corpuscles contain no sodium.

W. O. K.

Isatin as a Microchemical Reagent. J. B. MENKE (*Rec. trav. chim.*, 1923, 42, 199—203).—The silver and cuprous salts of isatoic acid have crystalline forms which are easily recognisable. They are precipitated on addition of a solution of the metallic salt to a 5% solution of ammonia in which isatin has been dissolved. The corresponding silver ammonium compound is also noted.

H. J. E.

The Application of Conductometric Titrations to Precipitation Analysis. VIII. Conductometric Titrations with Lithium Oxalate. I. M. KOLTHOFF (*Z. anal. Chem.*, 1923, 62, 161—177).—Silver, lead, and copper may be accurately titrated conductometrically with lithium oxalate, the end-point in each case being accompanied by a very abrupt change in the conductivity of the solution. Cadmium and zinc salts give much less trustworthy results, which become very erratic if alcohol is added. Nickel-, cobalt-, manganese-, and ferrous-ions appear to form complexes on the addition of the oxalate so that two deflections, neither of which is very definite, occur in the conductivity curve, the first corresponding with the addition of half the oxalate required to form the normal salt. Magnesium gives low results owing to the appreciable solubility of magnesium oxalate and its tendency to form complexes and supersaturated solutions. Barium, strontium, and calcium in neutral solutions may be satisfactorily estimated by the process; calcium also gives good results in ammoniacal solutions and at extreme dilutions, provided that 30% of alcohol is present. The presence of magnesium in the calcium solution gives very high results, but if a great preponderance of calcium ions is present the sum of the two metals is accurately estimated by titration conductometrically with lithium oxalate, so that this process may be applied to the determination of the hardness of potable water.

A. R. P.

Application of Conductometric Methods to Precipitation Analysis. X. Conductometric Titrations with Potassium Ferricyanide. I. M. KOLTHOFF (*Z. anal. Chem.*, 1923, 62, 214—215).—On account of the great mobility of the potassium-ions the

different points of inflection of the conductometric curves with potassium ferricyanide are not sharp and as an analytical reagent the latter finds only a little application. Lithium ferricyanide would be more suitable. Silver forms a red-coloured salt, $\text{Ag}_3\text{Fe}(\text{CN})_6$. The conductometric curve resembles that for potassium, being almost horizontal up to the point of inflection. Copper and cadmium can be accurately estimated. Lead does not form a precipitate with potassium ferricyanide and the conductometric curve is a straight line. Cobalt forms a blue precipitate, $\text{Co}_3[\text{Fe}(\text{CN})_6]_2$. A very dilute solution of cobalt containing 10 mg. of cobalt per litre gives a distinct red coloration. Nickel gives a faintly orange-coloured precipitate with the reagent. Nickel and cobalt are accurately estimated by this method. Manganese gives irregular results. Zinc also is not accurately estimated. With the exception of those of zinc and manganese the salts are of normal composition.

J. B. F.

Application of Conductometric Methods to Precipitation Analysis. XI. Conductometric Titrations with Sodium Nitroprusside. I. M. KOLTHOFF (*Z. anal. Chem.*, 1923, 62, 216—217).—Various metals give with sodium nitroprusside a precipitate of normal composition. Only silver is accurately estimated by conductometric titration.

J. B. F.

The Volumetric Estimation of Calcium. A. VÜRTHEIM and H. G. C. VAN BERS (*Chem. Weekblad*, 1923, 20, 68).—An answer to the criticisms of Grossfeld (this vol., ii, 183) on the method put forward by the authors (*A.*, 1922, ii, 869). Neutralisation with sodium hydroxide in the cold is more likely to cause precipitation of phosphate than addition of ammonia drop by drop at the boiling point.

S. I. L.

Method for the Quantitative Separation of Glucinum and Uranium. PAUL H. M.-P. BRINTON and REUBEN B. ELLESTAD (*J. Amer. Chem. Soc.*, 1923, 45, 395—398).—The quantitative separation and estimation of uranium and glucinum in mixtures of compounds of the two elements has been investigated and the following method evolved. To the hydrochloric acid solution about 5 g. of ammonium chloride and 5 g. of hydroxylamine hydrochloride are added, followed by a concentrated solution of ammonium carbonate, which is added until the precipitate at first formed is entirely redissolved. The solution is heated to boiling and the boiling continued for one minute after the appearance of a heavy precipitate of basic carbonate. The precipitate is filtered immediately and thoroughly washed with cold water. This basic carbonate precipitate is free from uranium. It is set aside to be ignited with the small amount of glucinum hydroxide which is to be separated from the filtrate. The filtrate is acidified with hydrochloric acid and boiled to expel carbon dioxide, then after the addition of 1 g. of hydroxylamine hydrochloride a slight excess of ammonia is added to the cold solution and the small precipitate of glucinum hydroxide is filtered and washed with 2% ammonium nitrate solution to which

have been added a few crystals of hydroxylamine hydrochloride and sufficient ammonia to make the solution faintly alkaline. The combined glucinum precipitates are ignited and weighed as oxide. The filtrate is acidified with hydrochloric acid and the hydroxylamine oxidised either by adding 75–100 c.c. of 3% hydrogen peroxide solution and boiling until the evolution of oxygen ceases, or by adding solid sodium or potassium bromate with constant stirring until the solution assumes an intense colour of bromine. The oxidised solution is heated nearly to the boiling point and a slight excess of ammonia is added with constant stirring. After settling, the ammonium uranate is filtered and washed with 2% ammonium nitrate solution which contains a little free ammonia. The precipitate is ignited and weighed as U_3O_8 . The method is good and gives trustworthy and accurate results. J. F. S.

A Rapid Volumetric Method for the Estimation of Magnesia in Carbonate Rocks. H. R. BRANDENBERG and A. H. AVAKIAN (*Concrete [Mill Section]*, 1922, 21, 78).—One g. of the sample is treated in an Erlenmeyer flask fitted with a reflux condenser with 60 c.c. of 0.4*N*-hydrochloric acid containing 2 c.c. of an alcoholic solution of phenolphthalein per litre. After boiling and cooling, the excess of hydrochloric acid is titrated with 0.4*N*-sodium hydroxide, the first pale pink colour being taken as the end-point. The mixture is again boiled, 1.5 g. of sodium oxalate and an excess of 0.4*N*-sodium hydroxide are added, and boiling is continued for a few minutes. The liquid is then cooled, diluted to 200 c.c., filtered, and 100 c.c. of the filtrate are titrated with 0.4*N*-hydrochloric acid. It is assumed that the loss of acidity in dissolving the substance is due entirely to the presence of calcium and magnesium carbonates, and that the final precipitate consists of calcium oxalate and magnesium hydroxide.

CHEMICAL ABSTRACTS.

The Alkalimetric Estimation of Magnesium and Calcium Salts. RICHARD WILLSTÄTTER and ERNST WALDSCHMIDT-LEITZ (*Ber.*, 1923, 56, [B], 488–491).—The methods depend on the observation that the solubility of magnesium and calcium hydroxides can be so depressed by the use of suitable solvents that the substances do not affect appropriate indicators.

The aqueous solution of a magnesium salt is gradually treated with an excess of alkali hydroxide solution (*N*/10–*N*/1) and so much ethyl alcohol is added that the concentration of the latter is 66–75%. After ten to fifteen minutes, the excess of alkali is titrated with hydrochloric acid in the presence of thymolphthalein (about 10 drops of a 0.5% alcoholic solution are used for each 100 c.c. of liquid); phenolphthalein cannot be employed. Ethyl alcohol may be replaced by methyl alcohol the suitable concentration of which is also 66–75%; in this case, the titration is complicated by the adsorption of the indicator by the precipitated magnesium hydroxide and the method is only suitable in certain circumstances (see later).

Aqueous alcoholic solutions are unsuitable for the estimation of

calcium, which is performed as follows. An excess of alkali hydroxide ($N/10$ to $N/1$) is added drop by drop to the aqueous solution of the calcium salt, which is subsequently treated with neutral acetone until the concentration of the latter is 85–90%. After fifteen minutes, the excess of alkali is titrated in the presence of thymolphthalein (10 drops in 200 c.c. of liquid) until the blue colour permanently disappears. Towards the end of the titration the colour is temporarily discharged, but returns as the adsorbed alkali hydroxide again passes into solution.

When magnesium and calcium hydroxides are simultaneously present, the sum of the bases is estimated in 90% acetone. Magnesium alone is estimated in 66% methyl or ethyl alcohol. If calcium is present in relatively small amount, ethyl alcohol is to be preferred on account of the sharper end-point. If, however, calcium is present in equal or excess quantity, the method is inaccurate, since the magnesium hydroxide carries down and retains small amounts of calcium hydroxide. In these circumstances, methyl alcohol (66–70%), in which calcium hydroxide is more freely soluble, must be used; the end-point of the titration is shown by the first complete disappearance of the blue colour of the thymolphthalein; no attention is paid to the bluish-violet coloration which gradually develops in the magnesium hydroxide.

If iron is also present, as in the analysis of dolomite, it is either precipitated with the aluminium hydroxide and the ammonium salt is expelled or is completely converted into the ferrous state by means of sulphur dioxide. Ferrous hydroxide behaves like magnesium hydroxide in the presence of ethyl alcohol or acetone and is estimated simultaneously; it is separately determined by titration with potassium permanganate.

H. W.

The Estimation of Zinc in Minerals. ET. OLIVIER (*Mon. Sci.*, 1923, 13, 31–35).—About 1.5 g. of the mineral, ground to pass an 80-mesh sieve, is dissolved in 20–25 c.c. of hydrochloric acid with subsequent addition of 10 c.c. of nitric acid. After evaporation to dryness, and dehydration of silica, the residue is taken up with 5 c.c. hydrochloric acid and diluted with 30 c.c. of warm water. Saturated hydrogen sulphide solution is added until the volume amounts to about 125 c.c. The precipitated lead, copper, antimony, arsenic, and cadmium sulphides are filtered, and washed with about 150 c.c. of warm water containing 5 c.c. of hydrochloric acid and a few c.c. of hydrogen sulphide solution. The filtrate is boiled to expel hydrogen sulphide, and brought to a volume of about 200 c.c. Ten c.c. of nitric acid, and, after cooling, 2–20 c.c. of hydrogen peroxide or 5–50 c.c. of bromine water (according to the amount of manganese present), are added to the solution. Iron, aluminium, and manganese are precipitated by the addition of 60 c.c. of ammonia, the liquid being allowed to remain over-night with free access to the air. The solution is filtered and titrated with sodium sulphide solution, using lead test-paper as an outside indicator. Titrations are compared with those of a standard zinc solution, which is prepared

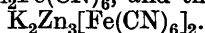
by a similar process to that to which the mineral has been subjected. The same tint of sulphide stain on the test-paper should be adopted as the end-point in each case, and this should be further confirmed by the addition of (say) 0.2 and 0.5 c.c. of sulphide solution, which should produce similar intensifications of the stain in both cases.

A. G. P.

Electrometric Estimation of Zinc by means of Silver Nitrate. ERICH MÜLLER and ALFRED ADAM (*Z. Elektrochem.*, 1923, 29, 49—53).—Using much the same method as was previously employed for the estimation of nickel and cobalt (A., 1922, ii, 875) the authors now show that zinc may be estimated electrometrically. The determination is carried out by treating 10 c.c. of the zinc solution with an excess of potassium cyanide solution and titrating the excess of potassium cyanide with *N*/10-silver nitrate solution, using a silver wire as indicator electrode. It is also possible to determine simultaneously the amount of silver which may be present with the zinc by the same process. Cadmium, lead, and copper cannot be estimated by this method.

J. F. S.

Application of Conductometric Methods to Precipitation Analysis. IX. Conductometric Titrations with Potassium Ferrocyanide. I. M. KOLTHOFF (*Z. anal. Chem.*, 1923, 62, 209—214).—Lead can be accurately estimated by conductometric titration with potassium ferrocyanide, since it forms only the normal salt. Zinc may also be accurately estimated in weak ammoniacal solution; stronger ammoniacal solutions require less reagent. A mixture made up of 20 c.c., 0.05 *M* of zinc sulphate, 20 c.c. of water, and 2.5 c.c. of a 10% solution of ammonia required 1.99 c.c. of 0.25 *M* reagent at the point of inflection, whereas with 18 c.c. of the ammonia solution this point was reached with 1.78 c.c. of the reagent, 2.00 c.c. being the calculated value. In the absence of ammonia, two points of inflection occur, the first corresponding with the normal salt, $\text{Zn}_2\text{Fe}(\text{CN})_6$, and the second with



Silver, copper, cadmium, manganese, nickel, and cobalt first give rise to a normal salt, which combines with a further quantity of reagent to form double salts. Silver gives a second point of inflection corresponding approximately with $\text{KAg}_3\text{Fe}(\text{CN})_6$, copper and cadmium at $\text{K}_2\text{Cu}_3[\text{Fe}(\text{CN})_6]_2$ and $\text{K}_2\text{Cd}_3[\text{Fe}(\text{CN})_6]_2$, respectively. Copper gives a third point at $\text{K}_4\text{Cu}_4[\text{Fe}(\text{CN})_6]_3$. Manganese, nickel, and cobalt behave similarly to copper, but with the formation of a further point corresponding with a composition of the type $[\text{3K}_4\text{Fe}(\text{CN})_6 + 4\text{MnFe}(\text{CN})_6]$.

J. B. F.

Electro-analytical Methods for the Estimation of Metals in Hydrochloric Acid Solution. ANNA J. ENGELENBURG (*Z. anal. Chem.*, 1923, 62, 257—284).—The methods proposed by Schoch and Brown (A., 1913, ii, 794) for the electrodeposition of tin, copper, antimony bismuth, lead, and cadmium from chloride solutions in the presence of hydroxylamine hydrochloride have

been further studied and modifications in the temperature, quantity of hydroxylamine hydrochloride added, and the current used are suggested. Application of the results to the separation of certain of the above metals from one another are also suggested.

The following new processes are described. Cadmium is deposited from a solution containing 10 c.c. of hydrochloric acid in 200 c.c. bulk by electrolysis for twenty minutes at 1 ampere, then adding 20 g. of ammonium oxalate and 10–20 g. of oxalic acid and continuing the electrolysis for a further forty minutes at 1.2 amperes. Zinc is estimated by electrolysis of a solution containing 1.5 c.c. of hydrochloric acid and 2 g. of hydroxylamine hydrochloride in 200 c.c.; the temperature is maintained at 18° and the current increased slowly from 4 to 8 amperes. In all the above processes hydrazine sulphate may be used instead of hydroxylamine hydrochloride, and in the case of copper 0.1–0.2 g. of ammonium persulphate in place of either of the other two reagents gives a more firmly adherent and smoother deposit. A mixture of 0.4 g. of ammonium persulphate and 0.5 g. of hydroxylamine hydrochloride in 150 c.c. of a tin solution containing 12 c.c. of hydrochloric acid improves the nature of the tin deposit. By measuring the cathode potentials of a solution containing the above metals, the presence or absence of each in the solution may be ascertained, by the potential changes as each metal is deposited. A. R. P.

Lead. II. Electrolytic Estimation of Lead in Biological Material. A. S. MINOT (*J. Biol. Chem.*, 1923, 55, 1–8).—The method described by Denis and Minot (*A.*, 1919, ii, 372) is inaccurate and is, in fact, untrustworthy even as a qualitative test for lead. This is due partly to the presence of manganese and partly to other factors. Fairhall's method (*A.*, 1922, ii, 659), however, gives accurate results. E. S.

The Carrying Down of Acids by Alumina Precipitates. ANDRÉ CHARRIQUÉ (*Compt. rend.*, 1923, 176, 679–682).—When alumina is precipitated by ammonia in presence of an alkali chromate, the precipitate remains yellow, even after prolonged washing with boiling water. The alkali metal could not be detected in the precipitate, and it is therefore only the acid which is carried down by the alumina, and it probably forms a layer of aluminium chromate on the alumina, which may constitute anything from 1–7% of the total weight. A similar absorption of chromic acid occurs when precipitated aluminium hydroxide is placed in contact with potassium chromate solutions. The precipitate cannot be freed from chromic acid by washing with ammonium nitrate, chloride, or acetate solutions, but when the alumina is precipitated with ammonium hydrogen carbonate or precipitated with ammonia and washed subsequently with 5% ammonium hydrogen carbonate solution, it is obtained perfectly colourless and free from chromate. A similar result is obtained with lithium or sodium carbonate, or with ammonium phosphate, the carbonic or phosphoric acid apparently displacing the chromic acid, and taking its place. In

analysis, it is sufficient, therefore, to wash the alumina with 5% ammonium hydrogen carbonate solution in order to eliminate chromic acid, the carbonic acid and ammonium salts remaining in the precipitate being subsequently removed during the calcination.

G. F. M.

Qualitative Analysis of the Iron Group. RALPH W. HUFFERD (*J. Amer. Chem. Soc.*, 1923, **45**, 438—439).—A modified method of treating the iron group precipitate in qualitative analysis is described. The precipitate is treated with a large excess of sodium hydroxide to remove the aluminium, zinc, and chromium. The precipitate is treated directly with nitric acid and potassium chlorate to remove the manganese. Iron is removed by adding a large excess of ammonia. The filtrate from the iron precipitate is evaporated until it has only a faint odour of ammonia and one-fifth of the solution treated with dimethyl-glyoxime to test for nickel. The remainder of the solution is evaporated to a syrup, treated with sufficient water to dissolve the salts, and tested for cobalt by adding 3 c.c. of 10% potassium thiocyanate followed by 3 c.c. of a mixture of amyl alcohol and ether (1:3). In the presence of cobalt the solution becomes bluish-green; if the colour is indistinct the careful addition of a few drops of 12*N*-hydrochloric acid will develop the colour if cobalt is present. In the absence of cobalt, the colour of the ether layer will be straw-coloured or colourless.

J. F. S.

Volumetric Estimation of Tervalent Iron and of Copper in the Presence of Iron. FRIEDRICH L. HAHN and HEINRICH WINDISCH (*Ber.*, 1923, **56**, [B], 598—601).—The iodometric estimation of ferric salts involves a large expenditure of time and iodide, since the reaction $\text{Fe}^{+++} + \text{I}^- \rightleftharpoons \text{Fe}^{++} + \text{I}$ is reversible, and dissociation only occurs slowly when the liberated iodine is removed. Since, however, cupric salts are instantaneously reduced by iodides to iodine and cuprous salts and the latter convert ferric salts into ferrous compounds, it is possible to catalyse the action of ferric salts and iodides by the addition of a small amount of cuprous compounds to such an extent that the titration can be performed immediately and in the presence of only a small quantity of iodide. The use of isolated cuprous iodide is unnecessary. It is sufficient if the potassium iodide solution is treated with a little copper sulphate and starch and subsequently with sodium thiosulphate until the blue colour is just discharged; the suspension is added to the solution of the ferric salt and the liberated iodine is immediately titrated with thiosulphate. The method is considered to be the most convenient and trustworthy for the standardisation of thiosulphate solutions.

It appears, therefore, that the sum of copper and iron can be immediately estimated by titration in mixtures of ferric and cupric salts. The action of the iron can be eliminated by the addition of a solution of sodium phosphate, which has been treated with phosphoric acid until it decolorises *p*-nitrophenol, to the

neutral or faintly acid solution. If the ferric solution is strongly acidic, it may be partly neutralised, phosphate without phosphoric acid may be used, or a larger proportion of the mixture may be employed. It is sufficient if two molecular proportions of phosphate are added for each molecule of ferric salt. It is immaterial whether ferric phosphate is precipitated or not. The estimation of copper is not influenced by the addition of phosphate. H. W.

Estimation of Bismuth as Phosphate and Its Separation from Lead, Copper, and Cadmium. G. LUFF (*Chem. Ztg.*, 1923, 47, 133—134).—The precipitation of bismuth as phosphate from a slightly acid solution of the nitrate serves to separate it from copper, lead, and cadmium if the operation is conducted as follows. The nitric acid solution of the metals is exactly neutralised with ammonia, using methyl-orange as indicator, 4 c.c. of nitric acid are added, and the bismuth is precipitated by the addition, drop by drop, to the boiling solution of a solution of 1 g. of ammonium phosphate in 40 c.c. of water and 2 c.c. of nitric acid. The dense, crystalline precipitate of bismuth phosphate is collected, washed with hot water, ignited wet together with the filter-paper, and weighed. If the filtrate contains only cadmium, this is precipitated as sulphide after the addition of an excess of ammonium acetate and the sulphide is dissolved in hydrochloric acid. The solution is rendered neutral to methyl-orange by the addition of potassium carbonate and the cadmium precipitated by a large excess of diammonium hydrogen phosphate. The precipitated cadmium ammonium phosphate is collected on a filter, washed first with dilute ammonium phosphate solution, then with 60% alcohol, ignited, and weighed as pyrophosphate (cf. Schoeller and Waterhouse, A., 1921, ii, 195). A. R. P.

New Compounds of Platinum, Palladium, Iridium, and Rhodium, and a New Method for their Estimation. W. N. IVANOV (*Chem. Ztg.*, 1923, 47, 209—210).—When 0.25% solutions of potassium chloroplatinite and sodium thiocyanate are mixed and left for five to six hours at the ordinary temperature, then shaken with 50 g. of ammonium nitrate or sulphate per litre, a light brown, flocculent precipitate of platinous thiocyanate is produced. The precipitate is soluble in aqua regia and in potassium cyanide solution, but not in single acids or alkalis. If the precipitation is carried out in boiling solutions, a black, flocculent precipitate having the composition $\text{Pt}_4(\text{OH})_4\text{S}(\text{CS}\cdot\text{NH}_2)_2$ is obtained. On ignition, a residue of platinum is left so that the compound is suitable for use in the estimation of platinum. Under similar conditions, palladium gives a precipitate of $\text{Pd}_3\text{S}_2(\text{CS}\cdot\text{NH}_2)_2$, which on ignition leaves a very fusible residue of Pd_3S which is slowly transformed, after prolonged heating, into the metal. Rhodium also gives a black precipitate the composition of which, however, was not ascertained. On ignition it yields metallic rhodium. Iridium is incompletely precipitated as a flocculent, yellow compound. A. R. P.

The Detection of Methyl Alcohol in Ethyl Alcohol. H. W. VAN URK (*Pharm. Weekblad*, 1923, 60, 273—276).—Distillation should be carried out as recommended in the German official method, the first 10 c.c. from 100 c.c. of the sample being again distilled and the first 1 c.c. taken. Oxidation may be conveniently carried out by means of the copper spiral, and formaldehyde detected by Denigès's method; a positive result should be confirmed by the morphine-sulphuric acid test. S. I. L.

Characterisation of the Alkylglycerols. RAYMOND DELABY (*Compt. rend.*, 1923, 176, 396—399; cf. this vol., i, 84, 85).—The author has tested the reactions described by Denigès ("Précis de Chimie analytique," 1920, 151) for glycerol with methyl-, ethyl-, propyl-, and butyl-glycerols to see how far they are specific. After oxidation with bromine, of the colours obtained in the presence of sulphuric acid with certain alkaloids or phenols only that with codeine, namely, a blue colour, is specific to glycerol. Similarly, if potassium bromide is added to the oxidation products before the sulphuric acid and then the colour tests described are applied, only the colour, blue, with guaiacol serves to distinguish glycerol from its homologues. If the osazone test is applied to the oxidation products, the osazone from methylglycerol is quite different from that obtained from glycerol and the other glycerols only give oily products. All the products of oxidation with bromine of the alkylglycerols reduce Nessler's reagent, Fehling's solution, and ammoniacal silver nitrate.

None of the oxidation reactions with potassium permanganate is specific to glycerol, and the same applies to the oxidation with lead peroxide. W. G.

Modification of Windaus's Method for the Estimation of Cholesterol. ROGER CAMINADE (*Bull. Soc. Chim. biol.*, 1922, 4, 601—613).—Windaus's method yields irregular results unless the precipitation of the digitonin cholesteride is made under definite conditions. More consistent results may, however, be obtained with much greater rapidity if the precipitate is formed in a solvent consisting of acetone (78 parts), water (18 parts), and alcohol (9 parts). A 5% solution of digitonin in the mixed solvent is added to the hot solution of cholesterol in the same solvent. The precipitate forms immediately, and, after a few minutes, is filtered and washed, first with hot water, then with the mixed solvent, and finally with ether to remove lecithin.

E. S.

Molybdo-manganimetry and its Applications. G. FONTÈS and L. THIVOLLE (*Bull. Soc. Chim. biol.*, 1922, 4, 614—622).—The authors have shown that the volumetric micro-estimation of dextrose (A., 1921, ii, 563) and of lactose (A., 1922, ii, 323) may be conveniently carried out by means of potassium permanganate when used in conjunction with a phosphomolybdic acid reagent. The method appears to be generally applicable to the micro-

estimation of reducing substances, and it is accordingly proposed to class such volumetric methods under the heading "molybdomanganimetry." The phosphomolybdic acid reagent is reduced by cuprous, ferrous, stannous, and mercurous salts, by sodium hyposulphite, and even by metallic copper, iron, zinc, and magnesium. The blue oxides of molybdenum so produced may be titrated with potassium permanganate, by which they are re-oxidised to molybdic acid, but the details of the method have not yet been worked out for each case. It is shown, however, that the copper deposited on the cathode in Pregl's apparatus for the micro-electrolysis of copper dissolves readily in the phosphomolybdic acid reagent, and that titration of the blue solution so obtained gives results agreeing with those obtained gravimetrically. For purposes of calculation, the reaction is regarded as a direct oxidation of the reducing substance by potassium permanganate; hence, in the estimation of dextrose, the use of a standard may be dispensed with if desired.

E. S.

Micro-estimation of Blood-sugar with Ferricyanide. H. C. HAGEDORN and B. NORMAN JENSEN (*Biochem. Z.*, 1923, 135, 46—58).—A new method which is claimed as superior to Bang's micro-method for the estimation of sugar in 0.1 c.c. of blood has been worked out in detail and depends on the oxidation of the sugar by excess of potassium ferricyanide, the excess being estimated by the iodine liberated in presence of zinc salts from potassium iodide. About eighteen analyses can be carried out in an hour. For details and tables, the original should be consulted. H. K.

Methods of Chemical Investigation on Blood. V. Estimation of Sugar in Blood. ALMA ROSENTHAL (*Biochem. Z.*, 1922, 133, 469—475).—Details are given of a slightly modified Hagedorn method for the estimation of blood-sugar. After precipitation of the protein by metaphosphoric acid or sodium tungstate, the filtrate is boiled with sodium ferricyanide, and the excess which is not reduced to ferrocyanide is estimated by adding potassium iodide and titrating the iodine liberated with thiosulphate. From the result, the content of the blood in dextrose can be obtained from a table.

W. O. K.

The Detection and Identification of Maltose, Galactose, Sucrose, and Inulin by a Mycological Method. ALDO CASTELLANI and F. E. TAYLOR (*J. Trop. Med.*, 1922, 25, 41—46).—An extension of the previously published method (*Brit. Med. J.*, 1917, Dec. Rep.; *Physiol. Abstr.*, 3, 263). A table shows the reaction of a number of bacteria and fungi with a great variety of carbohydrates. Fermentation tests with two suitable micro-organisms is sufficient to establish the identity of any of the sugars named (cf. A., 1922, ii, 879).

CHEMICAL ABSTRACTS.

Effects of the Method of Desiccation on the Carbohydrates of Plant-tissue. KARL PAUL LINK and W. E. TOTTINGHAM (*J. Amer. Chem. Soc.*, 1923, 45, 439—447).—In preparing plant-

tissues for carbohydrate estimations, a temperature of 98° should not be used for drying the fresh plant material when the sugar and starch contents are high. With tissue that can be dried rapidly, a temperature of 65° in a current of air at atmospheric pressure can be used safely if the tissue can be reduced to thin sections. When drying in a vacuum, 80° is a better working temperature than 65°, and in the case of coarse tissues improved results are obtained if the material is first heated in an autoclave to inhibit enzymatic and respiratory processes. The results obtained by this method in the case of beet leaves and corn ears were the same as when the alcohol method of preservation (cf. Davis and Daish, A., 1914, ii, 152) was used. Drying at low temperatures with a minimum error can be carried out only in a well-ventilated oven in which a large volume of air circulates continuously over the material.

W. G.

Estimation of Incrustating Substances on Flax Fibres by Saccharification of the Cellulose. P. P. BUDNIKOV and P. W. SOLOTAREV (*Z. angew. Chem.*, 1923, 36, 138—139).—In the purification of flax waste by digesting it under pressure with liquors containing sodium hydroxide and sodium hydrogen sulphite, the cellulose-content of the product was estimated by the method of Ost and Wilkening. In this method, which gave satisfactory results, 1 g. of the purified flax is dissolved in 7—8 c.c. of 72% sulphuric acid and the solution thereby obtained is afterwards diluted until its acid content is 3%, and is then heated for two hours at 120° in an autoclave. The reducing sugars present in the product are then estimated by means of Fehling's solution and the original cellulose-content calculated. (See further, *J.S.C.I.*, 1923, April.)

A. J. H.

The Estimation of the Iodine Number of Fats under Unfavourable Conditions. B. M. MARGOSCHES, RICHARD BARU, and LISBETH WOLF (*Z. anal. Chem.*, 1923, 62, 178—184).—The method of Aschman (*Chem. Ztg.*, 1898, 22, 59, 71) for the estimation of the iodine number of fats, in which an aqueous solution of iodine monochloride is allowed to react on the fat, gives accurate results, even without the use of a solvent for the fat and without continual shaking, provided that the solutions are left for a sufficient length of time (about twenty-four hours) before the excess of reagent is estimated. This period may be considerably reduced if the fat is dissolved in carbon tetrachloride or other suitable solvent and the mixture frequently agitated.

A. R. P.

A Simple Method for the Estimation of Lactic Acid in the Stomach-contents. RICH. EGE (*Biochem. Z.*, 1923, 134, 476—488).—A method is described for the estimation of lactic acid in the stomach contents, depending on the extraction of the lactic acid by ether, and re-extraction by water before titration. The distribution of lactic acid between ether and water is allowed for.

W. O. K.

Cyanogenesis. A Reaction of Citric Acid. A. M. JORISSEN (*Bull. Acad. roy. Belg.*, 1919, 731—737).—The author had previously shown (A., 1914, i, 813) that hydrocyanic acid was formed, under the influence of light, in solutions containing citric acid and traces of iron salts and nitrous acid. Hydrocyanic acid is not formed when citric acid is replaced by formaldehyde, acetaldehyde, formic, lactic, isobutyric, or lævulic acids, sucrose, dextrose, gelatin, vanillin, or ethyl acetoacetate (cf. *loc. cit.*). A test is developed using ferric chloride, acetic acid, and potassium nitrite as reagents. It fails in presence of tartaric acid. A more sensitive test is as follows: 100 c.c. of the solution to be tested are treated with 5 g. of manganese dioxide and 5 drops of acetic acid, and the mixture is left for twenty-four hours. After filtration, the liquid is treated with 5 to 10 drops of acetic acid and 5 c.c. of 1% potassium nitrite solution, the mixture left over-night, and then distilled in steam after adding calcium carbonate. The first 130 c.c. of distillate are tested for hydrocyanic acid (ferrous and ferric salt, sodium hydroxide, etc.). Glycerol, lactose, dextrin, and the other substances detailed above do not give rise to hydrocyanic acid under these conditions. E. E. T.

Comparison of the Pentabromoacetone Method, and Salant and Wise's Method for the Estimation of Citric Acid in Urine. W. B. MCCLURE and L. W. SAUER (*Amer. J. Physiol.*, 1922, 62, 140—144).—When known amounts of citric acid were added to normal urine the pentabromoacetone method (Amberg and McClure, A., 1918, i, 141) gave much better results than Salant and Wise's method (A., 1917, i, 106) in three cases. In the fourth case, there was close comparison between the results of the two methods. The pentabromoacetone method is preferred by the authors (cf. A., 1922, ii, 791). CHEMICAL ABSTRACTS.

Identification of Benzonaphthol [β -Naphthyl Benzoate], Salol [Phenyl Salicylate], Betol [β -Naphthyl Salicylate], Cresalol [*p*-Tolyl Salicylate], and Salophen [*p*-Acetamidophenyl Salicylate] by Microchemical Means. G. DENIGÈS (*Bull. Soc. pharm. Bordeaux*, 1922, 60, 163—169).— β -Naphthyl benzoate: a fraction of 1 mg. of the material is dissolved on a glass slide in a drop of chloroform from a tapered rod of end diameter 2—4 mm.; evaporation leaves crystal groups forming more or less concentric zones. A drop of glacial acetic acid, when placed at the centre of the dry residue and allowed to evaporate, yields arborisations often accompanied by isolated or crossed prisms. If the residue from chloroform or acetic acid is mixed with a drop of concentrated sulphuric acid, and a glass rod which has been dipped into formaldehyde solution inserted, a yellowish-brown colour develops, and on gentle heating the mixture blackens.

Phenyl salicylate, when similarly treated with chloroform, yields an oily droplet, which is not changed by treatment with acetic acid. The residue, by dissolution in a drop of ethyl alcohol, yields by evaporation groups of rhombic plates, similar crystals

being obtained also by seeding the oily droplet with the original material. Treatment as before with sulphuric acid and formaldehyde gives a white cloudiness followed by a red coloration which is intensified by heating.

β -Naphthyl salicylate is deposited from chloroform as an oily droplet; acetic acid then gives isolated rhombic plates mixed with clusters of prisms. With sulphuric acid and formaldehyde, the substance behaves in the same way as β -naphthyl benzoate.

p-Tolyl salicylate yields crystals (m. p. 36°) by seeding the oily droplets obtained from chloroform, acetic acid, ethyl alcohol, acetone, or pyridine. With sulphuric acid and formaldehyde, the substance behaves like phenyl salicylate.

p-Acetamidophenyl salicylate is deposited from acetone as isolated or tangled rhombic plates. When treated with sulphuric acid and formaldehyde, a rose colour develops in the cold; when heated, the colour is intensified at first, and then changes to brown.

CHEMICAL ABSTRACTS.

Demonstration of Salicylic Acid in Serum and Similar Fluids. H. HÉRISSEY (*Bull. Soc. Chim. biol.*, 1922, 4, 648—651).—The serum is acidified with sulphuric acid, extracted with ether, and the presence of salicylic acid in the latter demonstrated by means of the ferric chloride reaction. E. S.

Estimation of Formaldehyde and Acetaldehyde. E. W. BLAIR and T. S. WHEELER (*Analyst*, 1923, 48, 110—112).—Mixtures of formaldehyde, hydrogen peroxide, formic acid, and a trace of ozone obtained in investigations on the action of oxygen and ozone on hydrocarbons were analysed as follows. Formic acid was estimated in an aliquot part by titrating with *N*/100-alkali, methyl-red or phenolphthalein being used as indicator. Ozone was estimated in the neutralised solution by adding a 5% neutral solution of potassium iodide, acidifying with 5% hydrochloric acid free from chlorine, and immediately titrating the iodine liberated with *N*/100-thiosulphate solution. The hydrogen peroxide was estimated by Kingzett's method (T., 1880, 37, 802). To estimate the formaldehyde, the ozone and hydrogen peroxide were destroyed by adding potassium iodide and sulphuric acid. The iodine set free was not titrated, but the diluted solution was just neutralised, with thorough cooling, with sodium hydroxide solution. Twenty-five c.c. of *N*/10-iodine solution were then added and the formaldehyde estimated by Romijn's iodometric method (A., 1897, ii, 166), allowance being made for the iodine set free in previous reactions. If acetaldehyde was also present, Ripper's method (A., 1901, ii, 205) was used to obtain an iodine figure for both aldehydes, and the cyanide figure (Sutton, "Volumetric Analysis," 10th ed., p. 391) for formaldehyde applied to it to estimate the acetaldehyde present. H. C. R.

A Micro-method for the Estimation of Acetone and of β -Hydroxybutyric Acid in Urine and Blood. ALFRED LUBLIN (*Biochem. Z.*, 1922, 133, 626—641).—A micro-method is described

for the estimation of acetone and of β -hydroxybutyric acid in 0.2 c.c. of blood, or in 0.5 c.c. of urine, the estimation requiring thirty minutes in the first case and twenty minutes in the second. The acetone is distilled into an alkaline iodine solution, and the iodine left is titrated with thiosulphate.

W. O. K.

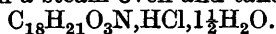
Reaction of Phenolphthalein. G. DE BENAVENT (*Anal. Fis. Quim.*, 1922, 20, 473—474).—An alkaline urine containing phenolphthalein, previously administered, and eliminated by the kidneys, was found to lose its red coloration on heating, whilst on cooling the red coloration reappeared. The reaction is shown to be due to the presence of uric acid. A number of other organic acids were examined for this reaction which was, however, only given by salicylic acid and benzoic acid in addition to uric acid.

G. W. R.

Estimation of Amino-acids and Ammonia, using an Apparatus to Control the Distillation. GIOVANNI REVOLTELLA (*Biochem. Z.*, 1922, 134, 349—353).—The formal titration of amino-acids in pigmented urine is facilitated by using a colour match of the same urine instead of water as used by Sørensen. An apparatus is also described which is designed to show when the evolution of ammonia is finished in a distillation.

H. K.

Estimation of Codeine. HAROLD EDWARD ANNETT and RAM RICHHPAL SANGHI (*Analyst*, 1923, 48, 16—18).—Eight g. of opium are triturated with 2 g. of freshly slaked lime and 80 c.c. of water for thirty minutes, 50 c.c. of the filtrate are extracted three times with 50 c.c. portions of toluene, the filtered extract is concentrated to 25 c.c., dry hydrogen chloride is passed through, and the precipitated codeine hydrochloride and colouring matter are dissolved in water and evaporated to dryness, thereby rendering the colouring matter insoluble. The residue is treated with hot water, the volume adjusted to 50 c.c., and the whole process is repeated from the beginning with 40 c.c. of the filtrate from the lime treatment (=4 g. of opium). In the final evaporation no further colour should develop, and the addition of a little alcohol when nearly all the water has evaporated causes the separation of codeine hydrochloride in small, colourless rosettes. The residue is dried to constant weight in a steam oven and taken as



The method was tested with pure codeine, and on opium with and without added amounts of codeine, and 95—96% of the codeine present was regularly recovered.

G. F. M.

Estimation of Narcotine and Papaverine in Opium. H. E. ANNETT and M. N. BOSE (*Analyst*, 1923, 48, 53—58).—Opium (1.5 g.) is triturated to a smooth paste with 30 c.c. of 0.5% sulphuric acid and after thirty minutes 20 c.c. of the filtrate are boiled with 16 g. of sodium acetate until complete solution of the salt has been effected. After keeping over-night the liquid is

filtered, the precipitate completely transferred to the filter-paper, washed, and dried. It is then extracted with 20—25 c.c. of hot toluene, the toluene extract is shaken with 20 c.c. of 10% sodium hydroxide to remove resins and colouring matters, and the washed toluene solution is evaporated almost to dryness with the addition of 2—3 c.c. of alcohol to facilitate crystallisation of the narcotine and papaverine, which after drying at 100° are weighed as such. The narcotine can then be estimated polarimetrically, papaverine being optically inactive. The rotation is measured in toluene solution as in acid solution papaverine considerably depresses the optical activity of narcotine. The process was tested on opium with and without the addition of known amounts of the two alkaloids, and satisfactory results were obtained without the use of any correction factor. G. F. M.

A Rapid Process for the Exact Estimation of Small Quantities of Uric Acid in Urine and in Blood-serum. HEINRICH CHANTRAINE (*Biochem. Z.*, 1922, 133, 605—612).—Uric acid in urine is separated as in Hopkin's method by the addition of ammonia and ammonium chloride, after precipitating it as the copper salt, and liberating it from that with hydrogen sulphide. Excess of potassium permanganate solution is added to the uric acid, and the excess is estimated iodometrically. A similar method may be used for estimating uric acid in blood-serum. W. O. K.

Behaviour of Uric Acid in Protein Solutions. LUDWIG PINCUSSEN (*Biochem. Z.*, 1923, 134, 447—458).—Uric acid in serum is only partly free, and results obtained on estimation are increased if the protein is first hydrolysed by a ferment or an acid, as only the free uric acid is determined by these methods. Other proteins and also fats, lipoids, etc., combine with uric acid.

W. O. K.

The Iodometric Estimation of Antipyrine. I. M. KOLTHOFF (*Pharm. Weekblad*, 1923, 60, 194—199).—Very good results are obtained by the method of Bougault (A., 1917, ii, 344), namely, addition of excess of *N*/10-iodine solution in presence of sodium hydrogen carbonate, acidification after one hour, and titration back with thiosulphate after addition of chloroform. The reaction is $C_{11}H_{12}ON_2 + I_2 = C_{11}H_{11}ON_2I + HI$. Sodium acetate may be used in place of the hydrogen carbonate, and alcohol in place of chloroform. The results are not affected by the presence of sodium salicylate, caffeine, acetanilide, phenacetin, or aspirin. S. I. L.

Measurement of the Colour of Brown Solutions, with Special Reference to Tannin Extracts. HENRY R. PROCTER (*J. Soc. Chem. Ind.*, 1923, 42, 73—79r).—The colours of brown solutions, more especially of tannin extracts, are determined by observing by means of a spectro-colorimeter the depth of solution required to reduce the light transmitted by the solution to a definite fraction of its initial value, e.g., one-half. Observations are made

with red, yellow, green, and blue light of definite wave-lengths. Alternatively, colour screens of copper-ruby and copper-green glass and a screen containing a solution of copper sulphate made alkaline with ammonia may be employed to afford light of sufficiently definite composition. In this case the rotating neutral tint sector of the spectro-colorimeter is replaced by a 20% solution of iron alum, and the colour of the tannin extract compared with the colour of this solution.

J. S. G. T.

The Estimation of Albumin by the so-called Nephelometric Processes. HENRI BÉNARD and ALBERT LABORDE (*Compt. rend.*, 1923, 176, 98—101).—A comparison of the results obtained by a diffusimeter of the type of Baudouin and Benard (*Compt. rend. Soc. Biol.*, 1920, May) and by an opacimeter of the type of Cheneveau and Audubert (*A.*, 1920, ii, 327) in the estimation of albumin in blood-serum, using trichloroacetic acid as a precipitant. The final dilutions were of the order of 2—40 per 100,000. In the diffusion method a control curve is necessary at the higher concentrations. The opacimeter can be used, if arranged vertically, in cases where the precipitate settles rapidly, as the thin sediment gives the same reading as the initial suspension. The diffusimeter is, however, more sensitive for very dilute emulsions.

W. G.

Estimation of Trypsin and Pepsin. JOHN H. NORTHPROP and RAYMOND G. HUSSEY (*J. Gen. Physiol.*, 1923, 5, 353—358).—Estimation of trypsin (or pepsin) may be effected by measuring the change in a definite time and at a given P_H and temperature in the viscosity of purified gelatin to which a given amount of the trypsin solution has been added. It is found that the time taken to cause a given percentage change in the viscosity is approximately inversely proportional to the amount of trypsin added.

W. O. K.

Arginase. VI. Modification of the Volumetric Method for Detecting Arginase. ANTONINO CLEMENTI (*Atti R. Accad. Lincei*, 1922, [v], 31, ii, 454—459).—If the acid liquid obtained by the acid hydrolysis of edestin, or the phosphotungstic precipitate of hexone bases obtained therefrom, is treated in vitro in presence of toluene with the pulped liver of a mammifer (monkey, man, rat) which contains arginase, a considerable increase is effected in the proportion of nitrogen titratable with formaldehyde. No such increase occurs, however, if the above liver is first boiled or if hen's liver, which is devoid of arginase, is used. The conclusion is drawn that the increase in nitrogen titratable with formaldehyde corresponds with the ornithine formed by scission of the arginine by the arginase, and that such increase furnishes an indication of the presence of arginase in an organ or in an organic liquid.

T. H. P.

A New Reaction of the Blood. GIUSEPPE BECCADELLI (*Biochem. Z.*, 1922, 134, 180—182).—If to 0.5 c.c. of serum or blood

there be added equal volumes of formaldehyde (40%), silver nitrate (0.75%), and ammonia (0.9%), after a few minutes the solution acquires a colour depending on the origin of the serum. Normal human serum gives an amber colour, that of various animals a shade of yellow, whilst that of syphilitics is decolorised.

H. K.

A Sensitive Reaction for Neo-salvarsan. K. SCHERINGA (*Pharm. Weekblad*, 1923, 60, 248).—One drop of a solution of one part in a thousand gives a violet coloration to a concentrated solution of ammonium persulphate. Colorations are given more or less quickly with other organic substances which form coloured oxidation products, salvarsan also giving a violet colour, but the reaction with neo-salvarsan is much more sensitive.

S. I. L.

Estimation of the Grignard Reagent. H. GILMAN, P. D. WILKINSON, W. P. FISHEL, and C. H. MEYERS (*J. Amr Chem. Soc.*, 1923, 45, 150—158).—Five methods for the estimation of Grignard's reagent have been studied, namely, titration with iodine (cf. Jolibois, A., 1912, i, 675), gravimetric analysis by the preparation of some insoluble compound, indirect analysis, gas analysis, and titration with acid.

Of these methods, the first was rejected as giving results which varied considerably with slight alterations in the conditions, the second was rejected as being unsuitable and giving low results. Of the three remaining methods, the last two, namely, the method of gas analysis and that of titration with acid, gave satisfactory results. They are based on the smooth decomposition of the Grignard compound with water, the gas evolved being measured in one method, and the basic magnesium halide titrated with standard acid in the other method. For the gas analysis method, an apparatus somewhat of the type of Van Slyke's apparatus for the estimation of amino-acids is used. For the titration method, the known volume of solution containing the Grignard reagent is warmed with a known excess of standard acid until all the basic magnesium halide is dissolved, and then the excess of standard acid is titrated back with standard sodium hydroxide, using methyl-orange as indicator.

W. G.

General and Physical Chemistry.

Refractivity of Organic Fluorine Compounds. FRÉD. SWARTS (*J. Chim. Phys.*, 1923, 20, 30—76).—The refractivity of a large number of organic fluorine derivatives is recorded. In the case of substituted paraffins, the introduction of fluorine decreases the molecular refraction by an amount which decreases the longer the carbon chain, and increases with the refrangibility of the light. Thus the molecular refractivity calculated by the Lorentz-Lorenz formula $[R_L]_\lambda$ has the following values: C_5H_{12} , α , 25.131; β , 25.522; γ , 25.748; $C_5H_{11}F$, α , 24.99; β , 25.350, γ , 25.569; C_7H_{16} , α , 34.452; $C_7H_{15}F$, α , 34.364; C_8H_{18} , α , 39.073; α , $C_8H_{17}F$, 39.032. Using the values of hydrogen found by Brühl, Landolt, and Falk, the atomic refractivity of fluorine is $[R_L]_\alpha$, 1.014, $[R_L]_\beta$, 1.005, and $[R_L]_\gamma$, 1.003. With methyl cyclohexane, the accumulation of fluorine does not produce any exaltation in the refractive value of the substitution $H \rightarrow F$. In the case of alcohols and esters, it is shown that the substitution of one fluorine atom produces a depression in the molecular refractivity of the same order as that observed with the paraffins, whereas the introduction of a second fluorine atom gives no depression with difluoroethyl alcohol, but a strong exaltation in difluoroethyl acetate. With acetic acid, the introduction of fluorine increases the molecular refractivity, which further increases with each fluorine atom introduced. Thus with H_α light, the increase for the first fluorine introduced is 0.13, for the second 0.31, and for the third 0.41. Measurements are also recorded for fluorine-substituted ketones, aldehydes, and amines. In the case of ethylene compounds, it is shown that the two stereoisomerides of bromofluoroethylene have practically the same molecular refractivity, although their densities are somewhat different. Tables of the dispersion of a large number of derivatives are given. In the case of aromatic compounds, it is shown that fluorine is unique in the fact that it alone gives derivatives which have a smaller refractivity than the corresponding open-chain compounds for all wave-lengths. The anomalies observed in the refractivity of fluorine compounds are considered in connexion with the structure of the fluorine atom. The following hitherto unpublished physical data for fluorine compounds are recorded: *Ethyl o-fluorobenzoate*, b. p. 216—216.5°/756 mm., m. p. —21.3°; *m-fluorobenzonitrile*, b. p. 182.6°/753 mm., m. p. —16.05°; *ethyl m-fluorobenzoate*, b. p. 208.8—208.84°/757.2 mm., m. p. —33.5°; $\alpha\alpha\alpha$ -3-tetrafluorotoluene, b. p. 101.2°; trifluoromethylcyclohexane, b. p. 103.20°, m. p. —103.4°; difluoromethylcyclohexane, b. p. 129.2°; ethyl trifluoroacetate, b. p. 5°.

J. F. S.

The Stark Effect on the Secondary Spectrum of Hydrogen. MASAZÔ KIUTTI (*Japan. J. Physics*, 1922, 1, 29—39).—An investigation into the behaviour of the lines in the secondary

spectrum of hydrogen of long wave-length, and including the Fulcher bands, under the influence of a powerful electrical field. From the blue to the red, more than one hundred lines are affected, but those lines on the long wave-length side of 5300 Å. do not usually show the Stark effect. The lines are normally displaced towards the red, or else separated in an asymmetrical manner. Groups of lines in the neighbourhood of 5400 Å. and 5930—5982 Å. are very largely affected. The amount of displacement increases either in proportion to, or more rapidly than, the field intensity. No simple rule can be found for the Stark effect on the Fulcher bands, except that the effect on the first and third members of both of the two bands is large and small alternately in the homologous succession of lines. This alternation may give some suggestion as to the structure of the centre of emission of the secondary spectrum.

W. E. G.

Line Spectrum of Chlorine in the Ultra-violet (Region λ 3354—2070 Å.). W. JEVONS (*Proc. Roy. Soc.*, 1923, [A], 103, 193—204).—Using a 10-foot concave grating and a quartz spectrograph, the author has investigated the ultra-violet spectrum of chlorine in the region λ 3354—2070 Å. A condensed discharge from a 12-inch induction coil with one, two, or three Leyden jars was employed, and a spark-gap of about 1 cm. was placed in series with the discharge tube. The spectrum was observed end-on to the capillary through a quartz window. Precautions were taken to eliminate lines due to impurities, and it is considered improbable that any oxygen lines remained unidentified, except possibly below λ 2228 Å. About two hundred lines due to chlorine were recorded, and the effect of capacity on the estimated intensities of more than one hundred of these was studied. The following lines, attributed by Exner and Haschek to chlorine were not observed: λ 3291.1, 3261.6, 3248.5, 3221.1, 2960.5, 2936.7, 2928.8 Å. The line λ 3129.5 Å., similarly attributed by Exner and Haschek, was observed but was probably due to oxygen. No triplets having constant differences of wave-number intervals 40.44, 67.10, and 107.88, respectively, as suggested by Paulson, were observed, but six pairs with a constant difference $\Delta\nu=40.4\pm1.0$, four pairs having $\Delta\nu=67.1\pm1.0$, and five pairs having $\Delta\nu=107.5\pm1.0$ were found.

J. S. G. T.

Band Spectra of Mercury. HANTARO NAGOAKA (*Japan. J. Physics*, 1922, 1, 1—6).—A *résumé* of preliminary work on the band spectra of mercury. The discordances between the results of different physicists on the band spectra of mercury may be attributed to the methods of construction of the lamps used. In this work, a lamp has been devised which gives nearly all the spectra previously recorded. Approximate measurements of the positions of the heads of the bands have been made. In some of the bands which could be easily measured, Deslandres's formula gives the positions of the lines accurately. Experiments were made to determine the structure of the lines in the bands, but no evidence was obtained of the presence of companions in the form of satellites.

Since this work was not conclusive, however, further experiments are being carried out with the aid of a high resolving spectrometer.
W. E. G.

Tesla-luminescence Spectra. III. The Effect of Varying Temperature and Pressure on the Benzene Spectrum. WILLIAM HAMILTON MCVICKER and JOSEPH KENNETH MARSH (T., 1923, 123, 817—820).

The Fluorescence Spectrum of Benzene Vapour. WILLIAM HAMILTON MCVICKER and JOSEPH KENNETH MARSH (T., 1923, 123, 820—822).

The Infra-red Absorption of Hydrogen Chloride in the Region $3.5\ \mu$, and at $200^\circ K$. B. J. SPENCE and C. HOLLEY (*J. Opt. Soc. Amer.*, 1923, 7, 169—173).—The infra-red absorption bands of hydrogen chloride have been measured at 291° and $200^\circ K$. They consist of two groups of bands of which the maxima of the envelopes occur at $3.397\ \mu$ and $3.538\ \mu$ at $291^\circ K$, and at $3.419\ \mu$ and $3.514\ \mu$ at $200^\circ K$. One-half of the frequency difference between the maxima of the envelope of the absorption bands corresponds with the most probable value of the frequency of rotation of the molecule. According to Kemble (*Physical Rev.*, 1916, 8, 689), this frequency $f_r = 1/4\pi\sqrt{RT/NJ}$, and thus should depend on the temperature. This equation is in fairly good agreement at $291^\circ K$, but at $200^\circ K$ there is a divergence indicating that it may require some modification at low temperatures. The position of the fine bands, in agreement with the theory of Bjerrum, is independent of the temperature. The results are also in accord with the theory of Reiche (*Ann. Physik*, 1919, 58, 657), according to which, at $291^\circ K$, the position of maximum absorption should occur at the third fine band, and at $200^\circ K$ at the second band on each side of the centre.
W. E. G.

The Limits of Absorption K of certain Elements. J. CABRERA (*Compt. rend.*, 1923, 176, 740—741).—The limits of absorption K of the elements of the rare earths were determined using de Broglie's method with a rotating crystal spectrograph and a lead screen with a window filled with the substance under examination. A Coolidge tube with a tungsten anticathode, or, in the case of thulium, where the limit of absorption K is very near the $K_{\alpha 1}$ line of tungsten, a gas tube with a platinum anticathode. The limit of absorption for tantalum was also measured. The results are given in tabular form, from which it is seen that the values of $\sqrt{\nu/R}$ depart more and more from a simple linear relation as the series of atomic numbers is ascended.
G. F. M.

The Law of the Distribution of the Bands in the Ultra-violet Absorption Spectrum of the Vapour of Toluene. VICTOR HENRI and E. WALTER (*Compt. rend.*, 1923, 176, 746—748).—The absorption spectrum of toluene vapour is composed of more than two hundred narrow bands distributed between $\lambda\ 2731$ and

λ 2325. The law of the distribution of these bands is expressed by the formula

$$1/\lambda = A + n \cdot a + p \cdot b - qc - h/(8\pi^2 \cdot 3 \cdot 10^{10} \cdot 3)(1 \pm 2m)$$

where A , corresponding with the electronic impulses, is 37493.2, a , b , and c with the vibrations of the atoms are 932.5, 263.6, and 180, respectively. 3 is the moment of inertia of the rotation of the molecule, m , n , p , and q are whole numbers, and $h/8\pi^2 \cdot 3 \cdot 10^{10} \cdot 3 = 1.3$. The intensity of the bands diminishes as the values of n , p , and q increase. The moment of inertia of the toluene molecule $3 = 21 \cdot 10^{-40}$.
G. F. M.

Ultra-violet Absorption Spectra of Benzoic Acid and the Three Hydroxybenzoic Acids. ARMAND CASTILLE and F. W. KLINGSTEDT (*Compt. rend.*, 1923, 176, 749—750).—The introduction of a carboxyl group into the benzene nucleus causes a displacement of the absorption spectrum by about 230 Å. towards the red, a quadruple increase in the coefficient of adsorption, and a widening of the absorption bands. The introduction of a hydroxyl group into the benzoic acid molecule in either the ortho- or meta-position is accompanied by a great increase in the absorption, a further widening of the narrow bands, and a considerable displacement of the spectrum towards the red. The two derivatives have almost the same spectrum. The para-derivative, on the other hand, is characterised by an entirely different spectrum, which shows five narrow bands between λ 2828 and 2671, then a wide and intense band at λ 2519, and an inflexion towards λ 2100, showing the existence of a band in this neighbourhood which is fused with a wide band in the extreme ultra-violet. These results are comparable with those obtained with other ortho-, meta-, and para-derivatives of benzene.
G. F. M.

The Ultra-violet Absorption Spectra of Veratrole and Vanillin. PIERRE STEINER (*Compt. rend.*, 1923, 176, 744—746).—The absorption curve of veratrole is very similar to that of pyrocatechol, the introduction of two methyl groups into the molecule having but little influence on the absorption. There is a group of three narrow bands in the middle ultra-violet, and a fourth band broad and very pronounced in the extreme ultra-violet. The absorption curve of vanillin can be compared with that of pyrocatechol and veratrole, on the one hand, and of benzaldehyde, on the other. The same three narrow bands are found as in veratrole, but displaced somewhat towards the red, and three times as intense. There is, in addition, a new broad band in the middle ultra-violet which is attributable to the aldehyde group, and the broad band of veratrole in the extreme ultra-violet appears again in vanillin, displaced slightly towards the right, and twice as intense.
G. F. M.

Studies in Organic Compounds containing Sulphur. I. The Effect on General Absorption due to the Valency and Mode of Linking of the Sulphur Atom. DAVID TEMPLETON GIBSON, HUGH GRAHAM, and JAMES REID (*T.*, 1923, 123, 874—881).

The Absorption of Light by Hæmatoporphyrin. I. KIKO GOTO (*Biochem. Z.*, 1923, **135**, 328—343).—Four different preparations of pure hæmatoporphyrin have been submitted to spectrophotometric measurements in dilute alcoholic solution with or without the addition of ammonia, acetic acid, or hydrochloric acid. In neutral, ammoniacal, or acetic acid solution, the curves obtained by plotting the specific extinction coefficient against the wave-lengths show very good agreement in detail over the four absorption bands. When, however, the solutions are left exposed to the light of a metallic filament lamp for periods up to twelve hours, the bands change, the first and fourth disappearing, and the second and third becoming merged more or less into one. In alcoholic solution to which concentrated hydrochloric acid had been added, there is only one absorption band, and it is unaffected by light.
H. K.

The Absorption of Light by Hæmatoporphyrin. II. PAUL HÁRI (*Biochem. Z.*, 1923, **135**, 344—352).—The author has examined, spectrophotometrically, the colouring matter in the urine of a patient in an undetermined pathological condition, and although the colouring matter was apparently closely allied to hæmatoporphyrin, it was not identical, the positions of the bands in alcoholic-ammoniacal solution and alcoholic-hydrochloric acid solution being different from those of hæmatoporphyrin (see preceding abstract).
H. K.

The Absorption of Light by several Components. N. P. PESKOV (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1924—1952).—Mixtures of coloured substances are examined spectrophotometrically with a view to ascertaining what mutual influences their components have on each other. Only crystalloids follow Beer's law, separately, or in mixtures. The use of dyes, which are mainly colloidal substances, together with crystalloids is useless for the purpose of testing Beer's law, and the absorption constants of such mixtures cannot be calculated by this law. The importance of this observation in connexion with the preparation of quantitative light filters for the determination of wave-lengths is pointed out. Mixtures of colloids only in exceptional cases follow Beer's law, but usually vary from it owing to inter-adsorption of the components, and light filters made from mixtures of such substances must therefore in each case be separately calibrated. Thus in the case of a mixture of colloidal iron and malachite-green, the latter substance distributes itself between the water and the colloidal hydrated ferric hydroxide in a constant ratio, depending on the concentrations of the two components. The value of spectrophotometric analysis for the investigation of the detailed processes of a reaction and the identification of intermediate products is emphasised.
R. T.

The Fluorescence and Coloration of Glass produced by β -Rays. J. R. CLARKE (*Phil. Mag.*, 1923, [vi], **45**, 735—736; cf. A., 1921, ii, 569).—Glass tubing, after treatment with radium

emanation until the colour change is complete, is heated at different temperatures and the duration of fluorescence measured. The time of fluorescence ranges from thirteen minutes at 110° to thirty seconds at 350° . At the annealing temperatures, the decolorisation will be practically instantaneous. Since at these temperatures complex molecular changes take place, it is probable that the fluorescence and decolorisation of the glass are associated with changes in the state of molecular aggregation. The normal colour of the radiated glass is brown, but when manganese is present it is purple.

W. E. G.

Rotatory Power of Organic Compounds. H. RUPE (*J. Chim. Phys.*, 1923, 20, 87—104).—A lecture on rotatory power delivered at Fribourg, Switzerland, April 30, 1922.

J. F. S.

Inhibition of the Photochemical Decomposition of Hydrogen Peroxide Solutions. I. WILLIAM THEODORE ANDERSON, jun., and HUGH STOTT TAYLOR (*J. Amer. Chem. Soc.*, 1923, 45, 650—662).—The rate of decomposition of hydrogen peroxide by ultra-violet light of wave-length $\lambda\lambda$ 2000, 2650, 2930, and 3050, respectively, has been determined, and the inhibitory effect of some twenty-five organic substances of widely differing character examined at 25° . All such substances inhibit the decomposition, due to the absorbing of the light by the organic compounds, and this has been found to be true in the case of benzene, several esters, acids, amines, ketones, and alkaloids. The retarding action of amines and alcohols requires an explanation based on causes other than absorption. It is shown that the inhibitors act more efficiently when placed in the peroxide solution than when used as a screening solution of similar thickness and concentration. The reason of the more efficient functioning of the inhibitor in the solution is probably that one quantum of energy is capable of activating more than one molecule. Thus if the stabiliser is acting as a screening solution, the peroxide being free from inhibitors, a quantum of light energy may slip through and enter the peroxide solution and by successive activation decompose a number of molecules. On the other hand, if the stabiliser is in the peroxide solution and one quantum of light energy should succeed in activating a peroxide molecule, this molecule will decompose, liberating the energy quantum, which in its turn may activate another peroxide molecule or, coming within the sphere of influence of a molecule of inhibitor, may be converted into the less active ultra-red energy.

J. F. S.

Application of the Photochemical Law of Equivalence to Dilute Solutions. HEINZ GRÜSS (*Z. Elektrochem.*, 1923, 29, 144—150).—In continuation of the work of Noddack (A., 1921, ii, 568), the author finds that the photochemical reaction $2\text{CCl}_3\text{Br} + \text{Cl}_2 + h\nu = 2\text{CCl}_4 + \text{Br}_2$, in a medium consisting either of carbon tetrachloride or silicon tetrachloride, proceeds in a manner independent of the concentration of the trichlorobromomethane, at least down to a molecular concentration of $1/80 \text{ CCl}_3\text{Br}$ in the former medium and $1/60 \text{ CCl}_3\text{Br}$ in the latter. The results obtained

indicate that pure carbon tetrachloride is a non-acceptor of chlorine under the influence of light. Results contrary to this conclusion, reached by Noddack (*loc. cit.*) and by Plotnikov (A., 1920, ii, 211; 1922, ii, 248) are attributed to the presence of impurities in the carbon tetrachloride employed by them. The reaction $2\text{CCl}_3\text{Br} + \text{O}_2 = 2\text{COCl}_2 + \text{Br}_2 + \text{Cl}_2$ can be influenced photochemically, and the velocity of reaction is independent of the concentration of CCl_3Br and O_2 in carbon tetrachloride. Einstein's photochemical law applies to the reaction, and one molecule of bromine is produced per quantum of illumination. The results obtained by Noddack and in the present work indicate that reaction occurs between trichlorobromomethane and illuminated chlorine molecules characterised by a large Bohr quantum number, without previous dissociation into atoms. The lower limit for the period of existence of the molecules in such quantised condition, found from the reaction $2\text{CCl}_3\text{Br} + \text{O}_2 + h\nu = 2\text{COCl}_2 + \text{Br}_2 + \text{Cl}_2$ is 10^{-7} sec., compared with 2×10^{-9} sec. in the case of the reaction studied by Noddack. J. S. G. T.

Photolysis of Tartaric Acid and Hydroxy-acids. VOLMAR (*Compt. rend.*, 1923, 176, 742—744).—Under the influence of ultra-violet light, and to a much lesser degree in sunlight, hydroxy-acids and their salts undergo photolysis. Tartaric acid in 1% solution after three hours' exposure gave 3.5 c.c. of gas having the composition CO_2 66%, CO 10%, H_2 21%, hydrocarbon 3%. The solution contained aldehydes and small quantities of a reducing substance of the nature of a sugar. In presence of alkalis, the carbon monoxide may disappear entirely, owing to condensation with a portion of the hydrogen with formation of the above-mentioned aldehydic substances. The homologues of tartaric acid behaved in a similar way. The decomposition is accelerated by the presence of catalysts such as uranyl acetate. G. F. M.

Spectrophotoelectrical Sensitivity of some Halide Salts of Thallium, Lead, and Silver. W. W. COBLENTZ and J. F. ECKFORD (*U.S. Bureau of Standards, Sci. Papers*, 1922, 18, 489—498; cf. this vol., ii, 51).—A definite relationship exists between crystal structure, chemical constitution, and atomic weight and spectrophotoelectrical sensitivity. The photoelectrical reaction of the halide salts of thallium, lead, and silver is confined to a narrow region at the violet end of the spectrum, being the narrowest and most sharply-defined reaction spectra of all substances yet investigated, including the photoelectrical gas ionic reaction spectra of the alkali metals. With increase in the atomic weight of the acid element, the maximum of photoelectrical reaction is shifted towards the long wave-lengths. The maximum of sensitivity of thallium chloride lies at 0.368μ , of the bromide at 0.413μ , and of the iodide at 0.455μ . The position of the maximum for the latter is unaffected by lowering the temperature. The reaction curves are unsymmetrical, terminating abruptly on the long wave-length side, and giving a high photoelectrical reaction on the short wave-length side of the maximum. Lead iodide is the only lead halide which is

sensitive, and this gives a complex curve, showing an ill-defined maximum in the region of $0.45\ \mu$ and a sharply defined maximum at $0.52\ \mu$. Silver halides are sensitive only when in a fused state, the chloride giving a maximum at $0.38\ \mu$, the bromide at $0.46\ \mu$, and the iodide at $0.47\ \mu$ and $0.50\ \mu$, respectively. Silver and potassium nitrates are not sensitive.

W. E. G.

Various Photoelectrical Investigations. W. W. COBLENTZ (*U.S. Bureau of Standards, Sci. Papers*, 1922, **18**, 585—607).—Artificial preparations of molybdenum disulphide are not nearly so photoelectrically sensitive as the native mineral, especially that containing a relatively high iron content. The sensitivity is destroyed by heating above 700° , whereas that of stibnite is unaffected under similar treatment.

Curves showing the photoelectrical sensitivity to light of different wave-lengths for cuprous oxide, a native lead-antimony sulphide, Pb_3SbS_3 , and iodine are given. Sulphides of tin, tungsten, and uranium, nitrates of silver and potassium, bismuth telluride, and molybdenum selenide are not photoelectrically sensitive. [Cf. *J.S.C.I.*, 1923; May.]

A. R. P.

Some Properties of Resonance Radiation and Excited Atoms. K. T. COMPTON (*Phil. Mag.*, 1923, [vi], **45**, 750—760; cf. Horton and Davies, this vol., ii, 4).—Atoms and molecules in states of partial or complete ionisation, produced by suitable excitation, give to a gas properties quite different from those of the normal unexcited gas. Such properties include new lines in the absorption and resonance spectra, the production of band spectra as the result of molecular combination between the excited atoms, and increased ease of ionisation. The excited state in helium gas was shown by Kannenstine to persist for 0.0024 sec. after the exciting voltage was removed. This permanence of excitation was ascribed to the occurrence of metastable helium atoms possessing a long life period. An alternative interpretation of this result is put forward in this paper. An electron the velocity of which exceeds that gained by falling through the resonance potential, V , collides with an atom, and displaces an electron from the normal to an outer orbit forming an excited atom. At the end of the average life of this atom, T , the electron falls back to the normal position, emitting its resonance radiation. Any other normal helium atom is capable of absorbing this radiation and emitting it after an interval, T . The radiation is thus passed from atom to atom until it finally escapes, or is degraded to a non-resonance radiation. The time, 0.0024 sec., in Kannenstine's work will thus represent the time required for the resonance radiation to escape from the gas. The passage of resonance radiation through a gas may be treated as a problem in diffusion, and it is shown that the number and persistence of excited atoms depend jointly on the time of activation, T , and on the square of the scattering coefficient, α^2 , of the resonance radiation. From this method of treatment, it appears that the average life of the excited helium atom is not noticeably larger than that predicted by theory, or

very different from that of other substances. In the presence of impurities, the resonance radiation may be altered in character by transformation into other wave-lengths to which the gas is more transparent. Thus the diffuse nature of the line corresponding with the helium atom excited by 20·4 volts may be ascribed to the production of unstable helium compounds between this atom and the impurities. W. E. G.

Critical Electron Energies in Helium, and the Extreme Ultra-violet Spectrum. ANN CATHARINE DAVIES (*Phil. Mag.*, 1923, [vi], 45, 786—798; cf. A., 1921, ii, 672).—The value of the ionisation voltage for electrons in helium deduced from the lines in the extreme ultra-violet observed by Lyman (cf. A., 1922, ii, 674) is greater than the experimental values of Horton and Davies, and those of Franck and Knipping by 0·7 volt. In the present paper, the errors likely to arise in the experimental values of the former workers are discussed. The discovery of two critical radiation voltages of helium separated by only 0·8 volt introduces the possibility that an error of interpretation of the observed effects has been made. The first of these voltages, at 19·7 volts (corrected), gives a much smaller radiation current than the second at 20·5 volts, and it is possible that the positive current due to the photoelectric effect of the former was so small that it was masked by the negative current from electrons escaping collision; hence the first critical stage was missed in the earlier investigation. Thus the second critical stage may have been taken for the first, in which case the true value for the first critical radiation voltage is $0·8 \pm 0·1$ volt lower than the value given originally for this constant. Since the values given in subsequent papers were measured relatively to the first, a correction of the same amount must be applied to them also. The selection principle of Bohr does not appear to hold for transitions of electrons to the normal state. Evidence is brought forward to show that the transitions $N-1\sigma$ or $N-1S$ must be possible. An explanation is given of the absence of the line $N-1S$ from the Lyman spectra. The ability of current-voltage observations to reveal the existence of ultra-violet series spectra is discussed, and it is concluded that whereas the method may be expected to indicate the first lines of a series involving the return of an electron to the normal state, it would probably not reveal the higher members of those series. W. E. G.

Excitation and Ionisation Potentials of Neon and Argon. G. HERTZ (*Proc. K. Akad. Wetensch. Amsterdam*, 1923, 25, 442).—In a recent paper (A., 1922, ii, 733) the author described the measurement of the excitation and ionisation potentials of argon and neon and based his calculations on the value 20·45 volts as the first ionisation potential of helium. Franck (A., 1922, ii, 811) has shown that this value is too high and that the figure 19·75 volts is much nearer the correct value. Using this value, the author has recalculated his results. The following values are recorded: Neon, excitation potentials 16·65 and 18·45 volts, ionisation potential 21·5 volts; argon, excitation potentials, 11·55, 13·0,

and 14.0 volts, ionisation potential 15.3 volts. The conclusions relating to the optical spectrum are not affected by this correction, since only the potential differences are used for them. Only the term 0.5 s, which corresponds with the normal state of the atom, must be diminished, and becomes 174000 ± 1000 for neon and 124000 ± 1000 for argon.

J. F. S.

Critical Velocity of Electrons in Krypton and Excitation of the Spectrum of the Gas. GEORGES DÉJARDIN (*Compt. rend.*, 1923, 176, 894—897).—The critical velocity of electrons in krypton and the development of its spectrum was studied by means of the apparatus and method previously employed for argon and helium (this vol., ii, 47, 112). An incandescent filament of tungsten was used as the source of the electrons. The ionisation potential of krypton was found to be 12.7 ± 0.2 volts, and the potential of double ionisation (simultaneous removal of two peripheral electrons) 28.25 ± 0.5 volts. A redetermination of the corresponding values for argon gave 15.2 ± 0.2 volts and 34.0 ± 0.5 volts, respectively. When the pressure is of the order of 1 mm., the ionisation of argon can be observed to commence at 11.5 volts and of krypton at 9.8 volts. These potentials are probably resonance potentials. The ratios of the simple and double ionisation potentials of argon and krypton are equal within the limits of experimental error, which points to the identity of the structure of the peripheral layers of the atoms of the two gases. Krypton has, like argon, two entirely distinct spectra; the first spectrum appears from the commencement of ionisation and consists of a small number of lines, amongst which are the well-known yellow and green lines and a group in the blue. The second spectrum, consisting of a considerable number of lines of which the most intense are situated in the blue and violet, commences to appear at a potential of 28.25 volts and the intensity increases to a maximum at 32—34 volts. The production of the first spectrum corresponds with the ionisation of the neutral atom, but the second spectrum, like the blue spectrum of argon, seems to be produced by several groups of different character. Certain lines result from the double ionisation of the atom, but others are probably emitted by atoms which have lost more than two peripheral electrons.

G. F. M.

The Separation of Isotopes. JAMES KENDALL and E. D. CRITTENDEN (*Proc. Nat. Acad. Sci.*, 1923, 9, 75—78).—An outline of two methods by which an attempt is being made to isolate pure isotopes in significant quantity. The ionic migration method is being tested with chlorine- and lithium-ions, the principle of the moving boundary being utilised. Sodium chloride dissolved in agar-agar gel is inserted in the middle horizontal section of a moving boundary tube, and on the two sides of this section are placed, respectively, other sections containing sodium hydroxide and sodium acetate gels. These gels continue up right-angle bends, in which are placed a solution of sodium hydroxide and a solution of sodium acetate in concentrated acetic acid, respectively. On passing a current, the boundaries keep perfectly sharp, and the

conditions are so fixed that they advance 12 to 18 inches a day. When the front chlorine boundary reaches the end of the last section, the apparatus is taken apart, the two rear sections are discarded, and two new sections containing hydroxide gel are fitted in front of the chloride tube. Chlorine-ions are forced to migrate into the two new sections, and the procedure is repeated until the chlorine-ions are passed through 100 ft. of gel. The chloride gel is then cut up into strips. Experiments with sodium iodide and thiocyanate have demonstrated that the front sections contain pure sodium iodide after the gel has moved only a few feet. Thus if the two chlorine-ions possess different mobilities, the faster moving ion should be found in the front section. No separation has been detected in the preliminary experiments, but the work is being continued. The method may be useful in the separation of the elements of the rare earths, and radium from barium.

A discharge potential method of separation is being tested which depends on the different concentration of the two isotopic chlorine-ions. Although it is unlikely that the decomposition potentials of the two isotopes are in any way different, if the Nernst concentration equation holds, the discharge potentials should differ by 0.03 volt. It should therefore be possible to effect an electrolytic fractionation by this means. Chlorine, mercury, magnesium, and lithium are under investigation in this connexion. W. E. G.

Discharge Processes in Gases using Tesla Currents. HERBERT FISCHER (*Z. physikal. Chem.*, 1923, **104**, 74—89).—A Tesla current of a maximum voltage of 25,000 has been allowed to pass through air, mixtures of nitrogen and oxygen, and other gases. The results show that oxygen, air, nitrogen, hydrogen, and argon give characteristic colours. The colour exhibited by hydrogen is noteworthy; with a Tesla current of 10,000 volts, hydrogen gives an intense ultramarine colour which after a while becomes greyish-blue. In all cases with oxygen and air, when a current of lower frequency and 9,200 volts is used, ozone is produced, the quantity of ozone increasing almost proportionately with the driving energy of the current. It appears, however, to be possible to increase the yield by increasing the number of plates. With increasing distance between the electrodes the yield of ozone decreases, and it increases with decreasing rate of flow of the gas. Glass and aluminium ozonisers under identical conditions furnish approximately the same concentration of ozone, but ozonisers with a brass electrode furnish extremely small yields of ozone. With Tesla currents, the apparatus becomes heated, so that external cooling becomes necessary. Nitrogen pentoxide is formed in small quantities, but nitrogen trioxide could not be detected. In mixtures of oxygen and nitrogen, the yield of ozone increases with the concentration of the oxygen. J. F. S.

Determination of the Dipole Length of the Hydrogen Chloride Molecule by Electrostriction Experiments. O. E. FRIVOLD and ODD HASSEL (*Physikal. Z.*, 1923, **24**, 82—87).—By

determining the increase of pressure in a dielectric composed of hydrogen chloride, due to charging the plates of a condenser, the authors find that the dipole length of the hydrogen chloride molecule is 0.31×10^{-8} cm., which is smaller than the value, 0.45×10^{-8} cm., deduced by Falkenhagen and Weigt (*ibid.*, 1922, **23**, 87) from measurements of the dielectric constant of the gas. The nuclear distance is found to be 1.265×10^{-8} cm., and the ratio of the two lengths is such that it is impossible to discriminate between the validity or otherwise of the formulæ for the dipole moment deduced, respectively, by Debye and by Pauli on the classical and quantum theories. Such discrimination is possible only when the dipole length is greater than half and less than the whole of the nuclear distance. J. S. G. T.

Recrystallisation of Alloys which Contain a Eutectic. G. TAMMANN and K. DAHL (*Z. anorg. Chem.*, 1923, **126**, 113—118).—The heating of a wire of a eutectic structure results in a decrease in its electrical resistance. In the case of pure metals, there is a temperature of minimum resistance, but with eutectic wires the minimum resistance is not connected with a definite temperature (cf. Credner, A., 1913, ii, 280). W. T.

Electrical Conductivity of some Gold-Iron Alloys. Examples of the Electrical Behaviour of Limited Mixed Crystal Series. W. GUERTLER and A. SCHULZE (*Z. physikal. Chem.*, 1923, **104**, 90—100).—The electrical conductivity of gold-iron alloys containing, respectively, 1, 2, 3, 5, 10, 20, and 40% of gold has been measured at a series of temperatures between 0° and 200° , with the object of testing the validity of Matthiessen's law (1861—1864). This law has been restated in the form that the absolute increase of the resistance on raising the temperature from 0° to 100° is independent of the increase of resistance brought about by the presence of mixed crystals, and has the same value as that calculated from the increase of resistance of the pure components when raised through the same temperature interval, that is, $dW_m/dt = dW/dt$. The experimental results show that the law in the form stated above is entirely true, and that it is not only true over the temperature range 0° to 100° , but also over any other temperature range. It may therefore be also stated in the form that within the range of a given state the differential quotient of the resistance and the temperature, dW/dt , increases in a given series of binary alloys proportionally to the volume concentration of the components. J. F. S.

New Dielectric Constants. RUDOLF KELLER (*Biochem. Z.*, 1923, **136**, 163—168).—The dielectric constants of a number of physiologically important substances have been determined. They include albumin, pepsin, trypsin, globulin, saliva, and sera. H. K.

The Theory of Electrolytic Ions. XXVIII. The Theory of the Determination of the Limiting Value of the Molecular Conductivity of Strong Electrolytes. RICHARD LORENZ and A. LANDÉ (*Z. anorg. Chem.*, 1923, **126**, 278—280).—Theoretical.

The authors' experimental formulæ, $1 - x_K/1 - y_{Cl} = \text{constant} = a$; $1 - x_{Na}/1 - y_{Cl} = \text{constant} = b$; $1 - x_{Na}/1 - x_K = \text{constant} = c = b/a$ (this vol., ii, 9), where x and y are the rates of increase of mobility with dilution of the anion and kation, respectively, are now shown to be generally applicable to binary electrolytes because they can be derived directly from Hertz's law (A., 1912, ii, 120). By a simple mathematical transformation it is shown that for any binary electrolyte the value of $1 - x/1 - y = gu_0/g'v_0 = \text{constant}$, where g and g' are constants dependent only on the nature of the ion and not on the concentration, and u_0 and v_0 are the limiting mobilities of the ions. H. H.

The Potentials of Lead-Tin Alloys. S. D. MUZAFFAR (*Z. anorg. Chem.*, 1923, 126, 254—256).—From measurements of the potentials of lead-tin alloys of compositions from 0% to 100% tin in potassium hydroxide solution and in a solution of lead acetate in acetic acid, in both of which electrolytes tin is more electro-positive than lead, the author concludes that it is highly probable that all these lead-tin alloys contain a complex containing about 9% of tin (cf. A., 1904, ii, 336, 818; 1907, ii, 774, 837). H. H.

Membrane Potentials and Cataphoretic Potentials of Proteins. JACQUES LOEB (*J. Gen. Physiol.*, 1923, 5, 505—519).—A comparison has been made of the membrane potentials of certain protein solutions and the cataphoretic potential difference of protein particles or collodion particles coated with protein, more particularly in respect of the influence of salts. The former potential difference is obtained by measuring the potential difference between the liquids on two sides of a membrane, that on one side containing the protein in solution, the latter from the velocity of the particles under a known potential gradient. Differences exist between the potentials, but in many points there is very marked similarity or identity. It is concluded that in both cases the forces inherent in the protein and linked with the membrane potential act as the determining factor, and that the forces inherent in the water surrounding the particles are secondary, and account for the differences. W. O. K.

An Electrochemical Method of Studying Irreversible Organic Reductions. JAMES B. CONANT and ROBERT E. LUTZ (*J. Amer. Chem. Soc.*, 1923, 45, 1047—1060).—Previous work on reversible reduction of organic substances (this vol., ii, 9) has been extended. The potential of the following combination is measured: Pt|Solution A : reducing agent|Solution A : quinhydrone|Pt. The material under investigation is then added to the half-cell containing the reducing agent (quinol), and it is noted whether the potential alters during the following thirty minutes. A rise of potential indicates that reduction occurs. In this way, upper potential limits for the reduction of a series of carbonyl derivatives of ethylene have been determined, in acetone and alcoholic solutions. The results show that the potential at which the substance is irreversibly reduced is approximately proportional to the reactivity

of the carbonyl group. The reduction of nitrosobenzene to phenylhydroxylamine is shown to be reversible, and the potential is measured. Preliminary values are given for a series of nitrogen compounds, which are irreversibly reduced.

A theory of irreversible reductions is advanced which qualitatively connects the "apparent reduction potential" with a true oxidation-reduction potential of the substance in question. W. S. N.

Concentration Cells in Non-aqueous Solvents. A. N. SACHANOV and A. M. GRINBAUM (*J. Russ. Phys. Chem. Soc.*, 1916, 48, 1794—1806).—The *E.M.F.* of concentration cells of silver nitrate in pyridine solution is investigated; it is for very small concentrations of silver nitrate (from 0.01*N* to 0.0004*N*) little different from that calculated by Nernst's theory, or obtained with aqueous solutions. With greater concentrations, wide variations from theory are observed, due to the formation of complex kations and to anomalous dissociation. The degree of dissociation of silver nitrate in pyridine solution is calculated, and found to decrease rapidly as the concentration becomes greater than 0.1*N*. Minimum dissociation occurs with a normal solution, whilst at higher concentrations the degree of dissociation again increases owing to anomalies in dissociation. R. T.

Action of Gelatin on Concentration Cells. RENÉ AUDUBERT (*Compt. rend.*, 1923, 176, 838—840).—The addition of gelatin to the concentration cells AgI-AgNO_3 , AgCl-AgNO_3 , and $\text{Ag}_2\text{S-AgNO}_3$ caused a diminution of the electromotive force when it was added to the silver nitrate solution, and an increase when the addition was made in the neighbourhood of the other electrode. The action of the gelatin is therefore to diminish the concentration of silver-ions, and given that $\epsilon = RT/96600LC/c$, where C is the concentration of silver-ions in the nitrate solution, and c that of the same ions at the other electrode, a measurement of ϵ with and without the addition of gelatin is all that is required to give the diminution in concentration of the silver-ions caused by the addition of varying amounts of gelatin, by substitution in the expression $C - C' = c[e^{96600\epsilon/RT} - e^{96600\epsilon'/RT}]$. The determinations showed that the quantity of ions fixed by the gelatin was a continuous function of the concentration C' of the ions in equilibrium with the colloid, which could be expressed as $C - C' = AC'^p$, where p is a coefficient independent of the concentration of the gelatin and of the nature of the cell. Its value approximated to 0.5, showing that the formula given by Freundlich to represent an adsorption isotherm can be applied to the equilibrium between the silver-ions and the gelatin. It seems therefore that the silver-ion forms an adsorption complex with the gelatin. The influence exercised by gelatin in the formation of a fine electrolytic deposit can be attributed to an increased cathodic polarisation. G. F. M.

Bimetallic Electrode System Applied to Neutralisation Reactions. H. H. WILLARD and FLORENCE FENWICK (*J. Amer. Chem. Soc.*, 1923, 45, 715—716).—In an attempt to use bimetallic

electrode systems in neutralisation reactions, it was found that the electrodes reacted very sluggishly in the region of the neutral point. The addition of potassium bromate to the solution did not improve matters, but on the addition of neutral hydrogen peroxide the electrodes regained their normal activity and retained it up to the neutral point. A potential difference persisted up to 0.3–0.4 c.c. of 0.1*N*-titrating solution of the end-point, it then began to decrease and at the neutral point a clear, sharp, downward break occurred. With the reversed titration, a rise preceded the end-point, which was marked by a break upwards of about 100 mv. In both cases, the point of the maximum velocity of potential change is exactly coincident with the "green point" of bromothymolsulphone-phthalein, which corresponds with a P_H value of 6.8. In neither case was the end-point permanent. Rapid stirring of the solution favoured the absorption of carbon dioxide to such an extent that variable results were obtained in consecutive titrations approaching the neutral point from the alkaline side. With the approach on the opposite side the crawl as the end-point was passed is not sufficient to impair seriously the clarity of the break. The method appears to offer possibilities for the development of a new type of hydrogen electrode which is unique in its independence of an external gas supply.

J. F. S.

Electrolytic Dissociation of Water in Salt Solutions. E. LINDE (*Z. Elektrochem.*, 1923, 29, 163–168).—The respective viscosities of solutions of lithium chloride and calcium chloride of various concentrations up to saturation (44.1% and 46.4%, respectively), at 25°, have been determined, and the results indicate that the product of viscosity and electrical conductivity in each case increases continuously with increase of concentration of the solutions. Values of the viscosities determined have been applied to correct the values found by Palmaer and Melander (*A.*, 1915, ii, 727) for the *E.M.F.* of hydrogen electrodes in aqueous solutions of lithium chloride and calcium chloride of various concentrations, such correction being necessary owing to the contact difference of potential between the two solutions employed, arising from a difference in their viscosities. Corresponding values of normality and corrected *E.M.F.* for lithium chloride solutions at 22° are: 1.5*N*, 0.124; 1.8*N*, 0.127; 3.0*N*, 0.115; 5.7*N*, 0.112; 7.2*N*, 0.052 volt. In the case of solutions of calcium chloride at 25.5°, corrected values were determined as follows: 0.65*N*, 0.168; 1.50*N*, 0.131; 2.18*N*, 0.098; 2.50*N*, 0.106; 4.00*N*, 0.053; 5.07*N*, 0.038 volt. The respective relative concentrations of hydrogen-ions in the various solutions are calculated from the corrected values of *E.M.F.* by Nernst's formula.

J. S. G. T.

The Electrochemistry of Non-aqueous Solutions. III. Electrolytic Deposition of Alkali Metals from Solutions in Anhydrous Pyridine. ROBERT MÜLLER, F. HÖLZL, A. PONTONI, and O. WINTERSTEINER (*Monatsh.*, 1923, 43, 419–437; cf. *A.*, 1922, ii, 612; Kahlenberg, *A.*, 1900, ii, 521, and Patten and Mott, *A.*, 1908, ii, 253).—Previous work is continued, the standard

electrode already described being used for measurements; in the following, potentials are referred to the electrode $\text{Ag}|0.1N\text{AgNO}_3$ in pyridine = 0, unless otherwise indicated. The decomposition potentials for 0.1*N*, *N*, and saturated solutions of lithium chloride in pyridine are, respectively, 4.18, 4.05, and 4.05 volts. With a mercury cathode, the three solutions give the same value, -2.83 volts. The deposition potential of lithium (*N*-LiCl solution) is 3.1 volts ($E_p=2.82$ volts), the corresponding anodic potential being 0.85 volt ($E_p=1.3$ volts). Using a more delicate electrometer, the following results were obtained: Lithium potentials for saturated and *N*-lithium chloride solutions are, respectively, 3.09 and 3.12 volts. The corresponding anodic potentials are 0.73 and 0.74 volt. For *N*-lithium chloride, the lithium potential referred to the hydrogen electrode is 2.83 volts. The decomposition potentials varied from 3.8 to 3.9 volts (values of deposition potential are obtained in all cases by producing the straight portion of the polarisation curves downwards, to meet the potential axis).

The presence of water in *N*-lithium chloride (pyridine) solutions gives rise to totally different cathodic and anodic polarisation curves, probably owing to the separation of lithium hydroxide (see Patten and Mott, *loc. cit.*).

The cell, $\text{Li}|\text{LiCl}|0.1N\text{AgNO}_3|\text{Ag}$, has E 3.16 and 3.2 volts for *N* and 0.1*N*-lithium chloride, respectively.

Similar measurements with lithium nitrate gave: Cathodic potentials, 2.00 and 1.90 volts, anodic potentials, 3.06 and 3.09 volts for saturated and *N*-lithium nitrate, respectively. Decomposition potentials (for saturated solution) 5.01 volts. The cell $\text{Li}|\text{LiNO}_3|0.1N\text{AgNO}_3|\text{Ag}$ has E 2.86, 3.05, 3.10, and 3.15 volts for the four concentrations, saturated, *N*-, 0.1*N*-, and 0.01*N*-lithium nitrate (in pyridine), respectively.

Sodium is not deposited from sodium iodide-pyridine solutions under conditions similar to those used in the case of lithium. With sodium thiocyanate no definite polarisation figures were obtainable. Emmert's dipyridine sodium (A., 1921, i, 268) may be responsible for these irregularities. The anodic polarisation in each case was more definite. Sodium nitrate solutions conducted too badly to allow of their investigation.

With potassium thiocyanate, one of the few potassium salts soluble in pyridine, no separation of metal occurred on a platinum electrode, but, using a mercury cathode, separation occurred readily and the constant potential of 1.77 volts was observed, the corresponding potential for the anode being 0.42 volt. The cell $\text{K}|\text{KCNS}(\text{saturated solution})|0.1N\text{AgNO}_3|\text{Ag}$ gave 2.58 volts.

E. E. T.

A New Method to Determine the Hydration of Ions. The Hydration of the Lithium-ion. GEORGE BABOROVSKÝ (*Rec. trav. chim.*, 1923, 42, 229—239).—The author describes a new form of apparatus for determining the transport number and hydration of ions, and gives the results of a series of experiments carried out with solutions of lithium chloride. The value for the hydration

of the lithium-ion was found by determining the change in mass and concentration of the electrode solutions and shows that the ion adds one molecule of water assuming that the hydration of the chlorine-ion is zero. The transport number of the lithium-ion in decinormal solution of the chloride is 0.3128 ± 0.0048 . H. J. E.

The Ionising Power of Molten Lithium Hydride. A. GUNTZ and BENOIT (*Compt. rend.*, 1923, **176**, 970—971).—The electrolysis of the solution of lithium carbide in molten lithium hydride obtained by the action of lithium on ethylene results in a separation of carbon at the anode. This is not due to the action of hydrogen on the carbide, which only occurs above 600° , and it is concluded that the carbide is ionised in the molten hydride. It was found that no hydrogen was evolved at the anode with a voltage below 0.1, whilst deposition of carbon occurred at 0.05 volt. Similar results were obtained with solutions of calcium carbide in lithium or calcium hydride, or a mixture of lithium or calcium hydride and chloride. The nitrides of the alkaline-earth metals are also soluble in the corresponding hydrides, and appear to be ionised in a similar way. G. F. M.

The Formation of a Reducing Substance at the Cathode by the Electrolysis of Acid and Alkaline Solutions. G. TAMMANN (*Z. anorg. Chem.*, 1923, **126**, 176—178).—The cathode liquid after the electrolysis of a dilute solution of sodium or potassium hydroxide or sulphuric acid has the property of reducing an alkaline solution of silver. The reducing agent is unstable, and one-half of it disappears in one day. It is shown that this reduction cannot be due to the presence of ferrous hydroxide or to active hydrogen (H_2). Attempts were made to extract the reducing agent with benzene, the benzene solution being then shaken with hydrochloric acid; the concentration of the substance was found to have thus increased tenfold. The author does not speculate as to the nature of the substance, pure specimens of which could not be obtained.

W. T.

The Electrophoresis of Chromic Solutions. F. L. SEYMOUR-JONES (*Ind. Eng. Chem.*, 1923, **15**, 265—266).—Thompson and Atkin have recently suggested (*J. Soc. Leather Trades Chem.*, 1922, **6**, 267) that in chrome liquors used in tanning, the active tanning agent is a negatively charged chromium complex, but electrophoresis experiments on normal and basic solutions of chromic chloride and sulphate and of chrome alum showed that anodic migration of chromium occurs only in basic sulphate solutions, and therefore no such negative complex can exist in solutions of the chloride or of chrome alum. Since, however, basic chloride solutions tan hide powder in a perfectly normal fashion, the theory that a negatively charged chromium complex is always the active tanning agent cannot be maintained. G. F. M.

The Magneto-chemical Effect. A. N. SCHTSCHUKAREV (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1785—1793).—Barium chloride solution is electrolysed in a strong magnetic field. A stream of positively charged particles is observed to emanate from the region

of the solution where liberation of ions take place. These particles move with great velocity, as they are able to penetrate a layer of solution 1 cm. in thickness, the minimum penetrative power observed being half as great. The nature of these particles is not certain, but it seems possible that they are produced as a result of the disintegration of the chlorine atom. A platinum-platino-iridium thermo-element placed in the solution within range of the particles gives a perceptible heat effect, so that they appear to possess considerable kinetic energy. A stream of negatively charged particles is also observed, but these have not up to the present been investigated.

R. T.

A New Method for the Control of Thermostats. D. J. BEAVER and J. J. BEAVER (*Ind. Eng. Chem.*, 1923, **15**, 359—361).—An apparatus is described by means of which it is possible to maintain water or oil thermostats of capacities of 10—300 litres constant to 0.001° over long periods of time with little attention. Sparking at the mercury contact which causes surface oxidation of the metal is eliminated by using a very small current across the contact, and amplifying it sufficiently by means of a vacuum tube to actuate a magnetic relay or other current controlling mechanism. With a 120 volt direct current supply, and a resistance of 1 megohm between the grid of the vacuum tube and the mercury contact, the current across the latter is approximately 2×10^{-5} amperes, which is far too small to produce an arc at the contact surface. When the thermoregulator is not fastened rigidly to the thermostat, the mercury surface oscillates rapidly. This increases the sensitiveness of regulation, but it is desirable to slow the oscillation down to a frequency of about 2 per second by placing a condenser of 0.1 microfarad capacity in parallel with the resistance between the grid and the filament. The thermoregulator consists of a glass spiral filled with toluene or turpentine, to the upper end of which a capillary U-tube of 1.5 mm. bore is sealed. This is filled with mercury, and a platinum wire sealed in the lower part of the U-tube is used to make one contact, whilst a fine iron or nickel wire makes the adjustable contact in the capillary. Back lash at the mercury contact is thus eliminated as neither of these metals is wetted by the mercury. A Monel metal tube charged with mercury provides a more sensitive regulator, and should be used if the room temperature is liable to fluctuate 5° or more from the bath temperature.

G. F. M.

The Heat of Vaporisation and the Difference in the Specific Heats of the Saturated Vapour and of the Liquid States for Neon. E. MATHIAS, C. A. CROMMELIN, and H. KAMERLINGH ONNES (*Compt. rend.*, 1923, **176**, 939—940).—The latent heat of vaporisation of neon was calculated from the Clapeyron-Clausius formula $L = T/J(1/\delta' - 1/\delta)dp/dT$, the densities δ and δ' of the liquid and saturated vapour at T° and a pressure p being obtained from earlier work (A., 1922, ii, 472). The values found for L as a function of the temperature are closely expressed by the equation $L^2 = 43.56922(T_c - T) - 1.744347(T_c - T)^2 + 0.0371203(T_c - T)^3$, where

T_c is the absolute critical temperature. The difference in the specific heats of the liquid m , and the saturated vapour m' was then obtained from the equation $m' - m = dL/dT - L/T$. The value was strongly negative at the critical point, and remains negative at all temperatures, with a maximum at a temperature $T/T_c = 0.74$. The values found for neon at a temperature $T/T_c = 0.6$ were as follows: T_c 44.38° , L 20.8, ML 420, and $L\Delta/p_c$ 0.374, where ML is the molecular heat of vaporisation, Δ the critical density, and p_c the critical pressure. A comparison with the corresponding values for oxygen, argon, nitrogen, and hydrogen shows that the deviations from the law of corresponding states increase as the critical temperature decreases.

G. F. M.

Relation between the Dipole Moment and Heat of Sublimation of the Hydrogen Halides. M. BORN and H. KORNFELD (*Physikal. Z.*, 1923, 24, 121—124).—The authors suggest that crystals of the hydrogen halides are built up of cubical crystal lattices, the unit cube of the lattice consisting of two congruent regular tetrahedra, at the corners of which molecular dipoles having their positive poles directed respectively towards and away from the centre of the cube are arranged. By considering the attractive and repulsive forces arising from such an arrangement of dipoles, an expression is deduced for the heat of sublimation of the respective halides, in the form $S = 1.565 \times 10^{40} p^2 d / M$, where S is the heat of sublimation, p the dipole moment, d the density, and M the molecular weight of the respective halides. Values of the dipole moment calculated from the respective heats of sublimation by means of this equation are: HCl, 2.90×10^{-18} ; HBr, 3.35×10^{-18} ; and HI, 3.89×10^{-18} . Frivold and Hassel (this vol., ii, 283) found 1.48×10^{-18} , and Falkenhagen and Weigt 2.15×10^{-18} for the dipole moment of HCl. The calculated values for HCl and HBr are respectively half those calculated from the experimental values of Kratzer for the nuclear distances in the two cases, and constitute an upper limit in each case. It is shown that values of the respective heats of ionisation of HCl and HBr calculated by means of the formula $2.388 \times 10^{-11} N \cdot e^2(1 + 4s/r_0)/r_0$ where N is the appropriate Loschmidt number, r_0 the nuclear distance, s the distance between the centre of gravity of the outer electrons of the halogen and the core, and e has the customary significance agree very closely with the experimental values found by Knipping (A., 1922, ii, 186).

J. S. G. T.

Vapour Pressure of Copper Oxide and of Copper. EDWARD MACK, GERARD G. OSTERHOF, and HOBART M. KRANER (*J. Amer. Chem. Soc.*, 1923, 45, 617—623).—The vapour pressure of copper and copper oxide has been determined by the dynamic method. A stream of nitrogen was led over the heated copper and passed into water which removed the whole of the copper vapour; in the case of the oxide oxygen was used instead of nitrogen. The amount of copper in the water was estimated by measuring the acceleration in the rate of oxidation of sodium sulphite by dissolved oxygen brought about by the copper in the water (Titof,

A., 1904, ii, 113). The following values of the vapour pressure are recorded: copper oxide, 600° , 10^{-7} mm.; 800° , 10^{-4} mm.; 900° , 7×10^{-4} mm., and 1000° , 10^{-4} mm.; copper, 810° , 5×10^{-7} mm. The value for copper oxide at 1000° does not represent a true vapour pressure for this substance, for at this temperature the vapour is a mixture of cupric and cuprous oxides. The heat of vaporisation of cupric oxide over the temperature range 600 — 800° has been calculated, and the value 63,000 cal. obtained. The present results have been compared with those of other workers and a satisfactory agreement has been found.

J. F. S.

Vapour Pressures of certain Hydrated Metal Sulphates.

CLIFFORD D. CARPENTER and ERIC R. JETTE (*J. Amer. Chem. Soc.*, 1923, 45, 578—590).—The vapour pressure of the tri- and penta-hydrates of copper sulphate, the heptahydrate of magnesium sulphate, the eight-thirds hydrate of cadmium sulphate, the heptahydrate of cobalt sulphate, and the monohydrate of manganese sulphate has been determined at a series of temperatures by the static method. A Bremer-Frowein tensimeter of modified structure has been used in the work, which is described together with manipulative details necessary to eliminate the usual errors. In all determinations, the value was reached from both sides. The vapour pressures of the saturated solutions of some of the hydrates have also been determined at 20 — 90° . A new transition point has been found for the heptahydrate of cobalt sulphate at 45.1° , and for the eight-thirds hydrate of cadmium sulphate at 41.5° . The transition point for the change from the heptahydrate of magnesium sulphate to the hexahydrate is found to lie at 48.4° ; this point was previously found by van der Heide (A., 1894, ii, 92) to lie between 48.0° and 48.5° . The heat of the reaction $AB \cdot xH_2O + H_2O \rightleftharpoons AB \cdot (1+x)H_2O + Qp$ has been calculated in each case, where Qp is given by the relation $Qp = RT^2 \cdot d \log p / dT$, so that Qp is therefore the heat of reaction per mol. of water at constant pressure. The average values of Q are $CuSO_4 \cdot 3H_2O$, 13256; $CuSO_4 \cdot 5H_2O$, 13268; $CdSO_4 \cdot 8/3H_2O$, 11170; $MgSO_4 \cdot 7H_2O$, 14035; $MgSO_4 \cdot 6H_2O$ (saturated solution), 9741; $CoSO_4 \cdot 7H_2O$, 12795; and $CoSO_4 \cdot 6H_2O$ (saturated solution), 9760. The value of Q usually changes most abruptly at the transition point, and it is nearly constant as long as the same phases are present. On account of this fact, most transition points are readily found by the intersection of the lines drawn through the points determined by the $\log p$ and $1/T$ relationship.

J. F. S.

The Vapour Pressures of Saturated Solutions of Alums.

STANISLAV MACISCHEVSKI (*J. Russ. Phys. Chem. Soc.*, 1916, 48, 1916—1923).—The vapour-pressure curves for potassium and ammonium alums are plotted, in order to see whether the empirical formula of Speranski (A., 1913, ii, 923) connecting vapour pressure, temperature, and concentration of solutions is applicable to double salts. These curves consist each of two curves, intersecting, in the case of potassium alum at 79.5° and in the case of ammonium alum, at 82.7 , indicating that at these points chemical change of

the alums occurs. Bertrand's formula connecting vapour pressure and temperature is not applicable to the curves for these two alums as a whole, but only to each portion separately. Speranski's formula is not applicable to the potassium alum curve, and is only applicable to the ammonium alum curve below 82.7° . R. T.

The Form of the Vapour-pressure Curve at High Temperatures. II. The Curve for Sodium Cyanide. CHRISTOPHER KELK INGOLD (T., 1923, 123, 885—891).

Relationship between the Properties of Liquid Substances. W. HERZ (*Z. Elektrochem.*, 1923, 29, 110—111).—An equation has been deduced from the revised Trouton rule and the Clausius-Clapeyron vapour-pressure formula which gives a connexion between the boiling point of a liquid and its vapour pressure at a given temperature. This equation has the form $\log p_1 = \log 760 - (9.5 \log T_s - 0.007T_s)(T_s - T_1)/4.57T_1$, where p_1 is the vapour pressure at the temperature T_1 and T_s the boiling point of the liquid. The agreement between the calculated and experimentally determined vapour pressure, whilst moderately good, is not sufficiently near to make the formula trustworthy for the calculation of vapour pressures. With liquids of medium boiling point which are not associated, the surface tension at the boiling point can be calculated from the density at the boiling point and the molecular weight by the formula $\gamma = T_s S^{2/3} (9.5 \log T_s - 0.007T_s) / 20M^{2/3}$, where M is the molecular weight, and S the density at the boiling point. The calculated results are sufficiently near the experimental values except in the case of carbon disulphide, where the two values differ by about 30%. The gas constant can also be calculated approximately from the boiling point by the formula $R = 3875(9.5 \log T_s - 0.007T_s)$. The calculated results are from 15—20% higher than the true value. J. F. S.

The Determination of Boiling Points by Distillation from Test-tubes. A. K. BOLDYREV (*J. Russ. Phys. Chem. Soc.*, 1916, 48, 1862—1870).—A slight modification of the method described by Pawlewski (A., 1881, 642) for the determination of the boiling point of small quantities of substances. A small test-tube, provided with a side-tube, and a cork through which a thermometer passes, is wrapped round with asbestos, and fits into an aperture cut in a sheet of the same material. The lower end of the tube which protrudes through the asbestos sheet is heated with a naked flame until the contents boil. The thermometer reading at first rises, then remains constant for some time, this temperature being taken as the boiling point, and then again rises, owing to superheating. The best results are obtained by keeping the bulb of the thermometer at least 4 cm. above the level of the liquid, so as to avoid the spattering of the superheated liquid. By this method triphenylamine gave b. p. 364.8° (corr.). Its solubility in 100 g. of ethyl and of methyl alcohol is measured, and is in the former solvent 0.74 g. at $19-20.5^{\circ}$, and 5.5 g. at 74° , and for the latter 0.73 g. at $19-20.5^{\circ}$, and 3.3 g. at 65° . R. T.

Distillation of Small Quantities of Liquids. FRANZ LANYAR and LUDWIG ZECHNER (*Monatsh.*, 1923, **43**, 405—412).—Fractional distillation of small quantities (1 to 3 drops) of liquid mixtures is readily effected, using a glass tube 50—60 mm. long and 5—8 mm. wide, sealed at one end, and constricted once or twice near the open end. The liquid (absorbed by a little asbestos wool at the closed end) may be separated, by careful heating with a micro-burner, into as many as ten fractions, which are drawn successively into capillary tubes suitable for b. p. determinations. Eleven separations effected in this manner show that the method is capable of general application.
E. E. T.

A Laboratory Fractionating Column. H. T. CLARKE and E. J. RAHRS (*Ind. Eng. Chem.*, 1923, **15**, 349).—The column consists of a Pyrex tube 90 cm. long and 20 mm. in diameter, having a series of semi-bulbs sucked in, beginning 15 cm. from the top and arranged at an angle of 90° on the periphery of the tube. Opposite each bulb a point is poked in to within 1 mm. of the upper part of the inner convex surface of the bulb. At 8 cm. from the upper end of the column a side arm is fused in, similar to that of a Claisen flask, and the delivery tube situated at the mid-point of its vertical portion is bent so as to ascend for a short distance before descending to the condenser. At the top of the column is fixed a Pyrex tube 16 cm. long and 15 mm. diameter through which cold water can be circulated, and the entire length of the column below the side arm to within 8 cm. of the lower end is jacketed with a glass tube, tubulated at each end, and secured by rubber stoppers. The position of the water-cooled tube is adjusted to suit the boiling point of the liquid which is being distilled so that 10 to 15 times as much condensate is returned to the flask as collects in the receiver. For very low boiling liquids, the jacket may be filled with water, or cold air drawn through at a regulated rate. For high boiling liquids, the tubulations are closed so that the jacket acts as a heat insulator.
G. F. M.

Calorimetric Researches. IV. Determination of the Heat of Combustion of Sucrose ; Suitability of this Substance as a Thermochemical Standard. P. E. VERKADE and J. COORS, jun. (*Rec. trav. chim.*, 1923, **42**, 205—228; cf. P. E. Verkade, A., 1922, ii, 740).—The authors consider that a second standard substance is necessary for thermochemical work and give reasons for testing sucrose as a possible substitute for naphthalene. As a result of a series of experiments, the ratio of the heat of combustion of benzoic acid to that of sucrose was found to be 1.6025 (air), the corresponding figure for naphthalene and sucrose being 2.4362 (air). In a review of the various objections which have been raised to the use of sucrose, the reasons in favour of using that substance are adduced but the tendency to incomplete combustion and the difficulty of ignition cannot be obviated. The conclusion is drawn that none of the substances hitherto investigated is quite satisfactory as a secondary standard. The values obtained for sucrose, on the assumption that the heat of combustion of

benzoic acid is 6324 cal._{15°} per g. (air), are 3946 (air) and 3944 (vacuum).
H. J. E.

The Variation of Heats of Solution with the Temperature.

PAUL MONDAIN-MONVAL (*Compt. rend.*, 1923, **176**, 889—892).—In order to demonstrate the influence of temperature on the heat effects of solution, dilution, etc., the following measurements were made at 0° and at the ordinary temperature of the heats of solution, etc., of sodium, potassium, and ammonium nitrates, potassium and ammonium chlorides, and potassium sulphate: molecular heat of solution in a large quantity of water, Q ; heat absorbed by dilution of the saturated solution to the above dilution, D ; heat of addition of 1 mol. H_2O to a large quantity of saturated solution, E' ; and heat of addition of a quantity of water sufficient to dissolve at saturation 1 mol. of the salt, E . L_1 representing the heat limit of solution in saturated solution, was calculated from the relation $L_1 = Q - D - E$, and as a check on the result the same quantity was obtained by a slight extrapolation of the experimental results obtained by the direct solution of the salt in solutions of increasing concentration. The complete results are given in tabular form, and they show in all cases a distinct difference in the values obtained at 0° and at the ordinary temperature (18—19°).
G. F. M.

Dilatometric Researches on Potassium Aluminium Sulphate. (MLLE) E. N. IVANOVA (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1905—1916).—It was noticed by Wiedeman (A., 1883, 780) that potassium alum contracts when heated above 51.3° in a dilatometer, and he explains this as being due to dissociation of the constituent molecules of the alum. This experiment was repeated, but no contraction was observed up to 87.3°, using either mercury or paraffin as the dilatometer liquid. The contraction observed by Wiedeman was probably due to the slow filling up of the interstices of the powdered alum by mercury. The use of paraffin above 75° is not recommended, as expansion of air adsorbed on the solid causes an abnormal expansion in the dilatometer. This adsorbed air is very difficult to eliminate.
R. T.

Force of Adhesion in Solutions. IV. Influence of Temperature on the Partition of Substances between two Phases. SERG. WOSNESSENSKI (*Z. physikal. Chem.*, 1923, **104**, 46—50).—A theoretical paper, in which, on the basis of Schilov and Lepin's work on the adsorption of substances by charcoal (A., 1920, ii, 591; 1922, ii, 626) and Iljin's theoretically deduced formula for the influence of temperature on the adsorption equilibrium (*Nachr. Moskauer physik-wiss. Inst.*, **1**, 219), the author has examined his previously published adsorption results and those of other authors. The calculated results show that the experimental values for the partition of succinic acid between ether and water, benzoic acid between benzene and water, ferric thiocyanate between water and ether, the adsorption of physiological salt solution by animal membrane and the adsorption of water by beans, are all in agree-

ment with the values calculated by Iljin's formula, $C_{\infty} = C_0 e^{\delta \sqrt{T}}$, thus showing that the essential process is the same in all cases.

J. F. S.

Adsorption of Gases by Solids and the Thickness of the Adsorbed Layer. M. H. EVANS and H. J. GEORGE (*Proc. Roy. Soc.*, 1923, [A], **103**, 190—193).—By direct determination, the authors find the thickness of the adsorbed layer of carbon dioxide on glass fibres having an average area of 9.093×10^2 sq. cm. per g. to be equivalent to that of 5.5 molecular layers, assuming the adsorbed gas to exist as a film having the density of liquid carbon dioxide. The equilibrium pressure was found to be 121.46 mm., and using Mülfarth's data (*Ann. Physik*, 1900, [iv], **3**, 328) for relative adsorption at 0° and at this pressure, the following results were calculated for the respective thicknesses of the adsorbed layer for the following gases: sulphur dioxide, 32.1; ammonia, 39.9; nitrous oxide, 4.5; acetylene, 3.5 molecular layers. These values are considerably greater than the values, not greater than the diameter of a single molecule, required by Langmuir's theory (A., 1918, ii, 430), and deduced from experiments with gases at low pressures.

J. S. G. T.

A Case of Simultaneous Positive and Negative Adsorption. M. A. RAKUZIN and (MLLE) G. F. PEKARSKAJA (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1889—1890).—The adsorption of Bismarck-brown by gelatin and by leather powder is found to consist of both positive and negative adsorption. The increase in the concentration of the solution, owing to adsorption of water, shows the latter, whilst the former is shown by the decolorisation of the solution. An increase in the optical rotation of the solution from 0° to +0.55° in the case of gelatin shows that some of the latter passes into solution.

R. T.

Sorption Equilibria. H. VON EULER and BIRGER BUCHT (*Z. anorg. Chem.*, 1923, **126**, 269—277).—The solubility of casein in aqueous and alcoholic solutions of monochloroacetic acid, and in alcoholic and benzene solutions of α -bromopropionic acid is measured. The corresponding sorptions of acid by the undissolved casein are also measured, and it is shown that the amount of acid sorbed per gram of casein is a linear function of the concentration of acid in the solution.

An attempt was made to obtain an asymmetric sorption of α -bromopropionic acid from benzene solution, but although in the most favourable experiment 0.64 g. of casein sorbed 0.555 g. of the acid from a solution containing 1.418 g., no optical activity was detected in the residual solution, and the authors draw the conclusion that any asymmetric sorption cannot exceed 10% of the whole.

H. H.

Dissociation of Molecular Hydrogen, [Deduced] from the Entropies of Diatomic and Monatomic Hydrogen. GRAHAM EDGAR (*J. Amer. Chem. Soc.*, 1923, **45**, 673—676).—A theoretical paper in which the free energy of dissociation, the dissociation constant, and

the degree of dissociation of molecular hydrogen have been calculated from the entropies of the substances and published data for the heat of dissociation. Tables are given of the values of the entropy, heats of reaction, and the equilibrium constants for 298.1° 1500°, 2000°, 2500°, and 3000° Abs., and a further table showing the fraction of hydrogen dissociated at the four higher temperatures at pressures 1, 0.1, and 0.001 atm. The results indicate, in keeping with the conclusions of Duffenback (A., 1922, ii, 620) and Saha (A., 1920, ii, 659), that hydrogen is much more dissociated at high temperatures than earlier calculations indicated. The following values of the fraction dissociated at 1 atm. pressure and various temperatures are recorded: 1500°, 0.000316; 2000°, 0.0063; 2500°, 0.0595, and 3000°, 0.26. J. F. S.

Velocity of Sound in Nitrogen Peroxide. HERMANN SELLE (*Z. physikal. Chem.*, 1923, 104, 1—9).—The velocity of sound in nitrogen peroxide has been determined at various pressures and temperatures by both the Kundt and Clément and Desormes methods. It is shown that there is a dispersion of sound in the region of vibration numbers 3670 to 1690. With decreasing vibration number this value sinks to about 3 m./sec. Sound dispersion is shown at the various temperatures and pressures investigated. Using the Clément and Desormes method, the values of $k=C_p/C_v$ and $\sqrt{\Delta p/\Delta \rho}$ were determined. This furnishes the velocity of sound for very slow vibrations. Taking account of this value, the sound dispersion at 21° and 500 mm. pressure is 4 m./sec. or 2.2% of the velocity. From the relationship between the velocity of sound and the course of the reaction $2\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$, the proportionality factors k_1 and k_2 were determined. Between 18° and 26°, the value of k_1 increases with the temperature from 376 to 617; in the case of k_2 , 4.8×10^6 is found as a mean value, and no dependence of this value on temperature was observed. A dependence on pressure was not found for either k_1 or k_2 . According to these determinations, 1 g.-mol. of N_2O_4 at 21° and 500 mm. pressure dissociates to the extent of 4.4% in 10^{-4} secs., and 1 g.-mol. of pure NO_2 associates to the extent of 4.6% to N_2O_4 in 10^{-8} secs. J. F. S.

Theory of the Capillary Layer of a Liquid in Contact with its Saturated Vapour. G. BAKKER (*Z. physikal. Chem.*, 1923, 104, 10—45).—A general discussion of the theory of the capillary layer as previously published (A., 1903, ii, 62; 1904, ii, 310, 540, 655, 806; 1905, ii, 304; 1910, ii, 106, 831; 1912, ii, 743; 1916, ii, 553). J. F. S.

Separation of Gas Mixtures by Diffusion in a Flowing Gas. G. HERTZ (*Proc. K. Akad. Wetensch. Amsterdam*, 1923, 25, 434—441).—When a gaseous mixture diffuses into a medium at rest the ratio of the partial pressures of the components of the mixture is constant, but if the mixture of gases diffuses into a medium in motion, the ratio of the partial pressures of the constituents is variable and this fact offers possibilities for the separation of the

constituents of gaseous mixtures. Equations are deduced showing the amount of separation which may be brought about by diffusion into a moving medium. The method has been applied to the case of mixtures of neon and helium. A jet of steam was allowed to enter a vessel containing the gas mixture through a number of narrow holes, a portion of the gas diffused through the holes against the steam jet and was pumped off, the steam was condensed after it entered the vessel, and so two fractions of gas were obtained. Using a 30% helium 70% neon mixture, pure helium was obtained by a single treatment. The separation was in accordance with the theory, but the amount of gas thus separated was small. Methods of increasing the amount separated are discussed, and the principle is also discussed generally in connexion with the separation of isotopes. It is shown that in the case of neon a separation of the isotopes to the extent of 30% may be expected from a single treatment.

J. F. S.

Anomalous Osmosis of Solutions of Electrolytes with Collodion Membranes. II. Effect of the Diameter of the Pores.

F. E. BARTELL and D. C. CARPENTER (*J. Physical Chem.*, 1923, 27, 252—269; cf. this vol., ii, 221).—The influence of the size of the pores of collodion membranes on the rate of osmosis has been investigated. It is shown that the rate at which solutions of potassium ferri-cyanide and aluminium chloride pass through a collodion membrane increases at all concentrations as the diameter of the pores increases. On the other hand, the relative diffusion values of potassium sulphate and calcium chloride decreases materially with increasing diameter of the pores. The rate of diffusion of solutions of potassium chloride remains approximately constant with the various membranes. In dilute solutions, potassium sulphate, calcium chloride, and aluminium chloride appear to pass through the membrane at a greater rate than the other salts. Comparisons of the rate of passage of potassium salts through the least porous membranes, that is, membranes with pores of diameter about 0.7 micron, in the case of dilute solutions gave the following anion order: $\text{SO}_4'' > \text{Cl}' > \text{Fe}(\text{CN})_6'''$. For concentrated solutions, the order for a similar membrane was $\text{Cl}' > \text{SO}_4'' > \text{Fe}(\text{CN})_6'''$. The latter order is the inverse of the order of magnitude of maximum osmosis. Comparisons of the rates of passage of chlorides into water showed the cation order in dilute solution to be $\text{Al}''' > \text{Ca}'' > \text{K}'$. Exactly the opposite order was found for concentrated solutions. The order of magnitude of osmosis with dilute solutions bears no apparent relation to the cation diffusion order; however, the order of magnitude of osmosis with concentrated solutions was the inverse of the cation diffusion order. With membranes of pore diameter about 0.93 micron, the anion order for the rate of diffusion of potassium salts from dilute solutions was $\text{SO}_4'' > \text{Cl}' > \text{Fe}(\text{CN})_6'''$, and with concentrated solutions $\text{Cl}' > \text{SO}_4'' > \text{Fe}(\text{CN})_6'''$. This was again the inverse of the maximum osmosis for concentrated solutions. The cation order for the rate of diffusion is $\text{Ca}'' > \text{K}' > \text{Al}'''$ in dilute solutions and $\text{Ca}'' > \text{Al}''' > \text{K}'$

in concentrated solutions. For very permeable membranes of pore diameter 1.6 microns, comparison of the amounts of potassium salts diffusing during the period of maximum osmosis gave the order for anions $\text{Cl}' > \text{SO}_4'' > \text{Fe}(\text{CN})_6'''$ for both dilute and concentrated solutions. This order is the inverse of that of maximum osmosis. For chlorides, the kation order is $\text{K}' > \text{Ca}'' > \text{Al}'''$ in all solutions. This order is the same as that of maximum osmosis in very dilute solutions, but the reverse of that in concentrated solutions. The work shows generally that the diameter of the pores is a highly important factor in determining the exact nature of osmosis, and it appears probable that the phenomena of anomalous osmosis and the attending salt diffusion is governed largely by the precise diameter of the pores of the osmotic membrane.

J. F. S.

Electroendosmosis through Carbon Filters. KOJIRO UMETSU (*Biochem. Z.*, 1923, **135**, 442—479).—With a specially designed apparatus, the author has examined the electroendosmotic behaviour of solutions through a carbon filter. Blood charcoal has an isoelectric point at p_H 3 and in general in acid solution is positively charged through adsorption of hydrogen-ions, but is negatively charged in alkaline solution through adsorption of hydroxyl-ions. Sulphosalicylic acid is a strong dibasic acid, but it is unexpectedly found that the anion is more strongly adsorbed than the hydrogen-ion by blood charcoal. A substance like charcoal which functions as an ampholyte but is not molecularly dispersed is termed an "ampholytoid." Unlike blood charcoal, sugar or benzoic acid charcoals are positively charged over the whole range examined and adsorb basic dyes well, blood charcoal adsorbing acid and basic dyes. This only applies to adsorption of ions, indifferent surface-active substances like octyl alcohol being adsorbed equally by all varieties of charcoal examined.

H. K.

Solubility Relations in Mixtures containing Polar Components. F. SPENCER MORTIMER (*J. Amer. Chem. Soc.*, 1923, **45**, 633—641).—In an earlier paper, the author described a graphical method for calculating the ratio of the experimental to the ideal slope of the curves obtained by plotting the logarithm of the molecular fraction of dissolved substance against the reciprocal of the absolute temperature of the solubility point of the mixture and, hence, for calculating the solubility in non-ideal solutions (*A.*, 1922, ii, 621). In the present paper, the author shows to what extent the generalisations previously discussed may be applied to such systems. Tables of solubilities of fluorene, *p*-dibromobenzene, benzoic acid, resorcinol, acetamide, and acetanilide in ethylene dichloride, chlorobenzene, nitrobenzene, *p*-xylene, toluene, benzene, pyridine, carbon tetrachloride, aniline, acetone; acetic acid, ethyl and methyl alcohols, phenol, acetophenone, urethane, and *p*-toluidine at various temperatures are given, many of which represent the results of new determinations. The ideal solubility of the solute has been calculated in every case. It is shown that the deviations from Raoult's ideal solubility law are

proportional to the magnitude of the differences of the internal pressures of the components of the system. The ratio of the experimental slope of the curve of $\log N$ against $1/T$ to the ideal slope, calculated from the latent heat of fusion, for any solute, is a measure of the relative internal pressures of the solute and the solvent. Not only may the latent heat of fusion of solids be determined, but relative values for the internal pressures of many solids and liquids may be calculated from solubility data by the application of the principles developed. The results of the calculations of relative internal pressures have been given and compared with those obtained by direct measurement or by other methods of calculation. A table of the relative internal pressures of sixty-eight substances referred to naphthalene as unity calculated from solubility data is included in the paper. The principles entering into the procedure for calculating solubilities of organic compounds in various solvents have been discussed both for polar and non-polar substances, and the limitations of the method pointed out.

J. F. S.

A Survey of Existing Crystal Structure Data. RALPH G. WYCKOFF (*J. Franklin Inst.*, 1923, 195, 182—210, 349—365, 531—549).—A critical summary of work published on X-ray diffraction effects made for the direct study of atomic arrangements.

Rhythmic Crystallisation. HANS KÄGI (*Helv. Chim. Acta*, 1923, 6, 264—266).—By crystallisation from a mixture of alcohol and glacial acetic acid or from benzene of *r*-menthyl benzylacetate, concentric crystalline rings are obtained, showing extremely well the phenomenon of rhythmic crystallisation. As crystallisation proceeds at the rate of about 1 cm. per minute, the phenomenon can be followed readily under the microscope. A number of photographs are reproduced. The *l*-ester does not crystallise in this manner.

E. H. R.

The Recrystallisation of Metals and Salts. G. TAMMANN and Q. A. MANSURI (*Z. anorg. Chem.*, 1923, 126, 119—128).—In a mass of metal some of the crystals grow at the expense of others, these crystallites being already in contact. In the case of powders the investigation is more difficult. Metallic powders are covered by a thin film of oxide, and when the powder is stirred these films are destroyed. When two particles having the same lattice structure touch they join; if, however, the lattice structure is different, then movement of atoms is necessary before union can take place. A stirrer was slowly rotated in the metallic powder and the temperature gradually increased. In the case of metals, the stirrer suddenly stopped at temperatures between 120° and 140°, this temperature being independent of the melting point of the metal. In the case of salts, the rate of stirring gradually decreased and finally stopped, this temperature being dependent on the melting point of the salt. These temperatures denote the temperature at which there is motion of the atoms in the solids.

W. T.

The Mutual Increase and Decrease in Size of Metallic Crystallites which are in Contact in a Conglomerate. RUDOLF VOGEL (*Z. anorg. Chem.*, 1923, 126, 1—38).—The crystallite conglomerate of a metal is not generally stable, because when the temperature is sufficiently high the frontiers between the crystallites change and a crystal which is itself invaded by one crystal may at the same time grow at the expense of another. This movement does not necessarily mean an increase in the size of the crystallites. Of two crystallites in contact, the one with the more stable structure, *i.e.*, the one containing the denser grouping of atoms on its surface, will grow at the expense of the other. When all the unstable contacts have disappeared, then movement of frontiers ceases. W. T.

Stability of Suspensions of Solid Particles of Proteins and Protective Action of Colloids. JACQUES LOEB (*J. Gen. Physiol.*, 1923, 5, 479—504).—The stability of a suspension of gelatin-coated collodion particles is minimal at the isoelectric point of gelatin, and at this point it is increased by the addition of small quantities of salt. Gelatin itself is least soluble at the isoelectric point, and its solubility is increased by salts. This is not due to the charge conferred on the gelatin particles by the salt, as cataphoretic experiments show that at the isoelectric point gelatin-coated collodion particles are practically as completely uncharged in the presence of salt as they are before salt is added, but it would appear that such effects are due to the increase in the real solubility of isoelectric gelatin on the addition of salts. This is borne out by the fact that approximately identical concentrations of salts are required to precipitate gelatin from solution, and to flocculate such suspensions. If, on the other hand, the collodion particles be coated with genuine egg-albumin, the stability of the suspension depends primarily on the potential difference between the particle and the surrounding liquid, and instability occurs as soon as the potential falls below 10—13 millivolts, a critical potential agreeing with that of particles of denatured egg-albumin. It is concluded that egg-albumin is denatured when it forms a film round a solid particle. Results similar to those obtained with egg-albumin are obtained with casein and with edestin.

These facts are discussed in the light of Langmuir's theory of the affinity of certain groups for water. The high protective power of gelatin depends on the greater affinity for water of the molecule of this substance, in other words, on the high true solubility of gelatin. W. O. K.

Action of Trypsin on Colloids and the Influence of Neutral Salts on this Action. E. STIASNY and W. ACKERMANN (*Koll. Chem. Beihefte*, 1923, 17, 219—255).—The action of trypsin on colloids depends on the previous history of the colloid, and in particular on the extent to which swelling has taken place. This fact probably explains the contradictory results obtained on the action of trypsin on colloids. A number of experiments on the action of neutral salts on the trypsin action have been carried out, chiefly with powdered hide. This substance has been used because

comparable results are more easily obtained than with pieces of hide and the experimental conditions can be kept nearer those obtaining in the tanning process. In all experiments, the hydrogen-ion concentration has been measured and taken into account in the subsequent discussion. In comparative swelling experiments, the swelling height of the hide powder has been measured in long tubes. Potassium thiocyanate, iodide, nitrate, and chloride show a moderate swelling action when present in $N/100$ - or $N/10$ -solutions, a sharp maximum in N -solutions, and a definite retarding effect in concentrated ($3N$ — $5N$) solutions. In the case of potassium sulphate the maximum swelling is with $N/10$ solution. At 37° , the swelling is always greater than at 20° . When arranged according to the height of the swollen material, the anions of the salts investigated fall into the Hofmeister series. That this regularity should occur at the same P_H value in the solutions investigated, is evidence against the views of Loeb, which questions the correctness of the Hofmeister series. The swelling in the present case is accompanied by a partial peptisation, which is greatest with most strongly swelling solutions of salts. When this peptisation is taken into account, the difference in the swelling action of the various salts is more strongly marked. Trypsin in the presence of neutral salts has been allowed to act on hide powder at 37° and 20° , and the proteolytic and peptolytic action measured after two hours, twenty-four hours, and six days. This has been carried out by observing the swelling height and the formol titration value, and by examining the filtrate from the hide powder for its content of tanning material and total nitrogen. Numerous experiments with potassium thiocyanate of various concentrations show that $N/100$ - and $N/10$ -solutions of this substance have no action on either the proteolytic or peptolytic action of trypsin, N -solutions increase the proteolytic action of pancreas tryptase strongly, but retard the action of pancreas peptase, and $5N$ -solutions completely stop both actions of trypsin. This shows that potassium thiocyanate influences the proteolytic trypsin action in exactly the same way as the swelling action. Increase of the trypsin concentration and the temperature accelerate the trypsin action without changing the regularity between the swelling and proteolytic trypsin action. Similar experiments have been carried out with potassium iodide, chlorate, nitrate, chloride, and sulphate, and the influence of various salt concentrations on the trypsin action investigated. The results show that the action of the salt on the substrate and that on the ferment must be differentiated. With strongly swelling salts and for the concentrations which most strongly promote the swelling, the action on the substrate is most noticeable and the swelling action and proteolytic action of the trypsin run parallel. In many cases, such as those of potassium nitrate and potassium chloride, the action of the salt in high concentrations appears to be overwhelmingly on the ferment; $4N$ -solutions of these salts retard the swelling, but have no retarding action on the proteolytic trypsin action which up to concentration of N has not shown a maximum. In the peptolytic trypsin action, the influence of the neutral salts is restricted to the ferment. The

independence of the peptolytic and the proteolytic actions is particularly marked with *N*-potassium thiocyanate and *N*-potassium iodide, which promote strongly the proteolytic trypsin action but retard the peptolytic action. Hide powder is much more sensitive to trypsin than pieces of hide, probably because in the powder the outer layer is so changed in the preparation that it is more easily peptised.

J. F. S.

Statistical Theory of Unimolecular Reactions. W. H. RODEBUSH (*J. Amer. Chem. Soc.*, 1923, **45**, 606—613).—A theoretical paper in which a statistical theory of unimolecular reactions has been developed. An equation has been derived from the kinetic theory for the rate of reaction of a unimolecular reaction. This equation has the form $\bar{N} = N\sqrt{RT/E_0\pi} \cdot e^{-E_0/RT}$, where \bar{N} is the number of molecules which possess vibrational energy in excess of the critical amount, and the other terms have their usual significance. In the two cases where data are available, namely, the vaporisation of mercury (Menzies, A., 1920, ii, 11) and Daniels and Johnston's experimental results on the decomposition of nitrogen pentoxide (A., 1921, ii, 249), the equation gives results which are probably as accurate as the data themselves.

J. F. S.

Decomposition of Nitrogen Pentoxide. M. BODENSTEIN (*Z. physikal. Chem.*, 1923, **104**, 51—54).—A discussion of a paper by Daniels and Johnston (A., 1921, ii, 249) on the decomposition of nitrogen pentoxide. The author points out that two values in the published results give constants not in keeping with the other measurements. These are shown to be due to the particular temperature at which the experiments were carried out. It follows therefore that the thermal decomposition of nitrogen pentoxide is a purely unimolecular reaction, $N_2O_5 \rightarrow N_2O_3 + O_2$, and constitutes the first case of the exact examination of a unimolecular gas reaction. The constants obtained by Daniels and Johnston are therefore to be multiplied by 5/6.

J. F. S.

Kinetic Interpretation of the Law of Van't Hoff. C. E. GUYE (*Compt. rend.*, 1923, **176**, 835—836).—It has already been shown that on the supposition that a dissociating action is a function of the impulse of the forces developed during collisions, the number of parietal collisions causing dissociation per unit of surface in unit time is given by the relation $\nu_0 = [n/2\sqrt{hm\pi}]e^{-hmv_*^2}$, and the number of collisions between molecules by the expression $\nu_0' = [n^2\sigma^2\sqrt{2\pi/hm}]e^{-2hmv_*^2}$ (*Arch. Sci. phys. nat.*, 1922, 132—153), the factors between brackets representing, respectively, the total number of collisions, and the exponentials the fractions of these numbers which are followed by dissociation. It is shown that this hypothesis accounts quantitatively for the approximate rule of van't Hoff, according to which at the ordinary temperature an elevation of temperature of 10° doubles the velocity of a reaction, and a numerical verification is given for the case of hydrogen, which can be extended to any gas, for in order to obtain the velocities of dissociation comprised between the same experimental limits,

it is only necessary to choose v_0 inversely proportional to the square root of the molecular weight, and the exponential, on which the velocity of dissociation mainly depends, retains then the same value.

G. F. M.

Halogenate Reductions. The Reduction of Iodate and Chlorate by Arsenious Acid. HANS KUBINA (*Monatsh.*, 1923, 43, 439—468).—The reduction of chlorate and iodate by arsenious acid has been investigated, and these two processes have been shown to be examples of coupled reactions. The reaction velocity is independent of the concentration of arsenious acid. The actual reaction measured is the slow reduction of halogenate by halide, this reaction being followed by the rapid oxidation of arsenite: $\text{XO}_3' + \text{X}' \rightarrow \text{A}$ (measurable); $\text{A} + \text{As}^{\text{III}} \rightarrow \text{X}' + \text{As}^{\text{V}}$ (rapid), where A is an intermediate compound.

The oxidation of arsenite by iodic acid proceeds with rapid initial acceleration, owing to the catalytic effect of the iodidion produced.

The reaction mechanism of chlorate reduction is probably: (a) Measurable reaction: $\text{ClO}_3' + \text{Cl}' + 2\text{H}' \rightarrow \text{H}_2\text{ClO}_3 + \text{Cl}$, followed by the rapid reactions, (b) $\text{H}_2\text{ClO}_3 + 4\text{Cl}' + 4\text{H}' \rightarrow 5\text{Cl} + 3\text{H}_2\text{O}$, and $3\text{Cl}_2 + 3\text{AsO}_3''' + 3\text{H}_2\text{O} \rightarrow 3\text{AsO}_4''' + 6\text{Cl}' + 6\text{H}'$. The initial velocity of interaction of chloric acid and arsenite does not increase rapidly; catalytic acceleration by chloridion is not observed, owing to the high initial concentration of this ion. Were the latter present, initially, in small quantities, such catalytic accelerative influence should be in evidence. On this supposition, the velocity of chlorate reduction by arsenite would be expressed by the equation: $dx/dt = [K_1 + K_2(\text{S})^2(\text{Cl}')] / (\text{ClO}_3')$.

In iodate reduction the mechanism is probably: (a) Measurable reaction: $\text{IO}_3' + 2\text{I}' + \text{H}' \rightarrow \text{HIO} + 2\text{IO}'$, followed by the rapid reactions (b) $2\text{IO} + 2\text{AsO}_3''' \rightarrow 2\text{AsO}_4''' + 2\text{I}'$, and $\text{HIO} + \text{AsO}_3''' \rightarrow \text{AsO}_4''' + \text{H}' + \text{I}'$, giving the velocity equation: $dx/dt = [K_1 + K_2(\text{I}')_2] / (\text{IO}_3')(\text{H}')$.

Schilov's work (A., 1903, ii, 276) on bromate reduction is also discussed. See also Bray (A., 1906, ii, 223) and Luther and McDougall (A., 1908, ii, 361).

E. E. T.

Rate of Reaction between Ethylene and Bromine. T. D. STEWART and K. R. EDLUND (*J. Amer. Chem. Soc.*, 1923, 45, 1014—1024).—If the apparently bimolecular additive reaction between ethylene and bromine is preceded by a dissociation or opening of the double bond of the ethylene with formation of tautomerides (Nef., A., 1905, i, 109), a purely bimolecular reaction may still be anticipated if the rate of tautomerism is rapid compared with the addition of bromine; this is true whether only one or all of the tautomerides can react. Positive conclusions respecting tautomerism can, therefore, be drawn only if a deviation from the bimolecular reaction is observed.

Such a deviation is found only to occur during the first twelve seconds after mixing the reagents, and is ascribed to surface catalysis;

the subsequent reaction is strictly bimolecular. The assumption of tautomeric forms of ethylene is therefore unnecessary.

Two air streams, containing known amounts of ethylene and of bromine, respectively, are completely mixed at 0° , in less than one second, in the apparatus described. The mixed gases are passed into a bulb to which a manometer is attached. A side tube allows the gas to be sampled immediately before it enters the reaction bulb. After sampling, the bulb is closed and the reaction followed by observing the decrease in pressure. The measured sample is analysed for bromine by absorbing the latter by means of potassium iodide solution and titrating the liberated iodine; the gas issuing from the sampler is collected and estimated for ethylene. The volume of the reaction bulb is varied in different experiments.

The reaction takes place for the most part, if not entirely, on the walls of the containing vessel; no gaseous reaction is detected. The reaction is promoted by the presence of moisture. With a constant surface, the rate of the reaction is proportional to both the concentration of ethylene and the concentration of bromine.

W. S. N.

Velocity of Hydrolysis of Acetic Anhydride. ANTON SKRABAL (*Monatsh.*, 1923, 43, 493—506).—The hydrion produced in the reaction: $\text{Ac}_2\text{O} + \text{H}_2\text{O} = 2\text{AcOH}$ is measured by its effect on the velocity of the interaction of iodide and iodate (cf. A., 1918, ii, 12, and Dushman, A., 1904, ii, 718). As solvent, aqueous acetone (containing 2.5 vols.% of the latter) is used. In order to obtain the end-point for total hydrolysis, it is necessary to use an excess of iodide-iodate mixture. With one minute as time unit and at 25° , the reaction velocity of hydrolysis of acetic anhydride is k_w 0.19. The same value was obtained in three different experiments in which the hydrion concentration varied considerably, and therefore is an accurate measure of the hydrolysis by water (i.e., k_s is negligible). The constant for the alkaline hydrolysis occurring in the same experiments was calculated and found to be $k_a \leq 4.4 \times 10^6$, a figure not appreciably larger than that for esters which are readily hydrolysed by alkalis.

In presence of larger quantities of acetone, k_w is decreased, this effect being due to the medium effect in addition to the mere dilution effect.

It is shown, by considering the hydrolysis of various substances containing the group $-\text{CO}\cdot\text{OR}$ (where R is alkyl or acyl), that, in addition to catalytic hydrolysis by hydrion or hydroxyl-ion, a considerable amount of hydrolysis by water (undissociated) occurs, if hydrolysis is not appreciably reversible.

E. E. T.

Hydrolysis of the Lactide from Lactic Acid. OTTO RINGER and ANTON SKRABAL (*Monatsh.*, 1923, 43, 507—523).—A continuation of work by Johansson and others (A., 1918, ii, 223; 1922, i, 425).—The velocity of the two-stage hydrolysis of lactide has been measured in aqueous acetone solution (2.5 vol.% of acetone) at 25° . For the first stage (lactide to lactyl-lactic acid), alkaline, acid, and water hydrolyses give k_{1a} 1.2×10^6 , k_{1s} 0.1088 and k_{1w} 0.00459. For

the second stage (lactyl-lactic acid to lactic acid), the values k_{2a} 19.5 and k_{2s} 0.00203 were obtained. The alkaline hydrolysis in the first stage proceeds with a rapidity similar to that observed in the first stage of the hydrolysis of dimethyl oxalate (A., 1918, ii, 12). In fact, lactide and the normal oxalic esters may be titrated as if they are free monobasic acids.

Acetone and alcohol decrease the velocity of the above hydrolysis.

The dissociation constant of lactyl-lactic acid (determined by means of indicators) is 9.9×10^{-4} at the ordinary temperature.

E. E. T.

Inversion of Lactose by Strong Acids. I. B. BLEYER and H. SCHMIDT (*Biochem. Z.*, 1923, 135, 546—557).—The velocity of inversion of lactose has been determined with hydrochloric acid (d 1.185), with perchloric acid (d 1.67), and with sulphuric acid (22 and 24*N*). The reaction is unimolecular, and from measurements at different temperatures the speed is shown to be quadrupled for a rise of 10° . The authors propose the formula $K = a \cdot t^{b \cdot t}$ for the relation between the temperature and the velocity constant. The velocity falls off with increasing content of lactose. H. K.

Inhibition Phenomena in Chemical Reactions (especially in the Solution of Metals in Acids). A. SIEVERTS and P. LUEG (*Z. anorg. Chem.*, 1923, 126, 193—225).—An investigation of the effect of various poisons on the rate of solution of metals in acids, particularly of iron in hydrochloric and sulphuric acids and aluminium and zinc in hydrochloric acid. It was found that ferrous sulphate, methyl sulphate, ammonium chloride, tetramethyl-ammonium chloride, choline hydrochloride, and taurine have no inhibiting effect. Potassium cyanide, caffeine, theobromine, coniine, pyrimidone, pyridine, atropine, quinoline, isoquinoline, and codeine had a slight inhibiting effect. Nicotine, veratrine, cocaine, and cinchonine were more effective, whilst α - and β -naphthaquinolines, strychnine, brucine, narcotine, and quinine were very effective. The most effective inhibitor was an "extract" consisting of the ether-soluble basic constituents of crude anthracene. It was found that the amount of inhibition was much the same in both acids, but with theobromine, nicotine, cinchonine, narcotine, and quinine, the inhibiting effect was more marked in hydrochloric acid. The authors conclude that all compounds containing pyridine nitrogen are more or less effective inhibitors. Analogous results were obtained with aluminium and zinc.

It is found that the velocity of solution of iron in hydrochloric acid at 78° is approximately proportional to the cube of the concentration of the acid. The temperature coefficient of the solution velocity is 2.0—2.3 per 10° between 50° and 78° . For slight amounts of poisoning, increase of temperature reduces the inhibition: for larger amounts, it has no effect. In the case of aluminium, the solution velocity also has a large temperature coefficient (1.4 from 20 —~~30~~³⁰), but it is reduced to zero in the presence of large amounts of poison. The poisoning and de-poisoning of metals occurs very quickly.

An empirical formula is proposed: $(K_0 - K_c)/K_c = ac^b$; where K_0 is the rate of solution with no poisoning, K_c is the rate of solution at poison concentration c , and a and b are constants depending on the nature of the poison. It is found to break down for inhibitions greater than 75–85%.

The influence of poisons on the overvoltage of metals was also investigated. α -Naphthaquinoline has little effect. "Extract" increases the overvoltage of nickel, iron, and copper, and, to a less extent, of mercury, silver, and lead: it has no effect on platinised platinum. No obvious connexion between the inhibition of solution in acid and the increase in overvoltage could be found, but it is considered that adsorption of the poison occurs on the metal surface, thus reducing the amount accessible to the acid. H. H.

The Solution Velocity of Copper in Dilute Benzaldehyde and its Dependence on the Viscosity. FRITZ SCHAAF (*Z. anorg. Chem.*, 1923, **126**, 237–253).—The experimental results of Bernoulli and Schaaf (A., 1922, i, 1029) are used, and an explanation of the form of the solution velocity-concentration curves is put forward. The solution velocity is a resultant of two effects, the concentration of benzaldehyde (that is, its active mass) and the fluidity of the solution, an increase in either factor increasing the velocity. An increase in the former factor, however, results in a decrease in the latter, so that the velocity-concentration curves rise to a maximum and subsequently fall to zero velocity at 100% concentration of benzaldehyde. At 50°, the maxima for benzene and toluene solutions occur at concentrations of 14 and 16%, respectively, of benzaldehyde, the solution having a fluidity of 127 c.g.s. units in each case. No reaction takes place between copper and benzaldehyde in any solution with a fluidity of less than 60.

It is found that the rate of solution is practically unaffected by stirring, and that in the tranquil state the rate of solution in the heterogeneous system depends on the temperature in the same way as does the velocity of a reaction in a homogeneous system. The temperature coefficient, however, is smaller in the former case.

H. H.

Catalytic Actions at Solid Surfaces. X. The Interaction of Carbon Monoxide and Hydrogen as Conditioned by Nickel at Relatively Low Temperatures. A Practical Synthesis of Methane. E. F. ARMSTRONG and T. P. HILDITCH (*Proc. Roy. Soc.*, 1923, [A], **103**, 25–34; cf. A., 1922, ii, 757).—Certain known interactions of carbon monoxide and hydrogen or steam in the presence of metallic catalysts are briefly reviewed, and attention is directed more especially to the behaviour of purified water-gas in the presence of various finely divided metals, other than copper, at temperatures between 200° and 300°. It is shown that, under these conditions, a new type of reaction represented by $2\text{CO} + 2\text{H}_2 = \text{CO}_2 + \text{CH}_4$ occurs, which, although never complete, proceeds to a very considerable extent. The mechanism of the action is briefly discussed, and it is suggested that in the presence of water vapour, considering two molecular volumes of water-gas, the following

reactions occur: $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$; $\text{CO}_2 + 2\text{H}_2 + \text{H}_2 = \text{CH}_4 + \text{H}_2\text{O}$. Nickel is the most efficient catalyst in this connexion. With cobalt, the reaction commences at a somewhat lower temperature, about 180° , and is subsidiary to the reactions $\text{CO} + 3\text{H}_2 = \text{CH}_4 + \text{H}_2\text{O}$; $2\text{CO} = \text{C} + \text{CO}_2$. Silver is inert, iron almost so, and platinum and palladium are of minor importance. Mixed catalysts, *e.g.*, copper-nickel, iron-nickel, cobalt-nickel, cobalt-platinum, and cobalt-palladium are less efficient than the corresponding single (cobalt or nickel) catalyst. At increased pressures up to 6 atmospheres, the process proceeds much as at atmospheric pressure, except that, in the case of nickel, the minimum temperature of interaction rises with increasing pressure. As by this reaction more methane is formed from water-gas than by other methods, the proportion of methane being 25% of the water-gas decomposed compared with a maximum of 20% by other reactions, it is suggested that the process may find application in increasing the methane content of town gas, or in the manufacture of pure methane. In technical practice, repeated passage of purified water-gas over nickel at 240 — 270° would remove all carbon monoxide. J. S. G. T.

Catalysis [of the Decomposition] of Hydrogen Peroxide by Colloidal [Basic] Ferric Salts. J. DUCLAUZ (*J. Chim. Phys.*, 1923, 20, 18—29).—The velocity of decomposition of hydrogen peroxide at 25° in the presence of colloidal solutions of ferric chloride has been investigated. The colloidal solutions were prepared by boiling solutions of ferric chloride and dialysing the sol thus obtained. The decomposition is shown to take place according to equations for a reaction of the first order. In solutions of the same acidity and containing a given hydrosol, the velocity constant is proportional to the concentration of the iron. The reaction is not due to the whole micella, but takes place through the active and ionisable portion of the micellae. The ferric-ion from a colloidal complex has the same activity as the ferric-ion from a molecule of ferric chloride. The demands of the electrochemical micellar theory put forward previously by the author (*A.*, 1910, ii, 108) are shown to be fulfilled both qualitatively and quantitatively in the present experiments. The general theory of the action of diastase has been considered from the point of view of this theory, and it is shown that the action of ions in the diastatic change appears to be fundamental. The poisoning of diastase is probably due to ordinary chemical processes between the active ions or the diastase-ions.

J. F. S.

Auto-oxidation and Antioxygen Action. Catalytic Properties of Iodine and its Compounds. The Case of Acraldehyde. CHARLES MOUREU and CHARLES DUFRAISSE (*Compt. rend.*, 1923, 176, 797—803).—The action of iodine as an antioxygen both free and in organic and inorganic combination was studied as regards its behaviour in the auto-oxidation of acraldehyde. Metallic iodides with the exception of those of mercury and silver, and the hydriodides of organic bases behaved distinctly as antioxygens in concentrations of 1 in 1000 or less, their power in this respect being of the same

order as that of the phenols. Thus methylamine hydriodide in a concentration of 1 in 1,000,000 showed a distinct retarding action on the oxidation, whilst 1 in 1,000 prevented oxidation for at least a month, differing in this way from the action of the phenols, which did not cause a complete cessation of oxidation, but rather a retardation of the velocity. With the iodides, on the contrary, the first phase, at all concentrations, was characterised by a complete cessation of oxidation for a certain period, followed by a second period in which the oxidation suddenly commences with a velocity equal to, or even exceeding, that of pure acetaldehyde. This positive catalysis, however, was infinitely less intense than the original negative catalysis. In the case of the organic iodine compounds, such as methyl iodide, iodoform, allyl iodide, iodosobenzene, etc., although their action is the same in principle, the period of negative catalysis is greatly abbreviated, and in general greater concentrations are required to produce any observable effect. Thus the period of negative catalysis or antioxygen action with methyl iodide 1 in 80 lasted only a few seconds, with methylene iodide 1 in 100, fifteen minutes, with iodoform 1 in 100, twenty hours, benzyl iodide 1 in 1000, seventy hours, etc. The retarding action of free iodine at 1 in 1000, lasts for several hours. The iodine-ion appears from these results to be the most energetic negative catalyst, and the transition to positive catalysis must be attributed to a change in the catalyst. The bearing of the results on the biological action of iodine compounds is discussed. G. F. M.

Reactions of Formic Acid at the Surface of Alumina. Selective Activation of Alumina. II. HOMER ADKINS and BRYNJULV H. NISSEN (*J. Amer. Chem. Soc.*, 1923, 45, 809—815).—Data are presented to show that by modifying the distance between the aluminium atoms, alumina may be selectively activated towards the following reactions: (1) $\text{H}\cdot\text{CO}_2\text{H}=\text{CO}_2+\text{H}_2$; (2) $\text{H}\cdot\text{CO}_2\text{H}=\text{CO}+\text{H}_2\text{O}$.

The experimental method is similar to that previously employed (Adkins, A., 1922, ii, 834); the following catalysts are used: (1) alumina from the action of water on aluminium amalgam, (2) alumina from aluminium isopropoxide on pumice, (3) alumina from aluminium isopropoxide in pills, (4) alumina from aluminium butoxide on pumice, (5) glass wool, and (6) pumice. For each catalyst a curve is constructed showing the relation between the temperature of reaction and the ratio (formic acid equivalent to CO)/(formic acid equivalent to CO_2). For the first and second catalysts this ratio is also plotted against the concentration of acid in the vapour phase.

From the first set of curves, it is evident that the velocity constants of the reactions (1) and (2) are not only differently affected by the same catalyst, but that different catalysts show different selective catalysing power. The second pair of curves show clearly that the presence of water alters the ratio of the two velocity constants (cf. Hinshelwood, Hartley, and Topley, A., 1922, ii, 274).

It is claimed that these results do not accord with the hypothesis of selective adsorption as to the mechanism of catalysed reactions,

but are more readily explained in terms of an extension of Langmuir's theory of the mechanism of reactions at surfaces. W. S. N.

Platinum Oxide as a Catalyst in the Reduction of Organic Compounds. II. Reduction of Aldehydes. Activation of the Catalyst by the Salts of certain Metals. WALLACE H. CAROTHERS and ROGER ADAMS (*J. Amer. Chem. Soc.*, 1923, **45**, 1071—1086).—Platinum black from platinum oxide prepared from absolutely pure chloroplatinic acid becomes very quickly inactive when shaken with an aldehyde in an atmosphere of hydrogen; only by frequent reactivation can the reduction be completed. The addition of as little as 4 parts per million of iron as ferrous or ferric chloride greatly accelerates the reduction. A systematic study of the effect of various amounts of ferrous and ferric chloride on the catalytic reduction of benzaldehyde, and of ferrous chloride on that of heptaldehyde, using the platinum oxide catalyst previously described (A., 1922, ii, 558) shows that an optimum effect is produced when an amount of iron chloride corresponding with about 0.0001 mol. in 100 c.c. is used. Larger concentrations of ferrous chloride only slightly diminish the rate of reduction, besides causing a tendency for the reduction to proceed beyond the alcohol stage. When ferric chloride is used, it is first reduced to ferrous chloride; with amounts exceeding 0.001 mol. per 100 c.c., an induction period appears, and the reduction is retarded because of the hydrogen chloride set free in the reduction of the ferric chloride. Moreover, the reduction proceeds beyond the formation of benzyl alcohol to toluene and even further. It is shown that impurities sufficient to increase the activity of the catalyst invariably appear during its recovery.

Evidence is given for the following interpretation of the effect of the ferrous salt. The inactivity of the pure platinum black is due to the fact that it is deprived of the oxygen necessary for its activity by the readily oxidisable aldehyde. The iron salt specifically inhibits this reaction and so prolongs the active life of the catalyst.

Using appropriate amounts of ferrous chloride and 0.23 g. of catalyst, it is shown that 21.2 g. of benzaldehyde may be smoothly reduced to the alcohol in twenty to twenty-five minutes. The reaction then stops and no further reduction occurs. A method is described for reducing 100 g. of benzaldehyde in four hours with 0.025 g. of catalyst. W. S. N.

The Dynamo-kinetic Theory of the Electron and the Atom. TH. TOMMASINA (*Compt. rend.*, 1923, **176**, 892—894).—A theoretical paper in which the author develops the conception of indivisible and indestructible units of energy termed *energons* as the ultimate constituents of the electron. As the movement of the energon is indestructible, its dynamo-kinetic value is invariable. The energon is to be regarded as being at the same time the indivisible quantum of energy, and the indivisible unit of matter. Its rotative velocity is the greatest that can exist and its energy being a function of its

velocity it combines in itself the maximum of energy with the minimum of matter.

G. F. M.

Whittaker's Quantum Mechanism in the Atom. H. A. LORENTZ (*Proc. K. Akad. Wetensch. Amsterdam*, 1923, 25, 414—422).—A theoretical paper in which, on the basis of Whittaker's quantum mechanism of the atom (A., 1922, ii, 632), the author evolves relationships to express the action between an electron and an atom during a collision. The author also attempts to generalise the ideas of Whittaker.

J. F. S.

Chemical Combination and Ewing's Magnetic Atom. A. P. LAURIE (*Proc. Roy. Soc. Edin.*, 1922, 42, 352—361).—In order to bring the Ewing magnetic atom (cf. A., 1922, ii, 632) into line with the ordinary conception of a chemical atom, it is assumed that the inner electrons form a fixed system of magnets with the *N*-poles pointing inwards, and that the outer electrons form a rotating unit around the first. Each of the outer electrons is capable of rotation about a central pivot. During chemical combination, the outer electrons oscillate about their centres, and fall into new positions with the conversion of work into heat. The mechanism of ionisation and catalysis is discussed from this point of view. A model is given in which eight electrons are arranged in a ring, so as to exert no external magnetic polarity, with an additional electron in an outer shell. The atoms in a chemical compound are considered to be held together by means of the outer electrons by the electrostatic and magnetic attractions brought into play. A Langmuir atom is constructed, in which eight ring electrons are arranged radially around a central nucleus, and a single electron in the outer shell is placed so that the lines of force passing through it are at a maximum. In chemical combination, the valency electrons swing through 90° to take up a new position under their mutual polar attractions. According to the arrangement of the ring electrons in the nucleus, combination may take place with or without ionisation. A simple explanation is given of the production of an electric current during a chemical reaction without local production of heat.

W. E. G.

The Hypothesis of Constant Atomic Radii. RALPH W. G. WYCKOFF (*Proc. Nat. Acad. Sci.*, 1923, 9, 33—38).—Calculations of the spheres of influence of atoms can be made from four independent starting points: (1) from metals, (2) through the diamond and the bivalent metal carbonates of the calcite group, (3) from pyrites (FeS₂), (4) from caesium dichloro-iodide (CsCl₂I). Atomic radii determined by these different methods of approach do not agree among themselves. The results from pyrites, and caesium dichloro-iodide are fairly concordant, however, and these have been employed in testing the hypothesis of constant radii (W. L. Bragg, A., 1920, ii, 537). The available data are grouped into two tables, in one the concordant results, and, in the other, those measurements in opposition to the hypothesis being given. The rule is obeyed only in those cases where the atomic environment is practically identical. Thus, the hypothesis is true in large groups of isomorphous

compounds, consisting of two kinds of atoms, like the alkali halides which have the sodium chloride arrangement. On the other hand, radical differences in atomic environment lead to marked changes in the interatomic distances.

W. E. G.

Twenty-ninth Annual Report of the Committee on Atomic Weights. GREGORY PAUL BAXTER (*J. Amer. Chem. Soc.*, 1923, 45, 563—572).—An account of the determinations of atomic weights published during 1922. The report includes new work on carbon, hydrogen, glucinum, boron, nitrogen, oxygen, sodium, chlorine, selenium, bromine, yttrium, silver, antimony, lanthanum, thallium, lead, and mercury, together with the references to the literature.

J. F. S.

Quantum Theory of Polyatomic Molecules. M. BORN and E. HÜCKEL (*Physikal. Z.*, 1923, 24, 1—12).—The method of quantisation of disturbed systems developed by Born and others (*Z. Physik*, 1921, 6, 140; 1922, 8, 205; 10, 137) is applied to deduce the theory of the mutual interdependence of degrees of freedom of rotation and vibration proposed by Kratzer (*A.*, 1921, ii, 140, 142) to explain the band spectra of diatomic molecules. On the assumption that the potential energy of a system of atoms depends only on the distances between nuclei, a mathematical theory applicable to the spectra of diatomic and polyatomic molecules is developed. In the case of diatomic molecules, and of triatomic molecules having atoms arranged in a straight line, the axis of rotation remains stationary in space. In general, with polyatomic molecules, the axis of rotation is not stationary. The theory is applied in detail to the case where the molecules in equilibrium are arranged over the surface of a symmetrical top.

J. S. G. T.

Two New Micro-methods for the Determination of Molecular Weights. K. RAST (*Z. physiol. Chem.*, 1923, 126, 100—119).—The first method is a modification of Barger's micro-method (*T.*, 1904, 85, 286). The modification consists in the fact that one single drop occupying two or three cm. of the capillary, of each of the two solutions that are to be compared—standard and unknown—is used. One of these drops is fixed at one end by being attached to the closed end of the capillary, and the other end of this fixed drop is observed at intervals, and changes in its position are noted. No change takes place if the solutions are isotonic. Full details are given of the method of filling the capillary tubes.

The second method makes use of the high depression of the freezing point obtained when camphor is used as a solvent. By the use of micro-apparatus and of small quantities of the solvent, determinations may be carried out with about 10 mg. of material.

W. O. K.

Electrovalency. I. The Polarity of Double Bonds. THOMAS MARTIN LOWRY (*T.*, 1923, 123, 822—831).

Co-ordination Compounds and the Bohr Atom. NEVIL VINCENT SIDGWICK (*T.*, 1923, 123, 725—730).

Some Factors Influencing Co-ordination. T. MARTIN LOWRY (*Chemistry and Industry*, 1923, 42, 316—319).—Co-ordination is the result of an attraction between ions which is similar, both in origin and in its geometrical effects, to the forces which bind together

the ions in crystals, such as rock-salt. In the compounds of Fe^{++} , Co^{++} , Rh^{++} , Ir^{++} , Pd^{++} , and Pt^{++} , six co-ordinated groups are just sufficient in number to complete the outer shell of electrons of the metal if each group shares one pair of electrons with the metal. The amines, such as $[\text{Ir}(\text{NH}_3)_6]\text{Cl}_3$ and $[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$, and the metallic carbonyls, such as $\text{Mo}(\text{CO})_6$, $\text{Fe}(\text{CO})_5$, and $\text{Ni}(\text{CO})_4$, appear to owe their formation and stability to this sharing of electrons. Whilst a deficiency of one, two, or three electrons can be tolerated readily, the surplus electron of potassium cobalticyanide is expelled with great violence from the co-ordinated complex, giving rise to the extremely stable cobalticyanide.

Co-ordination usually involves the attachment to a metal of more radicles than it can carry according to the old theory of valency. The theory of "mixed double bonds" allows this to be expressed by means of symmetrical formulæ in compounds such as ferric acetate.

Tautomeric ions, which can be written in two ways since they possess two possible points of attachment for a hydrogen nucleus or an alkyl group, often give co-ordinated complexes in which a multivalent ion is attracted to both points simultaneously. H. W.

Constitution of Hydrates. I. Hydrates of Salt-like Compounds. MAX E. LEMBERT (*Z. physikal. Chem.*, 1923, 104, 101—146).—A theoretical paper in which, on the basis of a simple geometrical conception of co-ordination linking, such as that of Werner and Kossel, steric numbers have been deduced which determine the possible co-ordination numbers for similar groups when added to a central atom. These steric numbers allow the drawing up of a system of the solid "whole number" hydrates of salt-like compounds, whereby the water molecules are arranged apart from the anion and kation. The mutual influence of the ions in hydrate formation is discussed in the light of Fajan's hypothesis, and this is confirmed. The system has been drawn up in special cases for the chlorides, sulphates, nitrates, and hydroxides of metals, and shown to be in keeping with facts. The lowest and highest hydrates in these groups can, with very few exceptions, be fitted into the system, and in the case of most of the exceptions, by means of a higher co-ordination number, which is shown to be likely, these can also be brought into the system. J. F. S.

Electrostatic Theory of Abnormal Liquids. JAKOB J. BIKERMAN (*Z. physikal. Chem.*, 1923, 104, 55—73).—A theoretical paper in which it is shown that when it is assumed that the molecular weights of the alcohols are normal, then the rules of Eötvös and van der Waals show that they have a slightly abnormal surface tension and vapour pressure. Both these abnormalities can be

explained by the assumption of the existence of an electric double layer on the surface of the alcohols. On the basis of this assumption, the thickness of the double layer is shown to be of ordinary molecular dimensions, and the potential spring has the same value as the electro-osmotically determined potential difference. The connexion of the anomaly with the power of the liquid to charge itself on contact with a foreign substance may be followed quantitatively. The connexion between the anomaly and the di-polar character is pointed out and the rôle of the partition of the dipoles in the establishment of the double layer is discussed. Since the Pictet-Trouton constant is unquestionably determined from the vapour-pressure formulæ, its unusual value in the case of the alcohols is explained by the present hypothesis. The abnormal viscosity and critical coefficients indicate the presence of large internal pressures which on calculation are found to have rational values. J. F. S.

The Dschâbir of the Eighth, and the so-called Geber (Pseudo-Geber) of the Thirteenth Century. EDMUND O. VON LIPPMANN (*Chem. Ztg.*, 1923, 47, 321; cf. Holmyard, this vol., ii, 148; Partington, *ibid.*).—In reply to Partington's criticism (*loc. cit.*), the author maintains that his disbelief in the authenticity of the Latin works ascribed to Geber, and of Avicenna's "De Anima" is well founded. A. A. E.

Glass to Metal Joint. MERLE L. DUNDON (*J. Amer. Chem. Soc.*, 1923, 45, 716—717).—A satisfactory glass-to-metal joint which is free from strain and capable of preserving high vacua may be made as follows. The glass tube is drawn out so that it fits easily for about 1 cm. into the copper tube. It is then coated with platinum and copper-plated over a length of 3—4 cm. by the usual electrolytic method. The coppered end is then polished until it fits tightly in the copper tube. Then copper is electrolytically deposited over the copper tube, joint, and a short length of the glass tube, so that an air-tight copper sleeve is formed which is free from strain and strong. J. F. S.

Inorganic Chemistry.

Apparatus for Electrolytic Preparation of Pure Hydrogen.
GERHARD NIESE (*Physikal. Z.*, 1923, **24**, 12—14).—An apparatus for preparing pure hydrogen by the electrolysis of a 30% solution of chemically pure sodium hydroxide employing pure nickel electrodes is described. A cylindrical anode surrounds a similar shaped cathode, and diffusion of oxygen from the former to the latter is prevented by the use of an auxiliary nickel cathode, having the form of a truncated cone.

J. S. G. T.

Hydrogen Hexasulphide and the Solubility of Sulphur in the Persulphides of Hydrogen. JAMES H. WALTON and EARL L. WHITFORD (*J. Amer. Chem. Soc.*, 1923, **45**, 601—606).—The solubility of sulphur in hydrogen disulphide and hydrogen trisulphide has been determined at temperatures from -34.72° to 55.3° . Both liquids dissolve large quantities of sulphur, the amount dissolved increasing very rapidly with increasing temperature up to -1.45° and above this temperature much less rapidly. The solubility curve shows a well defined break at -1.45° , and at this temperature the liquid has a composition very close to that required for hydrogen hexasulphide, H_2S_6 . It is found that if either sulphide is saturated with sulphur at a given temperature, the two resulting liquid phases have the same composition. The hexasulphide is stable at temperatures below -1.45° and decomposes rapidly at higher temperatures.
J. F. S.

Solubility. VIII. Solubility Relations of certain Gases. NELSON W. TALOR and JOEL H. HILDEBRAND (*J. Amer. Chem. Soc.*, 1923, **45**, 682—694; cf. A., 1919, ii, 392; 1922, ii, 141).—The solubility of chlorine has been determined in heptane, carbon tetrachloride, silicon tetrachloride, and ethylene dibromide at various temperatures from 0° to 40° . The following values are recorded in g. per g. of solvent: heptane at 0° , 0.2036; silicon tetrachloride at 0° , 0.131; carbon tetrachloride 0° , 0.156, 19° , 0.0848, 40° , 0.0433; ethylene dibromide 20° , 0.0813, 40° , 0.0469. These data together with other data on the freezing-point depression in liquid chlorine, are discussed in the light of the theory of solubility previously put forward, and shown to be in accordance with the earlier predictions. Solubility data for hydrogen, nitrogen, carbon monoxide, oxygen, methane, carbon dioxide, nitrous oxide, chlorine, carbonyl chloride, niton, and actinium emanation are summarised and their theoretical relations discussed.
J. F. S.

Behaviour of Ozone. E. H. RIESENFELD (*Z. Elektrochem.*, 1923, **29**, 119—121).—A résumé of the recent work on the preparation of pure ozone, its boiling point, critical constants, critical behaviour, and thermal equilibrium.
J. F. S.

Sulphur Trioxide. A. BERTHOUD (*J. Chim. Phys.*, 1923, **20**, 77—86).—Several physical properties of sulphur trioxide have been investigated. The following values are recorded: m. p. $16.85^{\circ} \pm 0.02^{\circ}$; b. p. $43.84^{\circ}/733.2$ mm.; vapour pressure of the liquid 24° , 240.5 mm., 25° , 253.5; 27.8° , 302.0; 30.45° , 352.0; 34.8° , 454.0; 37.8° , 534.7; 41.4° , 643.7; 43.68° , 726.5; 45.6° , 796.3; 47.8° , 887.2; by interpolation from these figures, the boiling point at 760 mm. is 44.52° ; critical pressure, 83.8 atms.; critical temperature, 218.3° ; d^{20}_{400} 1.9255; d^{25}_{400} 1.9040; d^{30}_{400} 1.8819; d^{35}_{400} 1.8588; d^{40}_{400} 1.8335; d^{45}_{400} 1.8090; d^{50}_{400} 1.7812, and d^{55}_{400} 1.7752. The orthobaric density of liquid and gaseous sulphur trioxide has been determined nearly up to the critical point, and the critical density found to be 0.633. The surface tension measured by the capillary rise is found to be 19° , 34.17; 44.9° , 29.47, and 78.0° , 22.63. The association
12*—2

constant calculated from these figures by the Eötvös method has the values 1.52 and 2.00, respectively. The van der Waals constants are calculated to $b=0.002684$ and $a=0.01629$. The observations made show that β -sulphur trioxide is not a simple polymeric modification of the α -variety, but probably an indefinite hydration compound. The law of rectilinear diameters could not be confirmed with sulphur trioxide.

J. F. S.

The Halides of Tellurium. M. DAMIENS (*Ann. Chim.*, 1923, 19, 44—119).—The author's work on tellurium iodide (A., 1921, ii, 110, 257, 399) and bromides (A., 1921, ii, 546, 636) is republished, together with similar work on the chlorides. The dichloride is only stable in the gaseous condition or in solution and in equilibrium with its decomposition products, tellurium and the tetrachloride.

In the solid state, it dissociates into a solid solution of the element in the tetrachloride. In ethereal solution, it absorbs bromine and iodine, yielding substances which appear to be the chlorobromide and chloriodide, respectively, but it was not found possible to isolate either of these. The dibromide, however, on addition of iodine under similar conditions, yields a bromiodide which may be crystallised from the solution. The methods used in the work were those of thermal analysis in conjunction with the study of the composition of the vapour obtained from mixtures of known composition.

H. J. E.

Determination of the Vapour Pressure of Metallic Arsenic. SHINKICHI HORIBA (*Proc. K. Akad. Wetensch. Amsterdam*, 1923, 25, 387—394).—The vapour pressure of the grey modification of arsenic and its liquid have been determined over the temperature ranges 450—815° and 808—853°, respectively, by the same method as that used by Smits and Bohkorst (A., 1916, ii, 317) in the examination of phosphorus. The following values are recorded: solid, 450°, 0.026 atm.; 500°, 0.076; 550°, 0.222; 604°, 0.785; 615.5°, 0.997; 658°, 2.392; 697°, 4.85; 741°, 9.7; 772°, 16.9; 790°, 22.3, and 815°, 33.6; liquid, 808°, 34.2 atm.; 817°, 35.7; 830°, 38.1; 843°, 40.5; 850°, 41.6, and 853°, 42.2. Extrapolation of the vapour-pressure curves gives the melting point as 817—818° at the corresponding pressure of 35.8 atm. The molecular heat of sublimation has been calculated to 33.6 Cal., the molecular heat of vaporisation of the liquid is 11.2 Cal., and the molecular heat of fusion is 22.4 Cal. Attempts to measure the vapour pressure of the black modification of arsenic failed owing to the rapid conversion of this substance into the grey modification at the temperature of the experiment.

J. F. S.

Preparation of Anhydrous Halides. GIUSEPPE ODDO and UGO GIACHERY (*Gazzetta*, 1923, 53, i, 56—63).—Oddo and Serra (A., 1900, ii, 74) showed that arsenic, antimony, and bismuth trichlorides may be readily prepared by heating the corresponding oxides in a reflux apparatus with sulphur monochloride. In the modification of this method now proposed, arsenic trichloride is obtained by passing a stream of chlorine through a heated mixture

of arsenious oxide and powdered sulphur. The tribromide and triiodide are prepared by heating a mixture, in stoicheiometric proportions, of arsenious oxide with sulphur and the halogen. The preliminary preparation of the sulphur monochloride is thus avoided.

T. H. P.

Preparation and Properties of Pure Graphite. M. PIRANI and W. FEHSE (*Z. Elektrochem.*, 1923, 29, 168—174).—Filaments of artificial silk were carbonised under slight tension for about twenty hours in an atmosphere of coal gas, the final temperature attained being 500°, and then at 2200—2500° in hydrogen. The ash content of the resulting filaments was about 0·3%. The filaments were then made incandescent at temperatures ranging from 1500° to 2000°, when surrounded by either gaseous or liquid carbon compounds. The former included hexachlorobenzene at 3 mm. mercury pressure, light petroleum under pressure of 3 to 30 mm. mercury, and carbon tetrachloride at 15 mm. pressure. The liquids used included light petroleum and carbon tetrachloride. Graphite was by this treatment deposited on the filaments, until their diameters were from 0·2 to 0·3 mm., corresponding with 200 to 300 times their initial diameters. The filaments were finally heated for about half an hour at about 3500° in carbon monoxide. The chemical, crystallographic, mechanical, thermal, and electrical properties of the resulting filaments are detailed, attention being directed more particularly to the fact that the filaments can be bent like lead.

J. S. G. T.

Some Properties of Graphite. R. M. BURNS and G. A. HULETT (*J. Amer. Chem. Soc.*, 1923, 45, 572—578).—The densities of natural graphites from Ceylon, Alabama, and Pennsylvania, Acheson electrode graphite, and carbon produced by the explosion of graphitic acid, have been determined by the liquid immersion method. The density of pure natural graphite is about 2·20 and that of Acheson graphite about 2·30. Carbon produced by the explosion of graphitic acid has a density of 2·215, and is therefore probably graphite. Samples of graphites originally showed no drift or increase in weight with time after immersion in the liquid. The natural graphites, however, after being swelled, or increased in volume by treatment with fuming nitric acid and heat, showed remarkable drifts. Pressure was used to hasten the completion of the drift. The tendency to drift was largely destroyed by a severe compression of the swollen material previous to the determination of density.

J. F. S.

Oxidation Processes by Means of the Carbon Model. O. MEYERHOF and H. WEBER (*Biochem. Z.*, 1923, 135, 558—575).—The authors have studied the self-oxidation of charcoal in alkaline solution. Animal charcoal suspended in dilute alkali takes up oxygen continuously with formation of carbon dioxide. The velocity of oxidation is increased 60% by replacing the air by oxygen. The respiratory quotient (*RQ*) lies in all cases between 0·5 and 1·0 and the heat evolved is 4 cal. per c.c. of oxygen used.

The temperature coefficient for a 10° rise of temperature is about 1.75. The self-oxidation is a surface effect and is inhibited by various urethanes to different extents; the inhibition is due to displacement of the adsorbed substance from the surface, the adsorbed hydroxyl-ion being uninfluenced. The degree of oxidation is proportional to the amount of hydroxyl-ion adsorbed. Among the usual physiologically important units, only the amino-acids are rapidly oxidised by charcoal. Hexose-phosphoric acid is slightly oxidised to carbon dioxide, but dextrose, lævulose, and lactic acid are not.

H. K.

The Structure of Silicon. HANS KÜSTNER and H. REMY (*Physikal. Z.*, 1923, **24**, 25—29).—X-Ray analyses of the respective crystal structures of five varieties of silicon containing from 2.7 to 72% of silica indicate that all conform to the diamond type of structure previously found by Debye and Scherrer (*ibid.*, 1916, **17**, 277). The length of side of the elementary cubical crystal cell is 5.4204 ± 0.00016 Å. The X-ray spectrum of "amorphous" silicon containing 72% of silica was identified with that of natural quartz. In all cases, spectra having sharp lines were obtained. The different chemical activities of varieties of silica are due solely to differences in the ratio of surface to mass of the sample.

J. S. G. T.

The Ammines of Silicic Acid. ROBERT SCHWARZ and ADOLF MATHIS (*Z. anorg. Chem.*, 1923, **126**, 55—84).—The only ammine of silicates described in the literature is $\text{CuO} \cdot 2\text{SiO}_2 \cdot 2\text{NH}_3$ by Schiff, but the method of preparation and the analysis given are not satisfactory. The present authors describe the preparation of the metasilicates of copper, silver, zinc, lead, nickel, and cobalt. Analysis gave too high values for the SiO_3 -ion, this being attributed to adsorption of silica from solution; precipitation from very dilute solutions is advisable. The following ammines were prepared: $\text{CuSiO}_3 \cdot 2\text{H}_2\text{O} \cdot \text{NH}_3$; $\text{CuSiO}_3 \cdot \text{H}_2\text{O} \cdot \text{NH}_3$; $\text{CuSiO}_3 \cdot 2\text{H}_2\text{O} \cdot 2\text{NH}_3$ (at -16°); $\text{Ag}_2\text{SiO}_3 \cdot 2\text{H}_2\text{O} \cdot 2\text{NH}_3$; $\text{ZnSiO}_3 \cdot \text{H}_2\text{O} \cdot \text{NH}_3$; $2\text{PbSiO}_3 \cdot 2\text{H}_2\text{O} \cdot \text{NH}_3$; $\text{NiSiO}_3 \cdot \text{H}_2\text{O} \cdot \text{NH}_3$; $\text{CoSiO}_3 \cdot \text{H}_2\text{O} \cdot \text{NH}_3$. The addition, therefore, is confined to one or two molecules of ammonia. It is only in the case of the copper salt that cooling increases the number of molecules of ammonia added; in other cases, the cooling merely accelerates the addition. Attempts to add ammonia to the anhydrous salts did not succeed, hence the molecular bound water is regarded as an essential part of the silicates, which influences their chemical reactions. Anhydrous zeolites, however, unite with ammonia readily.

W. T.

Separation of Radium from Other Elements. U. CIALDEA (*Gazzetta*, 1923, **53**, i, 42—48).—To recover radium bromide accidentally dropped on the pavement, the sweepings and washings of the pavement were evaporated on a water-bath and the residue was mixed and fused with a mixture of 2 parts of sodium carbonate, 2 parts of potassium carbonate, and 1 part of sodium nitrate. These salts carry into solution the radium, which may then be

recovered completely by the precipitation of barium sulphate, this being accompanied by total precipitation of the radium. Radium is also precipitated, to some extent, together with silica, with the sulphur of ammonium polysulphide, etc.; ferric salts are reduced to the ferrous condition by radium. T. H. P.

Electrolytic Production of Alkali Chlorates, Employing Magnetic Iron Oxide as Anode. G. GRUBE and F. PFUNDER (*Z. Elektrochem.*, 1923, 29, 150—163).—When neutral solutions of alkali chlorides are electrolysed with a view to the production of chlorates, employing magnetic iron oxide as anode, the current efficiency of the process is less than when a platinum anode is used, partly owing to catalytic decomposition at the anode of the hypochlorous acid produced to hydrochloric acid and oxygen. In acid solution at from 60—70°, with an anode current density of from 0.01 to 0.015 amp. per sq. cm. employing a magnetic iron oxide anode, the yield of chlorate is 85% to 90% of the theoretical value calculated from the current. The process of electrolysis of solutions of alkali hypochlorites and of free hypochlorous acid is the same, whether a platinum or magnetic iron oxide anode be employed. In cold, neutral solution, the main electrolytic process is represented by $6\text{ClO}' + 3\text{H}_2\text{O} + 6\oplus \rightarrow 6\text{H}' + 2\text{ClO}_3' + 4\text{Cl}' + 3\text{O}$. In hot acid solutions, chlorate is produced principally in accordance with the secondary reaction $2\text{HClO} + \text{NaClO} \rightarrow \text{NaClO}_3 + 2\text{HCl}$. J. S. G. T.

The Hydrogen Sulphates of the Alkali Metals and Ammonium. HORACE BARRATT DUNNICLIFF (T., 1923, 123, 731—738).

Electrolytic Preparation of Alkali Permanganate by Anodic Solution of Manganese under the Influence of Superimposed Alternating Current. G. GRUBE and H. METZGER (*Z. Elektrochem.*, 1923, 29, 100—105).—The electrolytic preparation of potassium permanganate by the anodic solution of metallic manganese in a solution of potassium carbonate has been investigated, and it is found that at the ordinary temperature the process takes place with a very unsatisfactory current yield (20.5—29.1%). The imposition of alternating current on the manganese anode improves the current yield, but only very slightly (32%). An increase in the current yield is found to occur with medium alternating current densities, whilst with a high alternating current density the current yield falls below that of the simple direct current electrolysis. The different actions brought about by the superimposed anodic alternating current are discussed, and it is shown that the favourable action of the alternating current in the preparation of potassium permanganate consists in the opposition of the alternating current to the removal of alkali from the anode layer. The reduction of the current yield with high alternating current densities depends on the depolarising action of this current, which results in the formation of manganate rather than permanganate. J. F. S.

Phase Relations in the System, Sodamide-Potassamide, as determined from Melting-point Curves. CHARLES A. KRAUS and EUSTACE J. CUY (*J. Amer. Chem. Soc.*, 1923, 45, 712—715).—The melting-point diagram of the system sodamide-potassamide has been obtained by the method of thermal analysis. The diagram indicates the existence of a compound between one molecule of sodamide and two molecules of potassamide, $\text{NaNH}_2 \cdot 2\text{KNH}_2$, having a transition point at approximately 120° . The eutectic between the compound and sodamide lies at a point corresponding with 33 mol.% of potassamide at a temperature in the neighbourhood of 92° . The flatness of the melting-point curve of the compound indicates that it is largely dissociated in the melted mixture.

J. F. S.

The Properties of Ammonium Nitrate. V. The Reciprocal Salt-pair, Ammonium Nitrate and Potassium Chloride. EDGAR PHILIP PERMAN and HORACE LEONARD SAUNDERS (*T.*, 1923, 123, 841—849).

Heteromorphism of Calcium Carbonate. Marble, Synthetic and Metamorphic. MAURICE COPISAROW (*T.*, 1923, 123, 785—796).

Heteromorphism of Calcium Sulphate. Alabaster and its Synthesis. MAURICE COPISAROW (*T.*, 1923, 123, 796—799).

Tricalcium Phosphate. ÉMILE LUCE (*J. Pharm. Chim.*, 1923, 27, 214—216).—Tricalcium phosphate, when properly prepared and dried at 100° , should not lose more than 5% of its weight when incinerated at a red heat. Several samples examined by the author yielded up to 20% loss on ignition indicating the presence of hydrated dicalcium phosphate in the substance, which was confirmed by the relative solubility of the samples in water and in ammonium citrate solution.

W. P. S.

[Molecular Volumes of] The Selenides of the Metals of the Alkaline Earths. FR. A. HENGLEIN and R. ROTH (*Z. anorg. Chem.*, 1923, 126, 227—236).—The linear relation between the molecular volumes of inorganic compounds of similar crystalline form and constant magnitudes characteristic of their kations or anions (*A.*, 1922, ii, 260) is shown to hold also for the selenides of calcium, strontium, and barium. These selenides were made by reduction of the corresponding selenates in a rapid stream of dry hydrogen at 400° for the calcium compound, at 600° for the strontium compound, and at 500° for the barium compound. The essential condition for success is the removal of the water formed before it has time to decompose the selenide.

The selenides are microcrystalline, white solids of cubic habit, which become coloured on exposure to air and decompose in water. Their densities were determined in a volumometer containing hydrogen, and the following values are recorded: calcium selenide, 3.57; strontium selenide, 4.38; barium selenide, 5.02. The distances between the atoms in the crystals are calculated

from the molecular volumes and shown to agree with Bragg's figures.

Attempts to prepare the corresponding tellurides were unsuccessful.
H. H.

The Structure of the Sulphides of Magnesium, Calcium, Strontium, and Barium. SVEN HOLGERSSON (*Z. anorg. Chem.*, 1923, 126, 179—182).—The lattice constant and the lattice structure of these salts were examined by the Debye-Scherrer method. They are all cubic; the unit cube containing 4.4 atoms, *i.e.*, four molecules. The results are tabulated.
W. T.

The Brittleness of Inter-metallic Compounds. G. TAMMANN and K. DAHL (*Z. anorg. Chem.*, 1923, 126, 104—112).—Pure metals and mixed crystals are plastic, this being due to the presence of gliding surfaces; intermetallic compounds, on the other hand, are brittle, this being due to a decrease in the number of gliding planes and to an increase in the tendency to fracture. Inter-metallic compounds were investigated at different temperatures by subjecting them to a sudden blow and to a high pressure. The authors found that almost all the compounds at the ordinary temperature show gliding planes and fractures. No gliding planes were found in the case of the alloys CuMg_2 , Fe_2Sb_3 , FeSb_2 , Zn_3Sb , ZnSb , and FeSi . Metallic compounds such as Cu_3Sn which are characterised by good cleavage lose this property at higher temperatures and they become plastic. All the compounds investigated become plastic at a temperature about 50° below their melting point.
W. T.

The Roasting Reaction Process of Copper. Equilibria in the System Copper-Sulphur-Oxygen. W. REINDERS and F. GOODRIAAN (*Z. anorg. Chem.*, 1923, 126, 85—103; cf. A., 1915, 773).—An application of the static method to the elucidation of the mechanism of the metallurgy of copper.
W. T.

Composition of Copper Hydroxides. L. LOSANA (*Gazzetta*, 1923, 53, i, 75—88).—The composition of the various hydrates of cupric oxide has been investigated by several methods, including that devised by Cohen for determining transformation points (A., 1894, ii, 340). The results obtained show that dehydration of normal cupric hydroxide takes place in two distinct ways, according as it occurs in presence of a liquid or with the dry compound. In the former case, the dehydration is marked by the formation of the definite compounds, $3\text{CuO}, \text{H}_2\text{O}$, $4\text{CuO}, \text{H}_2\text{O}$, and $8\text{CuO}, \text{H}_2\text{O}$. The loss in weight at various temperatures and the vapour-pressure curve show that loss of water by the dry compound is accompanied by formation of the above hydrates and, in addition, of $6\text{CuO}, \text{H}_2\text{O}$ and $7\text{CuO}, \text{H}_2\text{O}$. The compound $8\text{CuO}, \text{H}_2\text{O}$ loses water when heated to redness, but the magnitudes of the losses are not sufficiently constant to indicate the formation of further definite compounds.

The pronounced accelerating effect of alkali on the readiness with which the dehydration occurs is confirmed, and it is found that basic salts exert an opposite influence. In some instances, loss of

water, although with very low velocity, occurs at temperatures below the true temperatures of dehydration.

The various hydrates mentioned may be regarded as definite and moderately stable compounds. T. H. P.

Mercury Cleansing Apparatus. AUGUSTUS EDWARD DIXON and JAMES LYTTLE MCKEE (T., 1923, 123, 895—897).

Separation of Mercury into Isotopes in a Large Apparatus. WILLIAM D. HARKINS and S. L. MADORSKY (*J. Amer. Chem. Soc.*, 1923, 45, 591—601).—A partial separation of the isotopes of mercury has been obtained by evaporation in a vacuum in a large steel apparatus. A difference in density of four hundred and eighty parts per million between the light and heavy fractions is found, and the atomic weight of the fractions differs by 0.1 unit. This has been secured, without other cooling than that given by ice, in two hundred and sixty-eight hours of operation of the apparatus, which holds 2.5 kg. of mercury, together with thirty-seven hours of operation of the small glass apparatus used in earlier work (A., 1922, ii, 295). The weights of the end fractions were 3.8 g. for the heavy fraction and 4.4 g. for the light fraction. The increase in the atomic weight of the heavy fraction is 0.052, and the decrease in atomic weight of the light fraction is 0.440 unit. A multiple unit apparatus which would give the same separation in about thirty hours has been designed. A set of curves is given to show the relation between the increase in density of an isotopic mixture and the cut. These curves exhibit one curvature when the amount of the heavier isotope is less than 50%, and the opposite curvature when the amount is greater than 50% and a point of inflection when the heavier isotope constitutes exactly 50% of the mixture. When several isotopes are present, there may be several points of inflection in the curves. J. F. S.

Action of Mercuric Oxide on Sulphur Monochloride. GIUSEPPE ODDO and UGO GIACHERY (*Gazzetta*, 1923, 53, i, 63—64).—The reaction, $2\text{HgO} + 2\text{S}_2\text{Cl}_2 = 2\text{HgCl}_2 + \text{SO}_2 + 3\text{S}$, occurring when mercuric oxide is added gradually to sulphur monochloride, proceeds with great rapidity and is accompanied by the development of a large amount of heat. The yield of mercuric chloride is almost theoretical. T. H. P.

Rare Earths. XIV. Preparation and Properties of Metallic Lanthanum. H. C. KREMERS and R. G. STEVENS (*J. Amer. Chem. Soc.*, 1923, 45, 614—617).—Metallic lanthanum is best prepared by the electrolysis of fused lanthanum chloride in a graphite crucible which serves as cathode by a current of 40—50 amperes at 7—8 volts. Small quantities of potassium fluoride and sodium chloride were added to the fusion during the electrolysis to maintain proper fluidity. The metal, which usually contained some carbide, was washed with water to remove all adhering salts and carbide, and was then remelted in a graphite crucible under a flux of pure calcium chloride. The metal thus obtained was free from all other metals, and gave no odour of a carbide decomposition when treated with water.

When the electrolysis was carried out in iron crucibles, the product always contained this metal, but electrolysis with a tungsten cathode gave a metal which did not contain tungsten. Pure lanthanum is readily attacked even by dry air; it melts at 826° , and has the following physical properties: d_{15}^{25} , 6.1598; Brinnell hardness (500 kg.), 37; heat of combustion 1645 cal. per g.; kindling temperature 445° . The pure metal is not pyrophoric. Its alloys with iron are much harder than the pure metal and are not pyrophoric.

J. F. S.

Ceric Perchlorate. FR. FICHTER and ERNST JENNY (*Helv. Chim. Acta*, 1923, 6, 326—329).—Dilute solutions of ceric perchlorate can be obtained by dissolving freshly precipitated ceric hydroxide in 50% perchloric acid, or by the interaction of ceric sulphate and barium perchlorate, but the best method is by the electrolytic oxidation of cerous perchlorate, using a 27% solution with 22% of free perchloric acid. In nine hours, using a current of 0.01 ampere per sq. cm. at 30° , more than 96% of the cerous salt is oxidised. When the orange-red solution is heated, it gradually decomposes, forming the cerous salt with evolution of oxygen. On dilution of the concentrated solution with water, a yellow, basic salt is precipitated. When only a slight excess of perchloric acid is present, a basic salt can be obtained by merely warming the solution on the water-bath. It was obtained, mixed with some cerous salt, in the form of aggregates of fine needles having the composition $\text{Ce}_2^{\text{IV}}\text{O}_3(\text{ClO}_4)_2 \cdot 12\text{H}_2\text{O}$, the amount of water of hydration being, however, uncertain.

E. H. R.

The Ternary System, Aluminium-Zinc-Tin. I. The Binary Systems, Tin-Zinc and Aluminium-Tin. E. CREPAZ (*Giorn. Chim. Ind. Appl.*, 1923, 5, 115—122).—Thermal analysis of the system zinc-tin, gives results which agree with those of Heycock and Neville (T., 1897, 71, 392) and indicate that these metals form no compounds, but that, at high temperatures at least, a solid solution exists containing about 5% of tin. With the system aluminium-tin, thermal analysis, micrographic examination, and measurements of the hardness yield results indicating the existence of neither compounds nor mixed crystals.

Measurements of the values of E of the cell $\text{Zn}_x\text{Sn}_{(1-x)}|\text{N} - \text{H}_2\text{SO}_4|\text{normal calomel electrode}$, give -0.28 volt as the potential of pure tin with respect to hydrogen. In the neighbourhood of pure tin, the potential rises rapidly to that of zinc, this value being maintained almost constant for all the other alloys. For alloys highly concentrated in tin, solid solutions may be formed, but under the conditions employed not more than 5% (2.8 atom %) of tin can dissolve in the zinc (cf. Herschkowitsch, A., 1898, ii, 582).

Similar measurements have been made with the cells $\text{Al}_x\text{Sn}_{(1-x)}|0.1\text{N} - \text{KAl}(\text{SO}_4)_2|\text{normal calomel electrode}$ and $\text{Al}_x\text{Sn}_{(1-x)}|10\%\text{KCl}|\text{Al}$. The results obtained confirm Kremann's statement that the potential of aluminium is greatly influenced by the previous treatment of the surface of the metal (*Z. Metallkunde*, 1920, 12, 289). The value, -0.827 volt, for the potential with respect to

hydrogen of aluminium with a knife-scraped surface, agrees with Kremann's result. In all cases, the maximum value observed immediately after immersion of the metal diminishes rapidly to about 0.2 volt; such diminution cannot be ascribed to polarisation phenomena rather than to the formation of a surface layer. For aluminium-tin alloys, the potential throughout almost the whole range of concentration is virtually constant and higher than that of aluminium. On the assumption that the potential of alloys of the eutectic type is regulated only by that of the less noble metal, the potential of the aluminium in these alloys would be -1.139 volt. This value is sensibly below that obtained by Kremann with aluminium amalgams, namely -1.3 volts, and this author's suggestion that an aluminium-mercury compound, less noble than aluminium itself, is formed, is not applicable in the present case, as no compound or new crystalline form is detectable.

T. H. P.

The Fall in Conductivity of Aluminium Chloride during Melting and the Constitution of the Halides of Aluminium.

WILHELM BILTZ and ARTHUR VOIGT (*Z. anorg. Chem.*, 1923, 126, 39-53).—The molecular volumes of the solid aluminium halides do not show a linear relationship (cf. A., 1922, ii, 505), the abnormality being caused by the chloride. The molecular volumes of the molten halides, obtained from a determination of their densities at the boiling point, show a linear relationship when plotted against the molecular volumes of the solid potassium salts. The molecular state of aluminium chloride in the crystalline form differs from that of the molten salt, the molecules in the former being held together by stronger forces; this is also shown by its high melting point. The densities and molecular volumes determined were as follows. Aluminium chloride, molten d^{190} 1.33, mol. vol. 100, solid d^{25} 2.44, mol. vol. 54.7. Aluminium bromide, molten d^{265} 2.26, mol. vol. 118; solid d^{25} 3.01, mol. vol. 88.7. Aluminium iodide, molten d^{382} 2.78, mol. vol. 147; solid d^{25} 3.98, mol. vol. 102.5.

The electrical conductivity of crystalline aluminium chloride increases with the temperature from a zero value to a maximum of 10^{-6} reciprocal ohms; on melting it suddenly falls again to zero, and increases gradually with increasing temperature to 10^{-7} reciprocal ohms. This is attributed to the ions Al^{+++} and $(\text{AlCl}_6)^{---}$ in the crystals; on melting these combine to form the molecules (Al_2Cl_6) . The bromide and chloride of aluminium are non-conductors in the solid state.

W. T.

Basic Aluminium Sulphate. F. S. WILLIAMSON (*J. Physical Chem.*, 1923, 27, 284-289).—The formation of basic aluminium sulphate has been investigated. It is shown that when 2-4 g.-mols of sodium hydroxide are added to 1 mol. of potassium alum, the precipitate has a constant composition which corresponds with the formula $\text{Al}_2(\text{SO}_4)_3 \cdot (\text{Al}_2\text{O}_3)_4 \cdot 15\text{H}_2\text{O}$. The substance, $(\text{Al}[\text{OH}]_3)_4 \cdot \text{H}_2\text{SO}_4$, obtained by Schlumberger on adding five molecules of potassium hydroxide to 1 g.-mol. of potash alum is a mixture, because too large quantities of alkali hydroxide were added. The substance

$\text{Al}_2(\text{SO}_4)_3 \cdot (\text{Al}_2\text{O}_3)_4 \cdot 15\text{H}_2\text{O}$ loses less than 10% of its water when kept over concentrated sulphuric acid at the ordinary temperature. Practically all the water is expelled by heating at 150° , but less than one-third of it is taken up again at lower temperatures, so the substance is not a reversible hydrate. J. F. S.

Anodic Formation of a Perchloride of Manganese. ALAN NEWTON CAMPBELL (T., 1923, 123, 892—894).

General Colloid Chemistry. V. Connexion between Constitution and Stability of Iron Oxide Sols. WOLFGANG PAULI and GEORG WALTER (*Koll. Chem. Beihefte*, 1923, 17, 256—293; cf. A., 1921, ii, 246, 700; 1922, ii, 149).—The constitution of ferric oxide sols which had been subjected to prolonged dialysis has been determined by physico-chemical analysis. The complexes increase in size on prolonged dialysis, due to an increase in the number of neutral ferric hydroxide molecules associated with them; this number in no case is less than about one hundred and forty. The number of elementary complexes per c.c., Z , has been calculated from the chlorine-ion concentration, C_{Cl} , the molecular weight, M , the density, δ , and the average-diameter, d , of the particles by means of the formula $Z = N \cdot C_{\text{Cl}} / 1000$, where N is the Avogadro number and $d = 2\sqrt[3]{3M/4\pi SN}$. The following values of the four sols examined are recorded: I. $33\text{Fe}(\text{OH})_3 \cdot 4 \cdot 5\text{FeOCl} \cdot \text{FeO}^+/\text{Cl}'$, $M = 4000$, $Z = 9 \cdot 4 \times 10^{18}$ and $d(\mu\mu) 1 \cdot 3$; II. $60\text{Fe}(\text{OH})_3 \cdot 5\text{FeOCl} \cdot \text{FeO}^+/\text{Cl}'$, $M = 7000$, $Z = 4 \cdot 4 \times 10^{18}$, $d = 1 \cdot 6$; III. $70\text{Fe}(\text{OH})_3 \cdot 4\text{FeOCl} \cdot \text{FeO}^+/\text{Cl}'$, $M = 8000$, $Z = 3 \cdot 0 \times 10^{18}$, $d = 1 \cdot 7$; IV. $130 \cdot 5\text{Fe}(\text{OH})_3 \cdot 3 \cdot 5\text{FeOCl} \cdot \text{FeO}^+/\text{Cl}'$, $M = 14500$, $Z = 3 \cdot 6 \times 10^{17}$, $d = 2 \cdot 0$. These sols are evidently below the limits of ultramicroscopic visibility. On dilution, the sols undergo a slight reduction in size. The degree of dissociation calculated, for the three sols examined, by means of the ratio $C_{\text{Cl}} : n_{\text{Cl}}$, where n_{Cl} is the total chlorine concentration, is the same for all three cases. Investigation of changes brought about by ageing and by dilution, both of which result in an abnormal increase in the mobility of the colloidal ion and of the conductivity, shows that in both cases the change is due to the same cause, namely, an increase in the number of ions. The tendency to this change appears to become less the longer the sol is dialysed. The experiments show that ageing is a necessary condition for the formation of smaller particles. The addition of sulphates and similar salts to the sols causes coagulation, with the formation of insoluble precipitates. The anomalous action of typical electrolytes which only cause precipitation when they are present in concentrations nearly equivalent to that of the total chlorine is explained by an equilibrium between the free chlorine-ions and the chlorine bound in the complex. The precipitated sol is a complex double salt, a chloro-sulphate, which is rich in sulphate and poor in chlorine. J. F. S.

The Recent Formation of Blue Basic Ferrous Ferric Phosphate (Vivianite) on and in the Clods of an Arable Soil. HERMANN KUNZ-KRAUSE (*Ber. Deut. pharm. Ges.*, 1923, 33, 20—25).—A greyish-blue to dark blue coloration was found on, and

extending in some cases to a depth of several centimetres in, the clods of arable land in the neighbourhood of Dresden. The coloured material was soluble in hydrochloric acid, and both ferrous and ferric iron and phosphoric acid were found in the solution. The coloration is therefore ascribed to the presence of blue basic ferric ferrous phosphate (vivianite) formed from colourless ferrous phosphate, $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, by oxidation in air. The conditions governing the formation of this substance from ferruginous minerals and phosphoric acid, produced probably by the oxidation of organic phosphorus, its transport in solution in carbonic acid, and its reprecipitation by oxidation to the blue basic compound in the soil, are discussed. G. F. M.

Comparison of the Atomic Weights of Terrestrial Nickel and Meteoric Nickel. II. Analysis of Nickelous Chloride.

GREGORY PAUL BAXTER and FRANK ARTHUR HILTON, jun. (*J. Amer. Chem. Soc.*, 1923, **45**, 694—700).—The atomic weight of nickel has been redetermined with material of terrestrial origin and also with material extracted from the Cumpas meteorite. The determination with both kinds of material has been made by means of the ratios $\text{NiCl}_2 : 2\text{Ag}$ and $\text{NiCl}_2 : 2\text{AgCl}$, both being made nephelometrically. In the case of the ratio $\text{NiCl}_2 : 2\text{Ag}$, six determinations were made with terrestrial nickel, and the value of the mean ratio was found to be 0.600730, the extreme values being 0.600746 and 0.600715, whilst for four experiments with meteoric nickel the mean value is 0.600726, the extreme values being 0.600741 and 0.600716. In the case of the ratio $\text{NiCl}_2 : 2\text{AgCl}$ two experiments were made with terrestrial nickel, and the mean value was found to be 0.452118, whilst three experiments with meteoric nickel gave 0.452142 as the mean value of the ratio. The value of the atomic weight of nickel from both sources is therefore the same, namely, 58.70 ($\text{Ag}=107.880$, $\text{Cl}=35.458$). The mean of the present value and those of Richards and Cushman (*A.*, 1899, ii, 488), 58.68, and Baxter and Parsons (*ibid.*, 1921, **43**, 507) is 58.69 (see also *A.*, 1898, ii, 288). J. F. S.

Specific Gravity of Anhydrous Nickelous Chloride. Determination of the Specific Gravity by Displacement of Air.

GREGORY PAUL BAXTER and FRANK ARTHUR HILTON, jun. (*J. Amer. Chem. Soc.*, 1923, **45**, 700—702).—The specific gravity of anhydrous nickel chloride has been determined by displacement of air and also by displacement of toluene. In the former case, the value 3.52 is obtained and in the latter 3.54. The latter value is to be preferred. The experiments also indicate that anhydrous nickel chloride does not adsorb appreciable quantities of air. J. F. S.

Equilibrium in the Systems Nickel Chloride, Cobalt Chloride, Cupric Chloride-Hydrochloric Acid-Water. H. W. FOOTE (*J. Amer. Chem. Soc.*, 1923, **45**, 663—667).—The solubility of the chlorides of nickel, cobalt, and copper (cupric) has been determined at 0° in water containing various concentrations of

hydrochloric acid (0—40%). Cupric chloride has been similarly examined at 25°. The composition of the liquid and solid phases has been ascertained at each point, and it is shown that cupric chloride forms a single additive compound with hydrochloric acid, at 0°, namely, $\text{CuCl}_2 \cdot \text{HCl} \cdot 3\text{H}_2\text{O}$; nickel chloride yields a dihydrate and a tetrahydrate in addition to the usual hexahydrate, whilst cobalt chloride yields only a dihydrate in addition to the hexahydrate.

J. F. S.

Constitution of Aqueous Chromic Acid Solutions. FRIEDRICH AUERBACH (*Z. anorg. Chem.*, 1923, 126, 54).—In reference to Dhar's paper (A., 1922, ii, 382), it is stated that the dissociation constant of the first stage of ionisation of chromic acid is extremely large, but in the second stage it is only $4-8 \times 10^{-7}$.

W. T.

The Hydrates of Molybdenum Trioxide. GUSTAV F. HÜTTIG and BRUNO KURRE (*Z. anorg. Chem.*, 1923, 126, 167—175).—The existence of hydrates of molybdenum trioxide was investigated by means of the Hüttig tensi-eudiometer (A., 1921, ii, 195). The yellow precipitate obtained from a nitric acid solution of ammonium molybdate was shown to be the dihydrate $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$. A monohydrate, $\text{MoO}_3 \cdot \text{H}_2\text{O}$, was also shown to exist. Adsorption compounds were also indicated (cf. A., 1922, ii, 773). No stable hydrates of chromium trioxide were indicated.

W. T.

Production and Characteristics of the Carbides of Tungsten. MARY R. ANDREWS (*J. Physical Chem.*, 1923, 27, 270—283).—The reaction between incandescent tungsten filaments and naphthalene vapour has been investigated. The occurrence of two inflection points in the resistance-composition curve shows the existence of two carbides of the composition W_2C and WC . The mechanism of the reaction is discussed, and it is shown that the main factors are the rate of diffusion of carbon through tungsten carbide as a function of the temperature, the vapour pressure, and the value of the quantity, E , that is, the fraction of the total number of molecules which strikes the filament. The approximate resistivities of W_2C are given for various temperatures, and the conductivity of a partly carbonised tungsten filament is shown to be the sum of the conductivities of its two components. A few experiments with other carbonising agents are mentioned, particularly ethyl alcohol and acetylene. The rate of carbonisation with ethyl alcohol is only about one-fifth that with acetylene. Experiments with benzene, toluene, anthracene, methane, and illuminating gas are described. The results show that almost any hydrocarbon vapour will react with incandescent tungsten to give carbides. A complete vapour-pressure curve for naphthalene from -50° to $+200^\circ$ is given, which is represented by the equation $P = P_0 e^{-Q/RT}$, where Q is the latent heat of vaporisation; a few values for the vapour pressure of toluene at low temperatures are recorded which include the following: -90° , 3 bars, -80° , 31 bars, and -70° , 49 bars. Carbonised filaments heated in a vacuum decompose at rates depending on the temperature; above 2400°K

the rate of decomposition is moderately rapid. The carbon is volatilised without loss of tungsten, and this loss may be driven to completion at 2700°K , leaving metallic tungsten wires of the same conductivity as before carbonisation. J. F. S.

The Equilibrium of Tungsten and its Oxides with Hydrogen and Water Vapour; Carbon Monoxide and Carbon Dioxide and Oxygen. J. A. M. VAN LIEMPT (*Z. anorg. Chem.*, 1923, 126, 226; cf. A., 1922, ii, 301).—The author points out a mistake in his previous paper which necessitates a recalculation of his results. The recalculated vapour pressures at 1773° are: $\text{WO}_2 \rightleftharpoons \text{W} + \text{O}_2$, $p = 10^{-8.0}$; $2\text{W}_2\text{O}_5 \rightleftharpoons 4\text{W} + 5\text{O}_2$, $p = 10^{-7.6}$; $4\text{WO}_3 \rightleftharpoons 2\text{W}_2\text{O}_5 + \text{O}_2$, $p = 10^{-4.9}$ atmospheres. The recalculated heats of reaction are: $\text{W} + \text{O}_2 = \text{WO}_2 + 127,900 \text{ cal.}$; $4\text{WO}_2 + \text{O}_2 = 2\text{W}_2\text{O}_5 + 125,200 \text{ cal.}$; $2\text{W}_2\text{O}_5 + \text{O}_2 = 4\text{WO}_3 + 140,400 \text{ cal.}$ H. H.

The Preparation of Pure Tungsten Dioxide and Tungsten Pentoxide. J. A. M. VAN LIEMPT (*Z. anorg. Chem.*, 1923, 126, 183—184).—The methods of preparation are based on the equilibrium of the oxides of tungsten with hydrogen and water vapour (cf. A., 1922, ii, 301). A stream of hydrogen is passed through water kept at 85° and then the mixture of hydrogen and water vapour passed over tungsten trioxide kept at 900° ; the trioxide is thus reduced to the dioxide. If the water is kept at 97° , then the product is the pentoxide. The above temperatures for the water are those to give the necessary concentration of water vapour in the mixture (cf. Chaudron, A., 1920, ii, 379). W. T.

Isolation of the Oxide of a New Element. A Correction. ALEXANDER SCOTT (T., 1923, 123, 881—884).

Bismuth Subnitrate. E. ISNARD (*J. Pharm. Chim.*, 1923, 27, 216—217).—Certain samples of bismuth subnitrate examined yielded a reaction with Bougault's reagent indicating the presence of arsenic, but this element was not found to be present when the samples were submitted to the Marsh test. The impurity present which gave the reaction with the Bougault reagent was tellurium. W. P. S.

Cobaltinitrites of Bismuth and Cadmium. S. C. OGBURN, jun. (*J. Amer. Chem. Soc.*, 1923, 45, 641—645).—By simple double decomposition cadmium cobaltinitrite and three bismuthyl cobaltinitrites were obtained from the action of sodium cobaltinitrite on a saturated solution of cadmium sulphate or bismuth nitrate, respectively. The bismuthyl compounds, $(\text{BiO})_3\text{Co}(\text{NO}_2)_6$, $(\text{BiO})_3\text{Co}(\text{NO}_2)_5$ and $(\text{BiO})_3\text{Co}(\text{NO}_2)_4$, were obtained from the mother-liquor by rapid filtration at the various stages of the precipitation. Their structures may be represented by Werner's co-ordination grouping, and resemble those of the compounds $[\text{RuCl}_4\text{O}_2]\text{Cs}_2$ (Howe, A., 1904, ii, 490) and $[\text{OsCl}_4\text{O}_2]\text{Cs}_2$ and $[\text{OsCl}_3\text{O}_3]\text{Cs}_2$ (Wintrebert, Thesis, Bordeaux, 1902, 82). The compound $(\text{BiO})_3\text{Co}(\text{NO}_2)_4$ is the most stable; the compounds range from yellow to orange in colour, are insoluble in ether, and only sparingly soluble in alcohol. On

keeping either in solution or in the solid state, they are rapidly decomposed. They are very hygroscopic, and great care was necessary in the separation. *Cadmium cobaltinitrite*, $\text{Cd}_3[\text{Co}(\text{NO}_2)_6]_2$, was isolated from the mother-liquor by fractional crystallisation, and is a bright canary-yellow coloured compound. It is stable both in solution and in the solid form, slightly hygroscopic, insoluble in cold water, and only slightly soluble in alcohol or ether, but it dissolves readily in boiling water. J. F. S.

General Colloid Chemistry. VI. Analysis and Constitution of Colloidal Gold. I. ERNA KAUTZKY and WOLFGANG PAULI (*Koll. Chem. Beihefte*, 1923, 17, 294—312).—A large number of experiments are described which were designed to establish the constitution and composition of colloidal gold. Carefully prepared and dried gold colloids were heated in a current of carbon dioxide and the loss of weight and amount of oxygen evolved ascertained. The results make it very probable that colloidal gold does not contain oxygen compounds. This result is confirmed by the fact that when coagulated gold precipitates are boiled with hydrochloric acid gold does not go into solution. Similar gold precipitates are shown to contain only the smallest traces of chlorine. From these results it is concluded that the colloidal particle contains neither an oxygen-containing aurate group nor the anion of the gold salt used in the preparation of the sol. From conductivity measurements, it is shown that colloidal gold of specific conductivity $25\text{--}30 \times 10^{-6}$ ohms⁻¹ is free from foreign electrolytes, and that such a solution contains kations in the concentration $2.5 \times 10^{-4}N$. The precipitates formed by the addition of magnesium sulphate and barium chloride, respectively, to gold sols have been analysed after thorough washing and shown not to contain foreign elements. Colloidal gold retains a quantity of water when dried at 100°, an amount which is estimated at one molecule to each sixty gold atoms, and this can be accounted for on the assumption of an aquo-complex in the sense of Werner's hypothesis. The colloids examined in the present work were prepared by the action of tannin on solutions of gold chloride. J. F. S.

The Preparation of Ruthenium Pentoxide. HEINRICH REMY (*Z. anorg. Chem.*, 1923, 126, 185—192).—Ruthenous hydroxide is extremely unstable and undergoes spontaneous oxidation to the pentoxide; the pentoxide is also obtained by keeping the tetroxide in a sealed tube for some time. The product in each case contains water; whether this is to be regarded as combined water has not been investigated. It would seem that ruthenium can exert any valency from one to eight. W. T.

Mineralogical Chemistry.

Mendeléevite, a New Radioactive Mineral. V. I. VERNADSKI (*Compt. rend.*, 1923, **176**, 993—994).—This was described in Russian in 1914 as a calcium urano-titanocolumbate. It occurs with orthite in pegmatite veins at Uluntui, near Slyudianka, Lake Baikal, Siberia. The greyish-black cubic crystals (rhombohedral dodecahedra with small octahedral faces) have a dull surface with semimetallic lustre and reddish-brown streak; d 4.76 (4.46 for larger crystalline masses), H 4½. It contains U_3O_8 23.5, CaO 15%, some lead, and little iron and rare-earths. It belongs to the betafite group (A., 1913, ii, 232); but whilst the yellowish and greenish colours of betafite suggest the presence of uranyl or uranium trioxide, the reddish-brown colour of the new mineral suggests the presence of the dioxide. Columbates and tantalates have not originated in the superficial deposits of the earth's crust (biosphere), and in this situation they are very stable. L. J. S.

Analytical Chemistry.

Drying and Weighing in Micro-analysis. A. VON SZENT-GYÖRGI (*Biochem. Z.*, 1923, **136**, 102—106).—In using the Pregl micro-weighing tube and filter with asbestos, the difficulty was encountered that constancy of weight was not attained owing to the hygroscopic nature of the asbestos. This has been surmounted to a large extent by slightly modifying the Pregl tube by having the stem made of capillary bore and the top opening closed by a ground glass cap. The whole can be dried in an oven, a vacuum being applied to the capillary stem and the ground glass joint leaking sufficiently to allow a slow stream of air to pass. A suitable oven for a battery of tubes and a micro-thermo-regulator are also described.

H. K.

The Effect of Alcohol on the Sensitivity of Colour Indicators. I. M. KOLTHOFF (*Rec. trav. chim.*, 1923, **42**, 251—275).—Indicators of acid character are more sensitive towards hydrogen-ions in presence of alcohol, those of basic character less sensitive, but Congo red is an exception. Alteration of temperature has the reverse effect on an indicator in alcoholic solution to that which it exerts in aqueous solution; the magnitude of the variation from neutrality in alcoholic solution as determined for various indicators changes rapidly with temperature. Different indicators exert maximum or minimum ratios of sensitivity with alteration of the alcohol content of a solution, and the existence of these maxima or minima is determined by the influence of the alcohol in decreasing the dissociation of the acid or basic indicators and the ionisation of the water.

H. J. E.

Weighing Tube for Combustion Boats. RICHARD LANT (*Chem. Ztg.*, 1923, 47, 258).—The apparatus consists of a glass tube closed at both ends with glass stoppers and mounted horizontally on a glass foot; a projection on the upper side of the tube serves as a handle.

W. P. S.

New Method for the Electrolytic Separation and Estimation of the Halogens. GÉZA SCHAY (*Z. Elektrochem.*, 1923, 29, 123—126).—The conditions under which the halogens may be separated and estimated electrolytically have been investigated. It is shown that the halogens may be separated in the free state under the following conditions. The separated halogen must be removed by boiling immediately it is liberated; the cathode must, with respect to the anode, have a surface as small as possible, so that the cathodic reduction of the halogen is repressed to the minimum. Based on these conditions, a process is described whereby bromine and iodine may be quantitatively estimated and the three halogens separated. The method is accurate; the error is generally below 0.1% and rarely exceeds 0.2%.

J. F. S.

Electrometric Titration of the Halides in the Presence of One Another. H. H. WILLARD and FLORENCE FENWICK (*J. Amer. Chem. Soc.*, 1923, 45, 623—633).—The electrometric titration of the halogens has been investigated. It is shown that the direct titration of bromide in hydrocyanic acid solution to cyanogen bromide, BrCN , by potassium permanganate is too slow to be used with the bimetallic electrode system. If, however, the usual monometallic system is used and the titration curve plotted, the end-point may be quite easily determined. The oxidation takes place in accordance with the theoretical requirement of two equivalents of oxygen, and the oxalate factor for the permanganate may be used in the calculations. The maximum in the $\Delta E/\Delta V - V$ curve described usually lies a little too far to the right, but when a correction of -0.10 c.c. of $0.1N$ titrating solution is made the maximum error is less than 0.4 mg. of bromine. A sub-maximum often precedes the end-point maximum in the $\Delta E/\Delta V - V$ curve, and the intervening sub-minimum lies extremely close to the theoretical end-point. The sub-maximum does not always show. Iodide if present is oxidised to the corresponding iodine compound, ICN , but chloride in any quantity does not interfere with the reaction. Since a selective determination of iodide is possible, the proposed method provides an excellent means for the rapid estimation of bromide in the presence of any concentration of the other two halides. Iodide may be accurately titrated electrometrically by oxidation to cyanogen iodide with permanganate in hydrocyanic acid solution in all concentrations of chloride and in moderate concentrations of bromide. The effect of the bromide is a function of the ratio of its concentration to that of the iodide, and also of the absolute concentration of each. A more accurate method is the oxidation of iodide to iodate by an excess of alkali hypobromite, the excess being titrated electrometrically with arsenite. In this case, the presence of any amount of bromide

or chloride is without effect. Either the bimetallic or monometallic electrode system may be used in both methods. J. F. S.

Rapid Estimation of Total Iodine in Mineral Waters containing Sulphides. J. DUBIEF (*Ann. Falsif.*, 1923, 16, 80—82).—The sulphides and organic matter are oxidised with alkaline permanganate and the halogens then liberated by acidifying with sulphuric acid and dissolved in carbon disulphide. The excess of permanganate is removed with hydrogen peroxide. If the weight of bromine is less than five times that of the iodine, it does not interfere with the colorimetric estimation of the iodine in the carbon disulphide solution, and this can be immediately proceeded with. If more than this proportion of bromine is present, bromides of iodine are formed and the colour of the carbon disulphide solution becomes yellow. *N/10*-Potassium thiocyanate solution is then added drop by drop with agitation until the yellow colour disappears and the solution becomes violet. By this means 0.05 mg. of potassium iodide can be detected mixed with two thousand times its weight of the bromide. The solution should not contain more than 0.5 mg. of iodine, or the coloration is too intense for exact comparison. The iodine solution must be carefully cooled to avoid loss by sublimation. H. C. R.

Use of Phosphorus in Gas Analysis. AUGUST HOLMES (*Ind. Eng. Chem.*, 1923, 15, 357).—Phosphorus has not the disadvantages attendant on the use of pyrogallol for oxygen absorption, but its action is sometimes a little slow, particularly in the case of gas engine exhausts and the residue from an explosion in gas analysis. By passing such gases through bromine water, however, the oxygen is activated and easily absorbed. It is not necessary to pass the gas after this treatment through alkali hydroxide, since no change in reading takes place. If the room is cold bromine inoculation likewise assists absorption of the oxygen by phosphorus. If the phosphorus has been contaminated by the illuminants or by the cuprous chloride, the black spots may be removed by displacing the water with concentrated nitric acid, or nitric and hydrochloric acids, and then removing the acids by displacement with water. The phosphorus will then be light in appearance and very active for some time. G. F. M.

Electrometric Estimation of Sulphur in Soluble Sulphides. H. H. WILLARD and FLORENCE FENWICK (*J. Amer. Chem. Soc.*, 1923, 45, 645—649).—When the bimetallic electrode system previously described (this vol., ii, 33) is used, the end-point in the electrometric titration of sodium sulphide with an ammoniacal silver solution is unusually sharp. The *E.M.F.* rises slowly and sometimes irregularly at first, then there is a rise of 200—400 m. volts just before the end-point is reached, after which the completion of the reaction is marked by a very abrupt fall in potential. There is often a reversal of polarity during the titration which makes the first part of the rise apparently a fall. The proposed method is based on the reaction used by Lestelle (*Compt. rend.*,

1862, 55, 739), in which the sulphide is precipitated as silver sulphide in alkaline solution by titration with standard ammoniacal silver solution. It is, however, much more simple and accurate than his visual determination of complete precipitation. The change of *E.M.F.* at the end-point is so great that it is quite unnecessary to plot the curve. The method is very accurate, and may be carried out in the presence of sulphite, sulphate, chloride, thiosulphate, and polysulphides. The estimation of sulphur in steel by this method is carried out as follows: a 10 g. sample of the steel is placed in a 250 c.c. flask connected through a condenser with a hydrogen generator, a dropping funnel for admitting acid and a "10-bulb tube" containing 100 c.c. of a 10% sodium hydroxide solution. The apparatus is swept out with hydrogen, 100 c.c. of hydrochloric acid (*d* 1.1) are added, and when the rapid evolution of hydrogen abates the solution is boiled. The stream of hydrogen is continued for five minutes after the steel has dissolved. The sodium hydroxide solution is then washed into a beaker and titrated with standard ammoniacal silver solution as described above.

J. F. S.

Estimation of Sulphur in Organic Compounds. WALTER F. HOFFMANN and ROSS AIKEN GORTNER (*J. Amer. Chem. Soc.*, 1923, 45, 1033—1036).—The Benedict-Denis method for estimating sulphur in urine may be used to estimate sulphur in all kinds of organic compounds, excepting those which are volatile, and so escape before the thermal decomposition of the nitrates commences.

W. S. N.

Colorimetric Estimation of Traces of Thiosulphate in the presence of Sulphite. O. HACKL (*Chem. Ztg.*, 1923, 47, 266).—Thiosulphate may be conveniently estimated colorimetrically after the addition of silver nitrate when the concentration lies between 0.1 mg. and 2 mg. per 100 c.c., expressed as S_2O_3 . If sulphite is present, the solution may be acidified with a few drops of dilute sulphuric acid before the addition of the silver nitrate, without affecting the results of the colorimetric comparisons. Standards for comparison are prepared by adding a solution containing 0.1 mg. of S_2O_3 per c.c. to a volume of water equal to that of the sample being analysed. The solutions should be left for about five minutes before the comparison is made.

H. C. R.

Estimation of Trithionates in the Presence of Tetrathionates. E. H. RIESENFELD, E. JOSEPHY, and E. GRÜNTAL (*Z. anorg. Chem.*, 1923, 126, 281—284; cf. A., 1922, ii, 45).—A method of estimation of trithionates in the presence of tetrathionates is described in which advantage is taken of the fact that trithionates react quantitatively with copper sulphate to produce copper sulphide according to the equation: $S_3O_6^{--} + Cu^{++} + 2H_2O = CuS + 2SO_4^{--} + 4H^+$. Tetrathionates were found to be indifferent to this reagent, thus confirming the work of Kurtenacker and Fritsch (A., 1922, ii, 521).

To a solution of about 0.1 g. of the salt to be estimated is added

50 c.c. of a solution of 10 g. of copper sulphate crystals in 200 c.c. of water acidified with 10 c.c. of dilute sulphuric acid (30 c.c. of strong acid made up to 100 c.c.). The reaction mixture is maintained at 70° for one day, at the end of which time the copper sulphide is filtered, ignited, and weighed as copper oxide. Experimental results are quoted to show that the method is trustworthy for mixtures of potassium tri- and tetra-thionates containing from 0 to 100% of the latter.

H. H.

Estimation of Nitric Nitrogen and Total Nitrogen in Plant-tissue Extracts. PATRICK H. GALLAGHER (*J. Agric. Sci.*, 1923, 13, 63—68).—An examination of methods for the estimation of nitrates by reduction to ammonia is described and a method depending on reduction with Devada's alloy and distillation with magnesia recommended. In plant extracts, colloidal matter is first removed by precipitation with an equal volume of alcohol. A portion containing nitrate approximating to 0.1 g. of potassium nitrate is distilled in steam with 1 g. of Devada's alloy and 0.5 g. of magnesia for forty-five minutes. An air-cooled reflux still-head is suggested to regulate the concentration of ammonia solution reaching the receiver. In Kjeldahl estimations where nitrates are present, the latter may be reduced by the addition of 1 g. of Devada's alloy and 2 c.c. of 25% sodium hydroxide solution. The ammonia is distilled off for thirty minutes and added to that finally found after digestion of the residue with sulphuric acid. Blank determinations with magnesia are necessary.

A. G. P.

Volumetric Estimation of Small Amounts of Phosphorus, using a Standard Solution of Methylene-blue. WILLIAM M. THORNTON, jun., and H. I. ELDERDICE, jun. (*J. Amer. Chem. Soc.*, 1923, 45, 668—673).—An oxidimetric process for the estimation of small amounts of phosphorus has been satisfactorily worked out, which depends on the formation of the ammonium phosphomolybdate precipitate, dissolution of this compound in ammonium hydroxide, reduction of the solution to molybdenum trichloride by hydrochloric acid and zinc in an air-free atmosphere, and titration to molybdenum pentachloride with a standard solution of methylene-blue, on the assumption that the ammonium phosphomolybdate has the normal composition $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3 \cdot n\text{H}_2\text{O}$. The presence of iron does not interfere with the reaction. The solution of methylene-blue used contains about 4 g. per litre, and is standardised by means of a solution of titanous sulphate in hot hydrochloric acid solution. The solutions titrated must not contain much molybdenum or the end-point will not be observed sharply enough. The colour changes during the titration are salmon pink \rightarrow light yellow \rightarrow light green \rightarrow dark green; the final colour change indicates the end of the reaction. The method has been applied to the estimation of phosphorus in steel with satisfactory results.

J. F. S.

Estimation of the Supposed Assimilable Phosphoric Anhydride in Soil. CIRO RAVENNA (*Giorn. Chim. Ind. Appl.*, 1923, 5, 129).—After extraction of the soil with 1% citric acid solution,

the filtered liquid is evaporated to dryness and the residue oxidised with concentrated nitric acid in presence of a little manganese carbonate. The phosphoric acid is then estimated as usual by the molybdate method. [Cf. *J.S.C.I.*, 1923, May.] T. H. P.

Detection of Minute Quantities of Arsenic. II. O. BILLETER (*Helv. Chim. Acta*, 1923, 6, 258—259).—In the method previously described for the detection of minute quantities of arsenic (A., 1919, ii, 32) the hypochlorous acid used for the elimination of hydrochloric acid may be replaced with advantage by fuming nitric acid. The current of hydrogen chloride containing the arsenic is received into 4—5 c.c. of nitric acid, and on evaporation a residue of arsenic acid is obtained which can be introduced directly into the Marsh apparatus. The method is sensitive to one millionth of a milligram. E. H. R.

The Replacement of Bettendorf's Reagent by Hydrochloric Acid and Calcium Hypophosphite Solution. E. RUPP and E. MUSCHL (*Ber. Deut. pharm. Ges.*, 1923, 33, 62—64).—Bettendorf's reagent for arsenic can conveniently be replaced by a reagent prepared by dissolving calcium hypophosphite in 10 parts of hydrochloric acid (d 1.126). This reagent is equally sensitive, giving in all cases a very distinct brown coloration or precipitate within twenty minutes with as little as 0.1 mg. of arsenious oxide when heated in a boiling water-bath with the substance to be tested. In strongly acid solution the reduction proceeds still more rapidly. Satisfactory freedom from arsenic is in general indicated if no darkening in colour is produced within a quarter of an hour. The precipitation of calcium sulphate or the presence of selenium does not interfere with the test. In presence of antimony, the sodium sulphide test is to be preferred. G. F. M.

The Estimation of Arsenic in Organic Compounds. R. STOLLÉ and O. FECHTIG (*Ber. Deut. pharm. Ges.*, 1923, 33, 5—9).—A method of general applicability for the estimation of arsenic in arsenical organic compounds consists in destroying the organic matter by the Kjeldahl-Gunning method at a minimum temperature of 345—355°, and titrating the arsenic as arsenic or arsenious acid. 0.2 G. of the arsenical compound, 7 g. of potassium nitrate, and 15 c.c. of concentrated sulphuric acid are mixed in a 100 c.c. Kjeldahl flask with a neck 15 cm. long and 2.2 cm. wide, and heated for one hour, a further quantity of 1 g. of potassium nitrate is added, and the heating continued for a further half hour, when the above-mentioned temperature should have been attained, corresponding with a loss of 6—7 g. in weight. 3 G. of ammonium sulphate are then added in order to effect the destruction of excess of nitric and nitrous acids, and after heating for fifteen minutes the contents of the flask are diluted with 50 c.c. of water, and 1.5 g. of potassium iodide are added. After keeping for twenty minutes, the liberated iodine is titrated with $N/10$ -thiosulphate without an indicator. As a check on the figure obtained, the solution is nearly neutralised with sodium carbonate crystals, rendered alkaline with sodium

hydrogen carbonate, and the arsenious acid titrated with *N*/10-iodine until a permanent yellow colour is obtained. G. F. M.

Estimation of Carbon and Hydrogen in Organic Compounds containing Arsenic and Mercury. M. FALKOV and GEORGE W. RAIZISS (*J. Amer. Chem. Soc.*, 1923, 45, 998—1003).—The methods given are modifications of the method of Dennstedt.

For the analysis of organic arsenic compounds the wider part of the inner tube is 5—6 cm. longer than usual. The substance, mixed with sea sand if explosive, is placed in a porcelain boat; between this and the catalyst are inserted a porcelain boat containing red lead and a piece of broken porcelain. The red lead, prepared by heating lead peroxide in a current of oxygen after drying at 140°, reacts quantitatively with arsenic oxide, forming lead arsenate, which is stable at a high temperature. The analysis, which is performed in the usual manner, occupies at most two hours. Should poisoning of the catalyst occur, it may be revived by boiling for about three hours with 20% nitric acid, washing with hot water, and drying.

Compounds containing mercury are placed in a porcelain boat between which and the catalyst are inserted (a) a boat containing a mixture of red lead and sea sand, (b) a boat containing silvered asbestos, and (c) a piece of broken porcelain. The asbestos is silvered by mixing with a solution of silver nitrate (90 g. in 100 c.c.), evaporating to dryness, breaking into pieces the size of a pea, and gradually heating to redness in a porcelain crucible. During the combustion, the manipulation of which is described in detail, the mercury forms with the silver an amalgam which is stable to oxygen at comparatively high temperatures. In addition to carbon and hydrogen, mercury may be estimated from the increase in the weight of the boat containing the silvered asbestos; it is shown that the results so obtained are more accurate than by the gravimetric method, and that the operation is much more rapid. The silvered asbestos may be revived after each combustion by heating to a high temperature in a hard glass tube closed at one end; most of the mercury condenses in the sealed end of the tube, the remainder being trapped by means of a larger boat containing silvered asbestos, placed in the tube near the open end. W. S. N.

Simple Method for the Estimation of Carbon in Aqueous Liquids. E. FREUND and G. BOTSTIBER (*Biochem. Z.*, 1923, 136, 142—144).—The method used is a modification of the Messinger method. The substance is oxidised by potassium permanganate and dilute sulphuric acid in boiling solution and the carbon dioxide absorbed in alkali in a Peligot tube. For some substances, for instance, uric, tartaric, and benzoic acids, one hour is sufficient for complete oxidation, but aspartic acid requires three hours and casein much longer. H. K.

Estimation of Carbon Monoxide with Iodine Pentoxide. R. KATTWINKEL (*Brennstoff-Chem.*, 1923, 4, 104—105).—For the

estimation of small quantities of carbon monoxide, absorption in cuprous chloride is useless, but the reaction with iodine pentoxide ($\text{I}_2\text{O}_5 + 5\text{CO} = 5\text{CO}_2 + \text{I}_2$) may be employed. The pentoxide, which is best prepared by oxidising iodine with chloric acid and heating the iodic acid formed at about 200° , should, before use, be heated at 180° until it no longer loses free iodine or water. The estimation is carried out by passing the gas through a U-tube containing iodine pentoxide and glass wool and immersed in an oil-bath at 110 – 120° , at which temperature the reaction is rapid and quantitative. The iodine vapours are absorbed, without condensing, in a 10% solution of potassium iodide and the carbon dioxide in *N*/10-barium hydroxide. The iodine is titrated with *N*/1000-sodium thiosulphate and the barium carbonate converted into sulphate and weighed. The apparatus is finally swept out with air which has been purified by passing over heated copper oxide and through potassium hydroxide and sulphuric acid. With a gas containing 4–6% of carbon monoxide, the values obtained from the iodine liberated were high as compared with those found by absorption in cuprous chloride. By introducing a U-tube containing charcoal immediately before the pentoxide tube very concordant results were obtained from the iodine liberated and the barium carbonate formed, and these agreed closely with the cuprous chloride values. Iodine pentoxide is reduced by hydrogen sulphide, acetylene, ethylene, and, if present in quantity, *n*-pentane; methane has no action on it. Carbon monoxide is not absorbed by charcoal, whilst the latter removes all unsaturated compounds. A detailed survey of relevant literature is given. W. T. K. B.

A New Absorption Bottle for Carbon Dioxide and Moisture.

WILLIAM E. MORGAN (*Ind. Eng. Chem.*, 1923, **15**, 266).—An absorption bottle, for use with solid absorbents, consists of a cylindrical glass bottle with a ground glass cap at the base. The inlet and outlet tubes are sealed through the glass at the top, and the latter extends inside to the bottom of the bottle. To charge the bottle for carbon dioxide absorption, it is set, bottom up, on its flat top, the requisite amount of soda lime is introduced, a cotton or perforated rubber diaphragm is inserted if desired, and the calcium chloride is added. The ground joint at the base is greased, the cap fixed on, and the bottle, when inverted, is ready for use. The total weight of the bottle, filled, is about 80 g. G. F. M.

Estimation of Carbonate in Mineral Waters containing Sulphides. F. TOUPLAIN and J. DUBIEF (*Ann. Falsif.*, 1923, **16**, 76–80).—The direct estimation of carbonate-ion in mineral waters by evaporation to dryness, liberation of carbon dioxide with sulphuric acid, and subsequent absorption with soda lime, gives inaccurate results in the presence of sulphides owing to variations of the equilibrium between the acids hydrogen sulphide and carbonic acid, oxidation of sulphur to strong acids and to the production of sulphur dioxide, which is weighed as carbon dioxide. The sulphides may be eliminated by agitating the water with a small excess of lead peroxide for about fifteen minutes and subsequently

adding hydrogen peroxide and warming at 45° for half an hour. The water is cooled, filtered, and the carbon dioxide liberated with a mixture of sulphuric acid (2 vols.) and concentrated potassium dichromate (1 vol.), by which any thiosulphates not already completely oxidised are transformed into sulphates and sulphuric acid. The carbon dioxide evolved is then free from sulphur dioxide.

H. C. R.

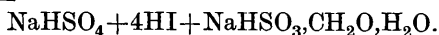
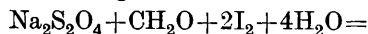
Detection of Peroxides and Per-salts. A. BLANKART (*Helv. Chim. Acta*, 1923, 6, 233—238).—Peroxides can be distinguished from per-salts by their action on an alcoholic solution of *p*-aminophenol. When shaken with this reagent, alkali peroxides give a deep blue to black colour; barium peroxide gives the same reaction more slowly, whilst magnesium peroxide and per-salts do not react. When the proportion of alkali peroxide in the mixture of salts to be tested is small, the alcoholic solution does not become coloured, but after a short time dark specks appear in the white precipitate.

It is impossible to distinguish between the different per-salts in solution, since they are hydrolysed more or less rapidly, giving hydrogen peroxide. In carrying out tests, the finely powdered substance must be added to the reagent. Percarbonates give, in this way, with a 30% neutral potassium iodide solution, an instantaneous strong brown coloration. A slower reaction is given by perborates, perhydro-orthophosphates, persulphates or by a mixture of perhydrocarbonate or perhydrophosphate with a hydrogen carbonate. With silver nitrate solution (0.05*N*), percarbonate gives a yellow precipitate of silver percarbonate, whilst perhydrocarbonate gives at once a black precipitate of silver with evolution of oxygen, although this reaction is masked in presence of much carbonate, or percarbonate. Perborates when pure give no reaction, but when contaminated with sodium peroxide they give at first a brown precipitate of silver oxide followed soon by a rapid evolution of oxygen and formation of a silver precipitate. Persulphates react slowly as hydrolysis occurs, giving a violet colloidal silver solution. Freshly prepared aniline water is slowly turned brown by percarbonate and persulphate, more slowly by perborate, whilst sodium peroxide and perhydro-salts are without action. A hot alcoholic solution of cochineal is decolorised by percarbonate, more slowly by perborate. The per-salts may also be distinguished to some extent by the colour change effected in cobaltous hydroxide. Thus with cobalt nitrate solution, percarbonate gives a green precipitate; perhydrocarbonate a greyish-brown; perborate a bright brown, greyish-brown in presence of sodium carbonate; perhydrophosphate a blue, greyish-green in presence of carbonate; perhydro-orthophosphate, rose, turned brown by carbonate, and persulphate a rose colour turned violet by carbonate.

E. H. R.

Estimation of Sodium Hyposulphite. R. W. MERRIMAN (*Chemistry and Industry*, 1923, 42, 290—292).—A method described for the estimation of sodium hyposulphite depends on the fact that this substance, in the presence of excess of formaldehyde, forms sodium formaldehydesulphoxylate and formaldehyde sodium

hydrogen sulphite, $\text{Na}_2\text{S}_2\text{O}_4 + 2\text{CH}_2\text{O} + 4\text{H}_2\text{O} = \text{NaHSO}_3 \cdot \text{CH}_2\text{O} \cdot 2\text{H}_2\text{O} + \text{NaHSO}_3 \cdot \text{CH}_2\text{O} \cdot \text{H}_2\text{O}$. The formaldehyde sodium hydrogen sulphite is not acted on by iodine in neutral or acid solution, whilst the sodium formaldehydesulphoxylate may be titrated with iodine solution. The action of iodine on sodium hyposulphite solution containing excess of formaldehyde is shown by the equation:



Each c.c. of *N*/10-iodine solution is equivalent to 0.004352 g. of sodium hyposulphite. The details of the estimation are as follows. Twenty c.c. of 40% formaldehyde solution and 930 c.c. of water are placed in a litre flask, the neck of which is cut off 1 inch above the graduation mark; 10 g. of the sample are added while the contents of the flask are shaken, the solution is then diluted to 1000 c.c., the flask is closed, and shaken thoroughly for five minutes. Twenty c.c. of this solution are now added to 100 c.c. of water contained in a beaker, 50 c.c. of *N*/10-iodine solution are added, and, after two minutes, the excess of iodine is titrated with *N*/10-thiosulphate solution.

W. P. S.

The Colorimetric Estimation of Calcium. ACH. GRÉGOIRE, E. CARPIAUX, E. LAROSE, and (MLLE) TH. SOLA (*Bull. Soc. chim. Belg.*, 1923, **32**, 123—130).—The method is based on observations of the pale yellow colour of the colloidal precipitate of calcium oleate obtained by the action of potassium oleate on the solution of a calcium salt in presence of potassium hydroxide and potassium sodium tartrate. When dilution is great, the excess of potassium oleate is hydrolysed and partly adsorbed on the precipitate. It is claimed that the method is practicable and of considerable accuracy. It is applicable only if the solution to be examined contains no other kation precipitated by potassium oleate under the same conditions. The presence of magnesium, if in quantities not greater than 30% of the calcium content, has no effect; beyond that proportion, the error due to magnesium increases rapidly with the proportion of that element. In these circumstances, an accurate estimation may be effected after preliminary separation of magnesium. Full experimental details are given.

H. J. E.

Criticism of de Waard's Micromethod. KURT BLÜHDORN and GRETE GENCK (*Biochem. Z.*, 1923, **135**, 581—584).—The authors have tested afresh de Waard's micro-method for the estimation of calcium in small quantities of serum by direct precipitation as oxalate and find it suitable for clinical use, although entailing the use of the micro-balance.

H. K.

Analytical Precipitation in Extreme Dilution. Barium Sulphate. FRIEDRICH L. HAHN; [with R. OTTO] (*Z. anorg. Chem.*, 1923, **126**, 257—268).—The author endeavours to overcome the well-known difficulty of complete precipitation of pure barium sulphate in the presence of other salts. This may be achieved in one of two ways: either by "precipitation in extreme dilution," by which he means the addition of the reacting solutions slowly

and at approximately equivalent rates to a small quantity of water or hydrochloric acid, thus securing very great effective dilution without undue increase of solution volume; or by heating the reagents in a sealed tube with hydrochloric acid to secure what is virtually a recrystallisation of the barium sulphate. Both methods give a coarsely crystalline precipitate of barium sulphate which is easily manipulated.

For the former method, about 20 c.c. of a solution containing about 9 g. of potassium sulphate per litre are allowed to flow simultaneously with a slight excess of an equivalent barium solution into 10 c.c. of boiling normal hydrochloric acid. The precipitate is filtered, washed, and weighed in the usual way. It is found that additions of potassium chloride up to 5 molecular proportions do not affect the results. Calcium chloride up to one molecule has no effect; up to two molecules, a slight effect, and thereafter, a marked effect on the results, but the error introduced in this way is much less than the error under the same conditions with the usual method. Potassium nitrate up to 4 molecules is practically without effect. Ferric chloride causes a large error and the precipitate is coloured, but by adding ammonia to the barium solution and carrying out the precipitation in water, subsequently removing the ferric hydroxide by washing with hydrochloric acid, the precipitate appears quite white and no appreciable error is introduced by the addition of 3 molecules of ferric chloride. Chromium chloride is treated in the same way as iron, and has no effect on the results when present in amounts up to 1.3 molecular proportions.

For the other method, the weighed sulphate is introduced into a tube with a slight excess of barium chloride and 2 c.c. of hydrochloric acid for every 100 mg. of barium sulphate. The tube is sealed and heated for three hours at 260°, when it is allowed to cool and the precipitate collected and weighed in the usual way. Longer heating or higher temperatures are unnecessary except when iron is present, when heating for three hours at 300° is requisite. Potassium chloride, calcium chloride, nitric acid, nickel and cobalt nitrates, iron, and aluminium chlorides are without effect on the results. It is shown that in the Carius method for the estimation of sulphur in organic compounds, it is unnecessary to remove the nitric acid by evaporation with hydrochloric acid provided that the barium chloride is introduced into the tube before heating. H. H.

The Colorimetric Estimation of Magnesium. ACH. GRÉGOIRE and (MLLE) TH. SOLA (*Bull. Soc. chim. Belg.*, 1923, **32**, 131—136; cf. this vol., ii, 339).—Magnesium may be estimated with considerable accuracy by colorimetric measurement of the precipitate of oleate obtained by means of potassium oleate in presence of ammonia and ammonium chloride. The conditions are similar to those in the case of calcium, as are the limits within which the method may be applied. The simultaneous estimation of calcium and magnesium by this method is regarded as impracticable owing to the difference in colour of the two oleates and to the number of corrections involved. H. J. E.

Estimation of Small Quantities of Aluminium. L. K. WOLFF, N. J. M. VORSTMAN, and P. SCHOENMAKER (*Chem. Weekblad*, 1923, **20**, 193—195).—The Alizarin-*S* method of Atack (*A.*, 1915, ii, 842) was not found to be accurate, but good results were obtained by using the sodium compound of alizarin itself instead of the sulphonic acid. All other common metals and silicon interfere, and must be removed; special precautions must be observed in the use of glass vessels. S. I. L.

The Reaction between Manganese, Lead Peroxide, and Sulphuric Acid. E. I. DYRMONT (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1807—1814).—A modification of the Crum-Volhard reaction for the detection of manganese, which consisted in the addition of the substance to be tested to a boiling suspension of lead peroxide in nitric acid, when a violet coloration is produced. It is shown that the substitution of dilute sulphuric acid for nitric acid in the above reaction enhances the delicacy of the reaction. This method is not suitable for quantitative estimations, as the maximum amount of manganese capable of being oxidised in this way to permanganic acid is only 30%. Maximum oxidation is obtained using 8—9% sulphuric acid, greater or smaller concentrations causing a rapid decrease in the amount of oxidation. R. T.

The Mechanism of the Crum-Volhard and of the Dyrmont Reactions for Manganese. N. A. VALIASCHKO (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1815—1820; cf. preceding abstract).—A comparative study is made of the above reactions for the detection of manganese. It is shown that the Dyrmont modification of the Crum-Volhard reaction, which consists of substituting sulphuric acid for the nitric acid used in the latter, gives a much more intense coloration, which has the further advantage of being stable towards sulphuric acid, whereas the permanganic acid produced by the Crum-Volhard reaction is decomposed by prolonged boiling with nitric acid. This decolorisation is explained by Volhard, and by Morse (*A.*, 1897, ii, 145), to be due to the precipitation of hydrated manganese dioxide, which is thus removed from the sphere of reaction. Hydrated manganese dioxide, however, is found to give the Crum-Volhard reaction for manganese, and the brown precipitates obtained by prolonged boiling of the reaction solutions in both cases are probably double compounds of lead peroxide and manganese dioxide. These compounds are not identical, the compound obtained from the Crum-Volhard reaction being more stable to acids than the substance obtained from the Dyrmont modification of this method, thus explaining the greater permanence of the coloration obtained by the latter. R. T.

Separation of Iron and Aluminium from Manganese and certain other Elements. G. E. F. LUNDELL and H. B. KNOWLES (*J. Amer. Chem. Soc.*, 1923, **45**, 676—681).—Moderate amounts of iron and aluminium can be separated from manganese and nickel as satisfactorily by precipitation with ammonium hydroxide solu-

tion as by the basic acetate or barium carbonate methods. The only requirements are those recommended by Blum for the complete precipitation of aluminium (A., 1916, ii, 493), namely, the presence of ammonium chloride, very low alkalinity ($P_H=6.5-7.5$, as indicated by methyl-red or other suitable indicator), and only one to two minutes' boiling of the alkaline solution. Phosphorus and vanadium interfere but slightly in the separation when iron or aluminium is present in preponderating quantity. When the reverse is the case, they form insoluble compounds with the manganese and interfere, not only in separations by ammonium hydroxide, but also in the methods using basic acetate or barium carbonate. Under the above conditions, the separation of iron and aluminium from cobalt, copper, and zinc is incomplete. A large excess of ammonium chloride improves the separation. An excess of both ammonium hydroxide and ammonium chloride improves the separation from copper and zinc. Under these conditions, however, the precipitation of aluminium is incomplete, and the separation from manganese, nickel, and cobalt is less satisfactory. J. F. S.

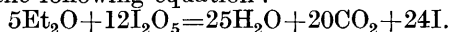
New Method of Detecting Nickel in Solution. C. G. VERNON (*Chem. News*, 1923, 126, 200).—Excess of concentrated ammonia was added to the solution containing nickel, and hydrogen sulphide was passed through it for a short time. The solution was then boiled and a bright mirror of metallic nickel was deposited. The test is not affected by the presence of cobalt. H. C. R.

Estimation of Small Quantities of Molybdenum in Tungsten. WALKER J. KING (*Ind. Eng. Chem.*, 1923, 15, 350—354).—Gravimetric methods for the estimation of molybdenum in tungsten are untrustworthy for quantities of less than 300 parts per million. For lesser proportions than this a colorimetric method is recommended depending on the formation of a blood red coloration of molybdenum thiocyanate when the alkali salts of tungsten and molybdenum are treated with an excess of hydrochloric acid in presence of tartaric acid, the solution treated with potassium thiocyanate, the molybdic acid reduced with stannous chloride, and the red coloured substance extracted with ether and matched against molybdenum standards prepared in a similar manner. A special modification of the Campbell and Hurley colorimeter is used for dealing with the volatile ethereal solutions, and a special flask made by fusing a 400 c.c. flask into the bottom of a 300 c.c. flask provided with a syphon, is used for the shaking-out process. None of the metals usually associated with tungsten ores interferes with the method, which is trustworthy for quantities of molybdenum as low as 10 parts per million of tungsten. The source of light for the colorimeter was standardised by using a 500 watt "Trutint" daylight unit. G. F. M.

Rapid and Sensitive Method for Detecting Bismuth in Urine. II. SERAFINO DEZANI (*Boll. Chim. Farm.*, 1923, 62, 97—101).—The author replies to Ganassini's criticisms (this vol., ii, 93) and produces further evidence supporting his method of

detecting bismuth in urine, this being instantaneous and capable of detecting 1 part of bismuth in 1,000,000 parts of aqueous solution or in 500,000—600,000 parts of urine. T. H. P.

Estimation of Small Amounts of Ethyl Ether in Air, Blood, and other Fluids, together with a Determination of the Coefficient of Distribution of Ethyl Ether between Air and Blood at various Temperatures. HOWARD W. HAGGARD (*J. Biol. Chem.*, 1923, **55**, 131—143).—The method, which is not suitable for quantities of ether greater than 6 mg., has been developed for use in connexion with studies of ether anaesthesia, and depends on the oxidation of ether by iodine pentoxide at 200°, which proceeds according to the following equation:



For the estimation, air, free from carbon monoxide, is drawn successively through a tower of calcium chloride, a bubbler containing the liquid to be analysed (heated at 40° during the later stages), a tower of solid potassium hydroxide, a U-tube filled with alternate layers of iodine pentoxide and glass wool and immersed in an oil bath at 200°, and finally an absorption tube containing a solution of potassium iodide. The iodine liberated is absorbed in the latter and is estimated by titration with thiosulphate. The result of a blank experiment must be deducted from the value so obtained. In order to render it suitable for use, the iodine pentoxide must be submitted to the preliminary treatment of heating it to 220—250° in a current of air for at least fifteen hours.

Using this method, estimations have been made of the distribution of ether between air and water and air and blood at various temperatures between 24° and 40°. E. S.

Estimation of Various Monohydric Phenols by the Phenol Reagent of Folin and Denis. CARLETON HENNINGSEN (*Ind. Eng. Chem.*, 1923, **15**, 406—407).—Monohydric phenols in dilute aqueous solution can be estimated by the phosphotungstic-phosphomolybdic acid reagent of Folin and Denis (*A.*, 1915, ii, 802) with a fair degree of accuracy without the use of an empirical factor, but employing β -naphthol or isoamylphenol as standards, since the intensity of the blue coloration produced appears in the case of all monohydric phenols to be proportional to the molecular concentration of the phenol. The strength of the solution for the actual colorimetric test should not exceed about 0.5 mg. of phenol per 100 c.c., and after the addition of the reagent and the sodium carbonate solution the mixture is maintained at 30° for thirty minutes before comparing the tints in a Duboscq colorimeter.

G. F. M.

Analysis of "Sodium Cresylate." E. ISNARD (*J. Pharm. Chim.*, 1923, **27**, 217—220).—The following method is proposed for the estimation of the total cresols in sodium tolyloxide. One hundred g. of the substance are treated with 2 g. of calcium chloride, diluted to 150 c.c., and filtered; 100 c.c. of the filtrate are acidified with hydrochloric acid and extracted twice with ether. Ten g.

of sodium chloride are then dissolved in the aqueous liquor and the extraction with ether is repeated several times. The united ethereal extracts are washed with water, dried with anhydrous sodium sulphate, filtered, the ether is evaporated, and the residue of cresols heated at 80°, cooled, and weighed. W. P. S.

Gravimetric Micro-cholesterol Estimation. A. VON SZENT-GYÖRGI (*Biochem. Z.*, 1923, **136**, 107—111).—Windaus's cholesterol estimation by means of digitonin is carried out on 0.1 to 0.5 mg. of cholesterol using the modified filter tube previously described (this vol., ii, 330) and with an error for pure cholesterol of about 3%. H. K.

Micro-cholesterol Estimation by Titration. A. VON SZENT-GYÖRGI (*Biochem. Z.*, 1923, **136**, 112—118).—This method depends on the oxidation of the cholesterol-digitonin complex with hot chromic acid and titration of the excess of chromic acid by potassium iodide and thiosulphate. The micro-filtration tube described previously (this vol., ii, 330) is surrounded by a jacket through which steam can be blown so as to effect the oxidation in situ at 100°. H. K.

New Reactions for the Detection of Sterols. GEORGE STAFFORD WHITBY (*Biochem. J.*, 1923, **17**, 5—12).—(1) Two c.c. of a reagent consisting of a mixture of sulphuric acid and formalin in the proportions of 50 volumes to 1 are added to 2 c.c. of a chloroform solution of the sterol (preferably 1—2 mg. of the sterol) and shaken. After shaking, the upper chloroform layer is found to be cherry-red in colour, whilst the lower sulphuric acid layer is brownish-red in colour and shows an intense green fluorescence. On pouring off the upper layer and treating it with two or three drops of acetic anhydride a bright blue colour, which lasts for a considerable time but passes into a green within an hour, is produced. This reaction is more than ten times as sensitive as the Salkowski reaction.

(2) On the addition of 25 drops of a reagent made up by mixing concentrated sulphuric acid and formalin in the proportion of 50 vols. : 1 vol. to 2 c.c. of a solution of 0.2—0.5 mg. of the sterol in glacial acetic acid, a rose-coloured, fluorescent solution is obtained. This reaction is claimed to be more sensitive than any colour reaction hitherto used for the detection of sterols—the limit of sensitiveness of the reaction is 1 in 200,000.

(3) A few mg. of a sterol are added to 1 drop of acetic anhydride on a piece of porcelain and gently heated until it has melted and the excess of anhydride has been driven off. When completely cooled the fused mass is moistened with concentrated nitric acid, when the substance assumes a blue or bluish-green colour. This reaction is of value for cholesterol, but is not suitable for phytosterol.

A differential test for sterolins is also described. One to two c.c. of concentrated sulphuric acid are poured on to a few particles of a sterolin in a test-tube and the mixture is warmed gently to effect solution; on cooling, a cold saturated aqueous solution of thymol is poured on top of it. The lower layer shows an orange colour

with strong green fluorescence. A violet ring is formed at the junction of the layers. When kept, the violet colour tends to spread through the upper layer. With sterols, the same colour is obtained in the lower layer, but no violet ring appears. The author suggests that all reactions for sterols in solution are in their essential features similar. S. S. Z.

The Effect of Soluble Calcium Salts on the Estimation of Dextrose, and its Cause. WILHELM BIEHLER (*Z. Biol.*, 1922, 77, 59—72).—In the estimation of dextrose by means of Fehling's solution, low results are obtained if soluble calcium salts are present, the error being approximately proportional to the quantity of calcium. Soluble salts of barium and strontium, but not of magnesium, zinc, or lithium, act similarly. This loss of reducing power is probably caused by the partial conversion of the dextrose into saccharinic acid under the influence of the alkaline-earth hydroxides. E. S.

Observations on the Method of Folin and Wu, and the Manganimetric Modification for the Estimation of Small Quantities of Reducing Sugar. PAUL FLEURY and LOUIS BOUTOT (*Bull. Soc. Chim. biol.*, 1923, 5, 148—152).—The shade and intensity of the blue colour produced in the Folin and Wu method varies with time, whilst the amount of potassium permanganate absorbed is more constant. W. O. K.

Electrometric Titration of Reducing Sugars. WANDA L. DAGGETT, ARTHUR W. CAMPBELL, and J. L. WHITMAN (*J. Amer. Chem. Soc.*, 1923, 45, 1043—1045).—The 'sugar solution is added rapidly to the boiling Fehling's solution, the course of the reaction being followed by comparing the potential of a platinum electrode immersed in the Fehling's solution with that of a normal calomel electrode. After each addition of sugar, the deflection of a galvanometer in circuit with the titration vessel is noted; this deflection is at first small and irregular, becoming large at the end-point. Further additions of sugar produce relatively small deflections. The method, as checked gravimetrically, is found to be accurate. W. S. N.

The Estimation of Sugar in the Blood. EDWIN GEORGE BLEAKLEY CALVERT (*Biochem. J.*, 1923, 17, 117—129).—A method based on Folin and Wu's and on Mackenzie Wallis and Gallagher's methods. The blood is collected in a platinum capsule which is introduced after weighing into a test-tube containing distilled water. The protein and other interfering substances are removed by the tungstic acid precipitation method of Folin and Wu and the cuprous oxide obtained with the reducing sugar is estimated colorimetrically with phospho-molybdic acid against permanent standards of coloured glass disks. A curve of correction for copper reductions is given. S. S. Z.

Estimation of Sugar by the Picric Acid Method in Liquids Poor in Protein. W. MESTREZAT and (Mlle) Y. GARREAU (*Bull. Soc. Chim. biol.*, 1923, 5, 41—58).—The sugar present in such

liquids as the cerebrospinal fluid may be advantageously estimated by the method of Benedict and Osterberg (A., 1921, ii, 660). Details are given of a macro- and a micro-method of carrying out the estimation, and comparison of these methods with the Folin-Wu-Guillaume method shows good agreement. If too much creatinine or similar reducing substance be present, this must first be separated.

W. O. K.

Estimation of Lactose. VINCENT EDWARDS (*Chem. News*, 1923, 126, 191).—In the volumetric estimation of lactose by means of Fehling's solution, the end-point of the titration is sharply defined if, in addition to a small quantity of magnesium tartrate, a piece of paraffin wax is added to the mixture of Fehling's solution and water.

W. P. S.

The Iodometric Estimation of Aldoses. I. M. KOLTHOFF (*Pharm. Weekblad*, 1923, 60, 362—375).—Aldoses are quantitatively oxidised to the corresponding carboxylic acids by iodine in alkaline solution. To the neutral sugar solution is added at least twice the theoretical quantity of iodine, and then with constant shaking not more than twice the theoretical quantity of sodium hydroxide; after five to ten minutes, the solution is acidified and the excess of iodine estimated by thiosulphate. Sodium carbonate may be used in place of the hydroxide, but the reaction is slower. By blank determinations under the same conditions, the amount of iodine taken up by other substances present may be allowed for.

S. I. L.

Application of the Iodometric Estimation of Aldoses to the Analysis of a Mixture containing Carbohydrates. I. M. KOLTHOFF (*Pharm. Weekblad*, 1923, 60, 394—402).—Lactose may be accurately estimated in milk by the iodine method (preceding abstract) after removal of proteins. In invert-sugar, honey, jam, and similar mixtures containing lævulose, dextrose, and possibly sucrose, the dextrose is estimated iodometrically without correction; the dextrose and lævulose are then estimated together by use of Fehling's solution, the lævulose so determined giving to the necessary accuracy the correction required for the iodine taken up by it in the iodometric estimation. The sucrose is then inverted, and the dextrose so formed estimated by another iodine titration, correcting for lævulose. If dextrin is also present, after the above procedure a more vigorous hydrolysis is carried out, and the dextrose so formed again estimated by difference.

S. I. L.

Estimation of Formic Acid. E. O. WHITTIER (*J. Amer. Chem. Soc.*, 1923, 45, 1087).—It is shown that in estimating formic acid by oxidation by means of alkaline potassium permanganate solution (Jones, A., 1895, ii, 463) at least twenty minutes are required for completion of the oxidation.

W. S. N.

Characteristic Colour Reaction of Oxalic Acid and Oxalates. MÜLLER (*Bull. Assoc. Chim. Sucr.*, 1922, 40, 169—171).—Ten c.c. of a solution of a small quantity of oxalic acid or an oxalate in

dilute sulphuric acid are treated in a test-tube with a few crystals of resorcinol and 2 c.c. of concentrated sulphuric acid are added so as to form a layer below the solution. A blue or bluish-green zone appears at the junction of the two liquids; on shaking the tube, the whole mixture is coloured blue, and this colour changes to violet when the mixture is heated slightly. Other organic acids yield yellow or red colorations with the test. W. P. S.

The Sulphuric Acid Test for Liver Oils. ARTHUR HARDEN and ROBERT ROBISON (*Biochem. J.*, 1923, 17, 115—116).—The purple coloration given by liver oils on addition of a few drops of sulphuric acid can be simulated by adding the sulphuric acid to a light petroleum solution of cholesterol and furfuraldehyde or ω -hydroxymethylfurfuraldehyde. Chloroform may also be used as a solvent, but unless the solutions are carefully dried more sulphuric acid will be required to produce the coloration. The addition of furfuraldehyde to oils such as butter, which by themselves give only a faint reaction, causes the production of a very intense purple coloration on adding sulphuric acid. Attempts to obtain furfuraldehyde, or a compound which could replace it in this reaction from coal fish oil by distillation and other means failed. The above reaction can also serve as a delicate test for cholesterol; a faint purple colour is slowly developed with 0.1 mg. in 5 c.c. of light petroleum containing excess of furfuraldehyde. With 0.5 mg. of cholesterol, the reaction takes place immediately. S. S. Z.

Estimation of Lipoids in Blood and Tissues. III. PIERRE LEMELAND (*Bull. Soc. Chim. biol.*, 1923, 5, 110—124).—A new method is described for the estimation of unsaponifiable fat and total fatty acids in blood and tissues, in which the free acids are converted into their potassium salts and the unsaponifiable fat is extracted by light petroleum.

In the estimation of lipid-phosphorus, it is considered that ether is the best solvent for the extraction of the lipoids. W. O. K.

Estimation of Chloral Hydrate. E. RUPP (*Pharm. Zentr.-h.*, 1923, 64, 151).—In the iodometric estimation of chloral in chloral hydrate it is essential that the iodine solution be added before the alkali solution. Ten c.c. of 1% chloral hydrate solution are treated with 25 c.c. of *N*/10-iodine solution and 2.5 c.c. of *N*/1-sodium hydroxide solution; after ten minutes, the mixture is acidified and the excess of iodine titrated with thiosulphate solution. W. P. S.

Perchloric Acid as a Micro-chemical Reagent. VIKTOR CORDIER (*Monatsh.*, 1923, 43, 525—536).—Perchloric acid may be used (cf. Deniges, A., 1917, ii, 345) as a sensitive microchemical reagent for the identification of some compounds (*A*, below). Other compounds (*B*) are less delicately responsive to the reagent. Hydrochloric acid, sulphuric acid, water, alcohol, ethylene glycol, glycerol, and nitrobenzene are the solvents used. The colour, crystalline form, and optical properties of the various precipitates obtained are described.

A.—Trimethylamine, tripropylamine, triisobutylamine, tetramethylammonium (iodide), tetraethylammonium (chloride), tetrapropylammonium (iodide), phenylhydrazine, hexamethylenetetramine, triphenylguanidine, pyridine, quinoline, quinaldine, acridine, cinchonamine, scopolamine, cinchonine, quinine, cocaine, veratrine, and guanine.

B.—Ethylenediamine, hydrazine, semicarbazide, aniline, dimethyl *p*-phenylenediamine, tribenzylamine, guanidine, *o*-phenylenediguamide, xanthine, piperine, codeine, sparteine, strychnine, and brucine.

The following compounds do not give crystalline perchlorates: Triamylamine, triethylamine, nitrophenylhydrazine, aminoguanidine, diphenylguanidine, benzyldiguanide, *p*-tolylidiguanide, creatine, diphenylamine, diphenylcarbazide, triphenylcarbinol, nicotine, atropine, berberine, and solanine.

E. E. T.

Use of Potassium or Sodium Bromide as a Source of Bromine for Urea Estimations. C. H. COLLINGS (*Chem. News*, 1923, 126, 180, 181).—A simple apparatus is described in which potassium or sodium bromide solution is decomposed by the gradual addition of nitric acid and the liberated bromine is removed by a current of air and conducted through sodium hydroxide solution, in which it is absorbed to form sodium hypobromite solution for use in the estimation of urea.

W. P. S.

Estimation of Carbamide by Hypobromite. B. M. MARGOSCHES and HEINRICH ROSE (*Biochem. Z.*, 1923, 136, 119—127).—Carbamide and ammonia compounds can be estimated by an alkalimetric hypobromite method. The carbamide (0.2 g.) is treated with 50 c.c. of *N*/10-hypobromite and heated for three minutes at 100°, then treated with 0.2 to 0.3 g. of sodium bromide and 50 c.c. of hydrochloric acid ($>N/5$). The bromine is driven off by gentle heating, and after cooling the excess of acid is titrated with $N/5$ -alkali, using methyl-red as indicator. Parallel blank experiments using sodium bromide are an essential feature.

H. K.

Reaction of Allantoin Applicable to its Estimation. J. MORE (*J. Pharm. Chim.*, 1923, 27, 209—214).—When a solution containing allantoin is treated with Nessler reagent, a yellow coloration is produced and mercurous salts are precipitated; other ureides and ammonium salts yield a precipitate with the reagent, but in this case the precipitate is soluble in dilute hydrochloric acid. For the estimation of allantoin, a solution of the substance in dilute sodium hydroxide solution is treated with an excess of Nessler reagent and, after twelve hours, the mixture is acidified with hydrochloric acid and treated with a known quantity (an excess) of *N*/10-iodine solution. The excess of iodine is titrated subsequently with thiosulphate solution. Two atoms of iodine are equivalent to one molecule of allantoin. The result obtained must be multiplied by 1.08, since only 92% of the allantoin is oxidised.

W. P. S.

General and Physical Chemistry.

Refractive Indices of Solutions of Hydrochloric Acid, Acetic Acid, and Ethyl Alcohol in Water at 25° and 30°. HOWARD M. ELSEY and GEORGE L. LYNN (*J. Physical Chem.*, 1923, 27, 342—345).—The refractive indices of aqueous solutions of hydrochloric acid, acetic acid, and ethyl alcohol have been measured at 25° and 30° for sodium light, using a dipping refractometer. The values of n_D are recorded in tables in the original. J. F. S.

The Atomic Refraction of Mercury. M. TIFFENEAU and CH. SOMMAIRE (*Bull. Soc. chim.*, 1923, [iv], 33, 293—296).—The atomic refraction of mercury was determined from observations of the refraction of four mercury alkyl compounds, their molecular refractions being calculated from the formula of Lorentz. The following values were obtained: mercury diethyl has n_D^{20} 1.504, d^{20} 2.4268, molecular refraction 33.39, whence, deducting 20.672 for 4C and 10H, the atomic refraction of mercury is 12.718. Mercury di-*n*-propyl has n_D^{22} 1.5138, d^{22} 2.0111, molecular refraction 42.79, whence the atomic refraction of mercury equals 12.882. Mercury diisopropyl has $n_D^{23.5}$ 1.52825, $d^{23.5}$ 2.0103, molecular refraction 43.82, and atomic refraction of mercury equals 13.91. Mercury di-*n*-butyl has n_D^{21} 1.5059, d^{21} 1.790, molecular refraction 52.09, and atomic refraction of mercury 12.946. The mean value derived from the unbranched chain compounds is therefore 12.848. The atomic refractions of mercury and the compounds increase as the chain lengthens, and also the introduction of the secondary radicle causes a notable exaltation. These results are in accordance with those previously obtained for lead. G. F. M.

The Molecular Refractions of Chloro-, Dichloro-, and Chlorobromo-acetates. PAULE LAURE VANDERSTICHELE (*T.*, 1923, 123, 1225—1229).

[The Graphitic Conception of Aromatic Carbon.] A. L. VON STEIGER (*Ber.*, 1923, 56, [B], 998).—In consequence of an error, the value $n_D^{90.35}$ 1.58932 instead of 1.59480 was cited for the index of refraction of anthracene dissolved in naphthalene (A., 1922, ii, 616). The recalculated value for the molecular refraction of anthracene is 65.46, which is in good agreement with the measurements of Krollpfeiffer (this vol., ii, 102). H. W.

A Method for the Separation of the Arc and Spark Lines of Emission Spectra. W. WIEN (*Ann. Physik*, 1922, [iv], 69, 325—334).—In order to distinguish between the arc and spark lines of a number of gases, positive rays were produced in a high vacuum, and the emission of light was examined. By means of a short condenser, the charged atoms were deviated from their path, and the lines due to these, the spark spectrum, separated from the

lines due to the uncharged atoms, the arc spectrum. The Balmer series for hydrogen were shown to be due to the uncharged atoms. On the other hand, the majority of the oxygen lines were deviated; the undeviated lines belong to the series spectrum. For nitrogen, the relationships are more complex, but the arc and spark spectra are found to agree with Stark's classification. The negative band spectrum was found to be given by positively charged molecules, and the positive band spectra from the uncharged molecules. The mercury lines observed were due to uncharged atoms. W. E. G.

Spark Spectra of Higher Order. LÉON BLOCH and EUGÈNE BLOCH (*Compt. rend.*, 1923, 176, 1062—1063).—The authors claim priority over Dunoyer for the method of resolving a spark spectrum into several spectra of different categories, and for the application of the method to the case of mercury (cf. *ibid.*, 1910, 153, 833, 933).
G. F. M.

Arc Spectra and Ionisation Potentials in Dissociated Gases. K. T. COMPTON (*Proc. Amer. Phil. Soc.*, 1922, 61, 212—226; cf. A., 1921, ii, 368).—The arc was studied in a new type of discharge tube permitting the use of an atmosphere of atomic hydrogen. Critical potentials were also studied by a modification of Lenard's method. For hydrogen, six critical potentials were observed: 10·1, 12·1, and 13·8 are associated with the atom, the first two being radiation potentials, and the last the ionisation potential. These values correspond respectively with the first and second lines and the convergence frequency of the Lyman series. The values 11·3, 12·8, and 16·2 refer to the molecule, being due, respectively, to ionisation without dissociation, dissociation plus radiation from an atom, and dissociation plus ionisation of an atom. The lowest voltage at which an arc can be maintained in hydrogen is 16·2 volts.

A similar study of nitrogen showed the arcing voltage to be 16·15 volts, at which value the positive bands were observed. One of these increased in intensity with further increase of voltage, and the other decreased. The negative band appeared at above 18 volts, and increased in strength with the voltage. The lines in the visible region of the spectrum were not seen at a potential below 70 volts. Whilst dissociation of nitrogen was impossible at temperatures obtained by the heated tube, dissociation by electronic bombardment was facilitated by electrically heated tungsten.

CHEMICAL ABSTRACTS.

Observations on the Structure of the Hydrogen Lines H_α and H_β . A. E. M. GEDDES (*Proc. Roy. Soc. Edin.*, 1923, 43, 37—42).—According to Sommerfeld's theory of the fine structure of spectral lines, the separation of the doublets for all members of the Balmer series of hydrogen lines should be constant, and correspond with a value $\delta\nu = 0\cdot365 \text{ cm}^{-1}$. The author finds for H_α and H_β , respectively, the values $\delta\nu = 0\cdot34$ and $0\cdot33 \text{ cm}^{-1}$. The result is held to support McLennan's view (A., 1921, ii, 666) that the value of $\delta\nu$ decreases with decrease of wave-length, so that the Balmer series must be regarded as a principal series, and not as a subordinate one.
J. S. G. T.

Spectra of Hydrogen, Nitrogen, and Oxygen in the Extreme Ultra-violet. J. J. HOPFIELD (*Physical Rev.*, 1922, 20, 573—588; cf. this vol., ii, 1).—Contrary to belief, oxygen and other gases are found not to be opaque in the extreme ultra-violet region, and a method has been developed for their examination. For hydrogen, wave-lengths are given for ninety lines from $\lambda 885\cdot6$ to $\lambda 1059\cdot2$. The resonance line is superimposed in the fourth order on the H_β line; hence its wave-length is $1215\cdot68 \pm 0\cdot03 \text{ \AA}$. This coincidence confirms the Bohr formula for this line. In the case of nitrogen, the continuous discharge gives chiefly the band spectrum, nineteen bands from $\lambda 1025\cdot8$ to $\lambda 1384\cdot7$ being measured; the disruptive discharge gave fifty new lines. It appears probable that Lyman's (*Astrophys. J.*, 1916, 43, 89) helium lines are really due to air. With the disruptive discharge, oxygen yielded about one hundred new lines, extending to $\lambda 507\cdot2$; when mercury vapour was present, about 15 additional lines, extending to $\lambda 433\cdot0$, were obtained.
A. A. E.

Emission and Absorption of Halogens in the Visible and Ultra-violet Regions. A. L. NARAYAN and D. GUNNAYYA (*Phil. Mag.*, 1923, [vi], 45, 827—830).—The emission spectra of bromine and chlorine are line spectra the nature of which depends on the intensity of the discharge and the temperature of the tube. As the temperature increases, some of the lines are reinforced and others disappear. The absorption spectra have been studied up to 2000 \AA . All these vapours give a banded spectrum in the yellowish-green region between 5800 \AA . and 5000 \AA ., and at the same time general absorption begins at the ultra-violet and extends up to 4900 \AA . With increase of pressure, the bands become darker and a few more are added at the red end, and the general absorption band extends more and more up to the green, where the banded spectrum begins. The absorption of bromine vapour gradually increases as the temperature rises from 30° to 600° , until at the latter temperature it absorbs almost the whole of the ultra-violet up to 2000 \AA .; this is the temperature of maximum absorption. In the case of chlorine, the absorption increases slightly towards the red end with rise in temperature, but towards the short wave-length side there is no appreciable change. The maximum absorption for iodine occurs at 300° . The emission and absorption spectra of the halogens are not complementary.
W. E. G.

Structure of the Band Spectrum of Helium. II. W. E. CURTIS (*Proc. Roy. Soc.*, 1923, [A], 103, 315—333).—In continuation of previous work (A., 1922, ii, 330), the author has investigated the structure of seven doublet bands, near $\lambda\lambda 4650$, 3680 , 3350 , 5130 , 4000 , 3630 , and 3460 \AA ., in the spectrum of helium. Each band consists of three series, two of which proceed to a head, whilst the third does not. Tables of wave-lengths and least square empirical formulæ are given for the constituent series of each band. The structure of the bands is considered in the light of the quantum theory, and it is shown that the doublet

separations should tend to decrease in passing to higher members of the series, but not to vanish, a result which is in accordance with the measurements of Fowler (A., 1915, ii, 118). Kratzer's half-quantum hypothesis (A., 1922, ii, 409) is applied to discuss the displacement of the more refrangible branches of the bands. A graphical method of calculating moments of inertia of the molecules concerned in the emission of the spectrum is detailed, and numerical values of the initial and final moment are calculated in the case of each of the bands. Initial values so calculated range from 2.00×10^{-40} to 2.17×10^{-40} whilst final values range from 1.71×10^{-40} to 1.76×10^{-40} . The differences between the stable and energised moments of inertia are large compared with the variation of the latter among themselves, and indicate that whilst the removal of the electron from the innermost to the next orbit considerably modifies the configuration of the molecule, subsequent transitions have relatively little effect. No perturbations were found in the bands $\lambda\lambda$ 6400, 4546, and 5730, previously studied, but in the main series of doublets, $\lambda\lambda$ 4650, 3680, and 3350, five cases occur. These displacements (obs.-calc.) range from -2.11 to $+1.50$ cm.⁻¹. They originate in disturbances of the initial energised state of the molecule. Their complete explanation requires possibly the postulation of an additional molecular type in addition to the whole- and half-quantum types. A new combination law in the form $R'(m) - P(m+1) = \text{constant}$, is shown to hold for bands of the same series and for the same value of m . J. S. G. T.

Series Spectra the Emission of which is Associated with more than One Electron. GREGOR WENTZEL (*Physikal. Z.*, 1923, 24, 104—109).—Certain lines in the neon spectrum are produced in pairs by the simultaneous transference of two electrons, one from the 2_2 to an outer orbit, and the other from 2_1 to 2_2 . The energy changes involved in these passages are discussed with the aid of a diagram and it is shown that the difference between the work of excitation for two such lines, will be nearly the same as the work involved in the transference of an electron from L_1 to L_2 which gives rise to a line in the Röntgen spectra. The Ritzsche term (A_1A_1') may be derived from the Ritzsche formula, but to obtain the non-Ritzsche term (A_2A_2') a constant amount 782 cm.⁻¹ must be added. The spectra of calcium, barium, and strontium are studied from this point of view, and values for the term differences, the ionisation work $I_2 - I_1$, and the work of excitation $A_2 - A_1$, are given for a number of lines. W. E. G.

Regularities in the Red Xenon Spectrum. L. A. SOMMER (*Z. Physik*, 1923, 13, 85—93).—This work was undertaken in order that a comparison might be possible between the spectrum of xenon and that of ionised caesium. The measurements of Baly, Merrill, and Meggers have been employed. In all, 148 lines have been arranged in pairs and groups on the basis of constant frequency differences. The intensities, λ and $\gamma_{\text{vac.}}$ are given. The comparison with the caesium spectrum will shortly be communicated.

W. E. G.

The Mass Spectra of the Chemical Elements. IV. F. W. ASTON (*Phil. Mag.*, 1923, [vi], 45, 934—954; cf. A., 1921, ii, 474).—The photographic plates used in this investigation have been improved by a process of Schumannisation, consisting in partly dissolving away the gelatin from the plate by means of sulphuric acid. The doubly-charged helium atom was sought for without success. The isotopes of nickel were investigated by employing nickel carbonyl diluted by carbon dioxide, and the atomic weights of its isotopes were 58 and 60, respectively. The intensity relation between the lines agrees with that predicted from the experimental atomic weight. The isotopes of titanium and chromium could not be determined when the chlorides were employed on account of the action of the chlorine atoms on the material composing the apparatus. Also lead ethyl and zinc methyl gave unsatisfactory results. The two weak xenon lines, 128, 130, previously suspected, have been confirmed, and two new components at 124 and 126 discovered after considerable over-exposure of the plate. Tin in the form of tin tetramethyl gave the isotopes 116, 117, 118, 119, 120, (121), 122, and 124; the values are less than whole numbers by 2—3 parts in 1000, as was detected by an examination of the line $\text{Sn}^{120}\text{CH}_3$, which is asymmetrically situated with respect to the two xenon lines, 134, 136. Only one iron line could be definitely identified, and this differed slightly from the whole number rule. Cadmium lines could not be obtained when the metal was volatilised inside the discharge tube, but its introduction led to the complete removal of the mercury lines. On volatilisation, selenium gave five strong lines, 76, 77, 78, 80, 82, and a faint sixth at 74, and these were confirmed by the occurrence of lines due to CSe , COSe , and CSe_2 . Three are isobaric with three of the krypton lines. No success was obtained with tellurium or beryllium. Aluminium appears to be a simple element, and no isotope of chlorine occurs at 39. Trimethylstibine gave two strong lines at 121, 123, the former being slightly the more intense, and these lines showed no appreciable deviation from the whole number rule. A complete list of the known isotopes is given. W. E. G.

The Relationship between the Arc Spectrum of Sodium, the First Spark Spectrum of Magnesium, and the Second Spark Spectrum of Aluminium. E. FUES (*Z. Physik*, 1923, 13, 211—220).—In a previous paper (cf. this vol., ii, 1, 103), it was shown how the terms in the arc spectrum of sodium could be utilised to determine the potential function in the inner field of the atom. It is now possible to extend these deductions from Na^I to the related spectra, Mg^{II} , and Al^{III} , although the configurations of these three systems are not exactly identical. For the calculation of the corresponding magnesium and aluminium spectra, only the data for Na^I and the value of the L_1 term of magnesium and aluminium are needed. The deviations between the experimental and calculated values, which increase with increasing atomic number, do not disturb the high degree of relationship between the three spectra. W. E. G.

Wave-length Measurements in the Arc Spectra of Neodymium and Samarium. C. C. KIESS (*U.S. Bur. Standards Sci. Papers*, 1922, 18, 201—219; cf. A., 1922, ii, 244).—The arc spectrum of neodymium has been investigated between λ 5474·72 and 8935·97, and that of samarium between λ 5475·20 and 9264·59, involving about 1500 lines in each, of which 130 are common to both. The latter are of unknown origin, and may possibly be characteristic of the intermediate unknown element of atomic number 61.

A. A. E.

Series-spectra of the Aluminium Sub-group. J. A. CARROLL (*Proc. Roy. Soc.*, 1923, [A], 103, 334—338).—The author has investigated the absorption spectrum of thallium vapour at a temperature of 500—600°, over the range λ 7000—2500 Å. No trace of absorption lines corresponding with the principal series was observed. Lines corresponding with the sharp series were observed at λ 5350·46, 3775·72, 3229·75, and 2580·14 Å., and to the diffuse series at λ 3529·43, 3519·24, 2767·87, 2921·52, and 2918·32 Å. The line λ 2768 Å. showed absorption on the red side only. The absence of the principal series of lines and the reversal of the subordinate series indicate that, in accordance with the latest developments of Bohr's theory, the normal state of the atoms in the aluminium sub-group of elements corresponds with a 1π orbit and not with a 1σ orbit as in the alkali metals. Of the three outermost electrons in the case of thallium, two are in 6_1 orbits and one in a 6_2 orbit, the latter giving rise to the arc spectrum.

J. S. G. T.

The Spark Spectrum of Gallium in Air and in Hydrogen. ELLIAS KLEIN (*Astrophys. J.*, 1923, 111, 373—379).—The wave-lengths of eighty-three lines, fourteen being questionable and forty-eight new, in the spark spectrum of gallium, between λ 2177 and λ 6414, in air and hydrogen have been measured with an accuracy of about $\pm 0\cdot05$ Å. It was found that in air, oxidation takes place, the gallium oxide formed superficially then radiating only the strongest lines of the metal, whilst in the case of nitrogen the bands masked the fainter gallium lines.

A. A. E.

The Electric Furnace Spectrum of Iron in the Ultra-violet, with Supplementary Data for the Blue and Violet. ARTHUR S. KING (*Astrophys. J.*, 1922, 55, 318—339; cf. *ibid.*, 1913, 37, 239).—Previous tables (λ 3884 to λ 7208) are extended to λ 2298. Furnace emission spectra extend into the ultra-violet only as far as the continuous spectrum of a black body at the same temperature, but by using a gas-filled tungsten lamp or by explosion of a series of fine wires, absorption spectra corresponding with either low or high temperatures of the vapour may be obtained extending to λ 2298 or beyond. Tables are given containing the temperature classification of 904 lines in the arc, and in low (1600°), medium (2000°), and high (2300°) temperature furnace spectra; a revised classification of 262 lines, λ 3884 to λ 4531 and a list of the most persistent low temperature lines are also given. Experiments with various metals indicate a parallelism between the

successive temperature excitation stages and the radiation stages as the potential is increased in low voltage vacuum arcs. The furnace method is suitable for the classification of spectra of substances of high b. p.

A. A. E.

Behaviour of Spectral Lines at the Positive Pole of the Metallic Arc. PAUL W. MERRILL (*Astrophys. J.*, 1922, 56, 475—482).—By using the Pfund type of arc, it was found possible to classify five hundred iron lines between λ 3849 and λ 5763 into six classes according to the degree of increase of the intensity of the lines at the boundary of the small region of luminous vapour just above the point where the core of the arc enters the molten bead which forms the positive electrode. Fair correlation was obtained with King's furnace classification. Similar relationships were found in the case of one hundred and eighty cobalt lines and some nickel lines.

A. A. E.

An Explanation of Complicated Spectra (Manganese, Chromium, etc.) by the Inner Quantum Number. A. SOMMERFELD (*Ann. Physik*, 1923, [iv], 70, 32—62).—The conception of the inner quantum number has been further extended (cf. *ibid.*, 1920, 63, 221) to provide an explanation of complicated line spectra. The choice of the combinations between the three quantum numbers k , n , and j is limited to the following: for the inner quantum number,

$$j \rightarrow \begin{cases} j-1 \\ j \\ j+1 \end{cases} \quad \text{and for the "azimutal" quantum number, } k \rightarrow k \pm 1.$$

The Landé condition that the combination $O \rightarrow O$ is impossible may be used to determine the absolute values of the quantum numbers. With the aid of the conception of the inner quantum number, it is possible to predict the intensities of the spectrum lines, those lines being the strongest in which j changes by the same amount as k ; the intensity becomes weaker the more the change of Δj deviates from the change Δk . These rules are applied to the members of the line spectra of manganese and chromium. For chromium, the passage $O \rightarrow O$ is absent and the existing lines are in agreement with the above principles, but in the scheme formulated for manganese the combination $O \rightarrow O$ is present, and doubt arises as to the absolute values for the quantum numbers. The number of levels into which the S , P , D , ... series or s , p , d , ... series are divided increases according to the numbers 1, 3, 5 ... The relationship between the inner quantum number and the impulse moment, and between the latter and the magneton number, is discussed. Doubt is expressed as to whether the paramagnetic moment is identical with the impulse moment derived from the inner quantum number.

W. E. G.

Series Relationships in the Arc Spectrum of Chromium. H. GIESELER (*Ann. Physik*, 1922, [iv], 69, 147—160).—From the observed Zeeman effect and with the aid of the Landé theory (*Z. Physik*, 1921, 5, 231), it has been possible to arrange and classify the arc spectrum of chromium. The key to the chromium spectrum

is given by the $3a/2$ -groups which had been already discovered for calcium, barium, and strontium. In the arc spectrum of chromium, three such groups occur, which consist of 12 lines. These are arranged in Rydberg schemes, giving the intensity λ_{air} in Å., $\nu=10^8\lambda^{-1}_{\text{vac}}$, and the differences between related lines. Also two pd series have been found, consisting of twelve lines, and from the Landé theory the separation factor g for the d terms has been calculated. The agreement between theory and experiment is good. The p differences also occur in combination with s terms in one series, and a second, somewhat faint group possibly with s term differences has been discovered, but it was not possible in this group to measure the Zeeman effect. A table is given of the Zeeman effect for lines in the chromium spectrum. W. E. G.

Spectral Series and Ionisation and Resonance Potentials of Chromium and Molybdenum. M. A. CATALAN (*Compt. rend.*, 1923, 176, 1063—1065).—One system of series of triplets of the arc spectrum of molybdenum has already been given (this vol., ii, 105) and a second parallel series is now tabulated. The diffuse term is also quintuple and the diffuse triplets are formed by nine components. By means of the terms $1s$ of chromium and molybdenum (54640·9 and 57420·4) the ionisation potentials of these elements are found to be 6·7 and 7·1 volts, respectively. The first resonance potentials calculated from the triplets λ 4254, 4275, 4290, and λ 3798, 3864, 3902 are 2·89 and 3·19 volts from chromium and molybdenum, respectively. G. F. M.

The Existence of New Lines, including a Sommerfeld Doublet, excluded by the Principle of Selection in the L -series of the Heavy Elements. PIERRE AUGER and A. DAUVILLIER (*Compt. rend.*, 1923, 176, 1297—1298).—A record of observations of new lines in the X-ray spectra of certain heavy elements. They correspond with the combinations M_4L_1 and M_5L_1 , the former forming a Sommerfeld doublet with the β_{11} line. Details are also given of twenty-five L lines in the spectrum of tantalum and of 4 K lines in that of ruthenium. H. J. E.

An Extension of the Fundamental Ultra-red Absorption Band of Hydrogen Chloride. W. F. COLBY, C. F. MEYER, and D. W. BRONK (*Astrophys. J.*, 1923, 57, 7—19).—The fundamental absorption band of hydrogen chloride at $3\cdot4\mu$ has been further studied (cf. A., 1922, ii, 5) and extended from $3\cdot9$ to $4\cdot2\mu$ by the aid of a grating having 2,800 lines to the inch. Seven new principal lines have been measured, and a series of faint lines has been discovered between the principal lines in the region $m = -12$ to $m = -17$. The possibility of these faint lines being Rowland ghosts, Lyman ghosts, or secondary reflections is discussed and rejected. They are observed only when the gas is heated at about 500° . A table and a diagram of the thirty-nine lines of the entire known spectrum of hydrogen chloride are given, and revised constants have been computed for Kratzer's theoretical formula. A. A. E.

The Effect of certain Dissolved Substances on the Ultra-red Absorption of Water. J. R. COLLINS (*Physical Rev.*, 1922, 20, 486—498).—In a study of the absorption of water from 0·8 to 2·3 μ , the wave-lengths of maximum absorption were found to be 0·97, 1·20, 1·44, and 2·00 μ , the corresponding coefficients of absorption being 0·448, 1·220, 29·4, and 103, respectively. In the absorption spectrum of water vapour, the bands at 1·44 and 2·00 μ are stronger, and the other two bands weaker than for liquid water; it is suggested that the former and the latter bands are associated with different kinds of molecules. The ultra-red absorption spectra of aqueous solutions of the following substances from 0·8 to 2·3 μ have been determined: sodium, potassium, and lithium hydroxides; aluminium, calcium, magnesium, sodium, and strontium chlorides; silver, aluminium, magnesium, ammonium, and zinc nitrates; aluminium and zinc sulphates; sodium thiosulphate. In all cases, the solutes decreased the absorption in the water band at 1·44 μ and probably also in that at 2·00 μ , whereas all except aluminium and zinc sulphates and the hydroxides increased the absorption in the bands at 0·97 and 1·20 μ . The results do not agree with the solvate theory which ascribes the effect to the formation of hydrates.

A. A. E.

Absorption of Potassium Vapour. A. L. NARRAYAN and D. GUNNAYYA (*Phil. Mag.*, 1923, [vi], 45, 831—834; cf. A., 1922, ii, 679).—The absorption spectrum of potassium vapour has been studied at high vapour densities up to 950° with the view of extending the Balmer series for this element. Between 750° and 800°, this series could be observed up to the thirtieth member, and at slightly higher temperatures evidence of the presence of some members of the diffuse series was obtained. In the red-channelled spectrum 15 bands were measured.

W. E. G.

The Fluorescence and Channelled Absorption Spectra of Cæsium and other Alkali Elements. J. C. MCLENNAN and D. S. AINSLIE (*Proc. Roy. Soc.*, 1923, [A], 103, 304—314).—Experiments are described showing that potassium vapour, in addition to the banded fluorescence and absorption spectra observed by Wood and Carter (*Physical Rev.*, 1908), possesses a closely-banded absorption spectrum in the region of wave-lengths λ 8625—8200 Å., longer than that of the first member, λ 7699·01 Å., of its doublet series, and also a more widely spaced one in the region, λ 4500—4150 Å., of the second member of the series. The channelled absorption spectrum of rubidium was shown to consist of at least seventeen bands, four additional to those observed by Carter (A., 1910, ii, 672) and to extend from λ 6700 Å. to λ 7100 Å. The fluorescence spectrum of rubidium was found to consist of a wide band between λ 6540 Å. and λ 7100 Å. It was channelled on the long wave-length side, but continuous on the side of shorter wave-lengths. With cæsium vapour, a channelled absorption spectrum consisting of bands at $\lambda\lambda$ 7585, 7659, 7706, 7749, and 7778 Å., was found, and a fluorescence spectrum consisting of an unresolved band extending from about λ 7540 Å. to λ 8000 Å. Lithium probably possesses

a banded absorption spectrum in the ultra-violet. It is considered very probable that the complete fluorescence and channelled absorption spectra of caesium and rubidium have the same characteristics as the corresponding spectra of sodium and potassium. J. S. G. T.

Rare Earths. XIII. Absorption Spectra. L. F. YNTEMA (*J. Amer. Chem. Soc.*, 1923, **45**, 907—915).—The absorption spectra of solutions of chlorides of praseodymium, neodymium, samarium, dysprosium, holmium, erbium, and thulium in the visible region have been measured at various concentrations and thicknesses of solution. Absorption curves have been drawn and the last appearance of each band on dilution has been tabulated. In the case of praseodymium, five bands are recorded with maxima at $\lambda\lambda$ 4441, 4690, 4891, 5890, and 5974 Å.; with neodymium twenty-two bands were photographed with maxima at $\lambda\lambda$ 3803, 4185, 4273, 4331, 4612, 4691, 4755, 4803, 5091, 5123, 5205, 5222, 5319, 5726, 5748, 5782, 6228, 6251, 6286, 6374, 6786, and 6877 Å., and in addition faint bands were observed by visual methods at 4293, 4869, 5253, 5731, 5816, 5823, 5888, and 6720 Å. The band 5816 is stated by Baxter and Chapin to occur only in nitrate solutions, and the band 5470, which also occurs in nitrate solutions, was not observed in the present work (A., 1911, ii, 285). With samarium, bands were photographed with maxima at $\lambda\lambda$ 3740, 3905, 4013, 4071, 4154, 4177, 4411, 4636, 4794, 4893, 4995, 5297, and 5594 Å., and faint bands were also found by visual methods at $\lambda\lambda$ 4509, 4744, 5277, and 5572 Å. Seven bands were photographed with dysprosium, the maxima lying at $\lambda\lambda$ 3800, 3873, 3990, 4275, 4502, 4534, and 4754 Å., and a faint band found visually at λ 4778 Å. Twenty-two bands are recorded for holmium, the maxima lying at $\lambda\lambda$ 3865, 4159, 4174, 4192, 4220, 4273, 4505, 4522, 4549, 4678, 4735, 4799, 4831, 4853, 4910, 5365, 5435, 5493, 6405, 6433, 6530, and 6567 Å. Nineteen bands were photographed for erbium with maxima lying at $\lambda\lambda$ 4050, 4060, 4072, 4104, 4123, 4422, 4479, 4537, 4555, 4849, 4871, 4913, 5208, 5232, 5416, 5490, 6490, 6526, and 6669 Å., and two faint bands at $\lambda\lambda$ 5396 and 5515 Å. observed visually. Thulium gives four bands with maxima at $\lambda\lambda$ 4643, 6588, 6835, and 6999 Å. It is pointed out that the close coincidence of the two holmium bands at $\lambda\lambda$ 4273 and 4505 Å. with the dysprosium bands at $\lambda\lambda$ 4275 and 4502 Å. may lead to confusion in the identification of either element in the presence of the other. A method for the quantitative estimation of the rare earths is outlined, which consists in diluting the mixture until the most persistent band has disappeared and taking the ratio between the equivalent thickness of the last appearance in the mixture and in the pure salt. There appears to be no definite periodic arrangement of the absorption bands. J. F. S.

Production of Narrow and Broad Bands in the Absorption Spectra of Substances in Solution and in the Vapour State.

VICTOR HENRI (*Compt. rend.*, 1923, **176**, 1142—1145).—From a comparative study of a large number of organic compounds, the following general rules were deduced. A substance having only a single double bond in its molecule, *e.g.*, $C=C$, $C=O$, $C=N$,

or $\text{N}=\text{O}$, has only broad bands in its absorption spectrum both in solution and in the state of vapour. A substance with a single molecule containing two or more double bonds either adjacent or conjugated presents numerous narrow bands both in solution or as vapour, distributed in series conforming with the theory of quanta. If the two double bonds in molecules of this type are separated by the introduction of CH_2 -groups, the narrow bands fuse together, and only broad bands appear in the spectrum. If the molecule is weighted by the introduction of more and more complicated atomic groups, the narrow bands are widened, and eventually form themselves into broad, continuous bands. Examples of these changes are given in acraldehyde, crotonaldehyde, and mesityl oxide, mono- and di-substitution products of benzene, etc. The mechanism of the production of these bands is discussed, and it is concluded that for molecules containing only a single double bond the first postulate of Bohr does not apply, and only the second is valid, whilst for molecules with two neighbouring double bonds both postulates apply, the first being determined by the existence of an electric polarity in the molecule. G. F. M.

The Ultra-violet Absorption Spectrum of Chlorobenzene Vapour. Determination of the Molecular Structure. VICTOR HENRI (*Compt. rend.*, 1923, 176, 1298—1301).—A more complete study of the absorption spectrum resulted in the measurement of more than seven hundred and fifty bands between 2755 and 2262 Å., the greater number of these being observed at a pressure of 3 mm. The spectrum consists of eight groups of bands each of which is made up of several series. The conclusion is drawn that the molecule has two separate moments of inertia in relation to two axes of rotation; one of these corresponds with that of benzene and is about an axis passing through the CCl -group and the CH -group in the para-position with respect to it, the other is smaller and perpendicular to this. The molecule is regarded as a flattened octahedron, the centre of gravity of the CCl -group being half the distance of that of the opposite CH -group from the median plane. H. J. E.

Relation between Absorption and Structure. IV. Structure and the Absorption of Light of Acid Additive Products of Benzylideneimines. V. A. IZMAILSKI (*J. Russ. Phys. Chem. Soc.*, 1918, 50, 167—189; cf. A., 1915, ii, 198; 1916, i, 287).—The absorption spectra of different acid salts of various substituted benzylideneanils are measured, and the structure of these salts discussed from these data. In view of the fact that many of these salts can exist in two chromoisomeric forms, so-called meso-formulæ are given them, as follows :



where X is an acidic radicle and the broken lines represent partial valency linkings. Those substances in which the para-position in the aldehydic benzene ring is occupied by atoms or groups more

unsaturated with regard to valency than the corresponding carbon atom, as, for example, the amino- and dimethylamino-groups, exhibit more strongly marked tendencies to exist in forms represented by the two meso-formulæ shown above. Absorption of light by organic substances is concluded to be due, not to any particular group or radicle of the molecule, but to be a function of the molecule as a whole, as is shown by the very similar absorption constants obtained for *p*-dimethylaminobenzylideneanil, $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{NPh}$, and benzylidene-*p*-dimethylaminoanil, $\text{CHPh} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2$. Absorption curves are drawn for the following substances: Benzylideneanil, its sulphate, and its hydriodide, which exists in two forms; for diphenylmethylenephénylimine, $\text{Ph}_2\text{C} \cdot \text{NPh}$, its hydriodide and hydrobromide; for *p*-dimethylaminobenzylideneanil, its hydrobromide, dihydrobromide, acetate, and diacetate, and for benzylidene-*p*-dimethylaminoanil. R. T.

The Absorption Spectra of Vegetable Dyes of the Flavone Series. I. YUJI SHIBATA and KENSHÔ KIMOTSUKI (*Acta Phytochim.*, 1923, 1, 91—104).—The vegetable colouring matters of the flavone series show two characteristic absorption curves in the ultra-violet, and since the position of these bands is affected by the number and orientation of the hydroxyl groups, the ultra-violet absorption spectra serve as a ready means of identifying the different members of the series. The observations are best made in 1/10,000 molar alcoholic solution. Flavone itself has the two bands at frequencies 3500 and 4050. The position of the second band is scarcely influenced by hydroxyl groups, but the first is shifted towards the red by hydroxyl groups in the benzopyrone nucleus, and in the opposite direction by hydroxyl in the side phenyl group. Moreover, the depth of this band increases with the number of hydroxyl groups, as in the series kaempferol, quercetin, myricetin, containing, respectively, one, two, and three hydroxyls in the side phenyl group. Acetylation neutralises the influence of the hydroxyl groups, and diacetylchrysin and penta-acetylquercetin have exactly the same absorption spectrum as flavone.

In chrysin, apigenin, and luteolin, the head of the first absorption band is near 3500; chrysin is exceptional in that the second band is also shifted considerably towards the red. Galangin, kaempferol, and kaempferide form a closely-related group with the first band at 2650. In quercetin, isorhamnetin, and myricetin, this band is also at 2650 but is deeper.

The absorption bands of the flavone colouring matters from seventeen different plants were examined, and by comparison of the curves obtained with those of the above substances it was possible to determine to what type the unknown substances belonged. Exact correspondence was not obtained, probably on account of impurities in the plant preparations. E. H. R.

Absorption Spectra of Pyrrole and its Derivatives. I. The Absorption Spectrum of Pyrrole. T. V. KORSHUN and KLARA VLADIMIROVA ROLL (*J. Russ. Phys. Chem. Soc.*, 1917, 49, 153—156).—The absorption spectrum of pyrrole is found to contain

two bands, occurring at $1/\lambda$ 3200—3500, and $1/\gamma$ 3750—4000, these positions being close to those found for pyrrole derivatives at concentrations more than a thousand times smaller. These bands were not observed by Hartley and Dobbie (T., 1897, **73**, 603), who used weaker solutions, or by Purvis (T., 1910, **97**, 1657), who did not take readings of the part of the curve corresponding with the second band. The existence of these bands confirms Valiaschko's law (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1820), that the absorption spectra of cyclic substances are essentially a feature of the nucleus, and that substitution merely intensifies and modifies them. R. T.

The Low-voltage Arc in Mercury Vapour and its Relation to Fluorescence. Y. T. YAO (*Physical Rev.*, 1923, [ii], **21**, 1—21).—The effect of initial emission velocities of electrons on minimum ionising potentials is examined, and a proof of the fundamental importance of the critical point of 4.9 volts for mercury vapour is held to have been obtained. Low voltage arc phenomena were studied under identical conditions for the two cases, (a) when the vapour was very near to the liquid surface, and (b) when it was far removed from it. The difference (about 1.2 volts) in the minimum voltage for maintenance of the arc, together with the known dependence of fluorescence on the continuance of distillation of mercury, demonstrate the close relation existing between the production of arcs and the excitation of fluorescence and resonance radiation in mercury vapour. It is suggested that there may be some influence, due either to the arrangement of internal electrons or to the influence of neighbouring molecules, which increases the probability of ionisation along the $1S\text{--}mp_2$ path as compared with the $1S\text{--}mP$ path in freshly distilled vapour, but that this influence does not appreciably affect the potential energy of the electron in the $1S$ state. A. A. E.

Phosphorescence Caused by Active Nitrogen. E. P. LEWIS (*Nature*, 1923, **111**, 599—600).—Active nitrogen excites a green or bluish-green phosphorescence in a number of solid substances; the spectra are nearly all continuous. A strong effect is produced with uranium nitrate, uranium ammonium fluoride, zinc sulphide, barium chloride, strontium chloride, calcium chloride, and caesium chloride, whereas a weak effect is given by lithium chloride, sodium chloride, potassium chloride, sodium iodide, potassium iodide, sodium carbonate, and strontium bromide. The phenomenon may be due to chemical reaction with the active nitrogen, or to the presence of free electrons. A possible reason for the afterglow is briefly discussed, it being suggested that if there is enough oxygen present to remove most, but not all, of the electrons, recombination may proceed slowly, the spectrum of the afterglow being due to the recombination of electrons with positive molecular ions. A. A. E.

The Establishment of Einstein's Equivalence Law, and its Significance in Photochemical and Chemical Processes. FRITZ WEIGERT (*Z. Physik*, 1923, **14**, 383—409).—Einstein's

thermodynamic deduction of the photochemical equivalence law is based on the conception of an ideal perfectly reversible photochemical reaction, and leads to the relation $Q=Nh\nu$ between the heat tone, Q , of the reaction and the number of quanta N absorbed in the reaction. It is shown that a stable photochemical equilibrium is a physical impossibility. Einstein's expression for the velocity of a photochemical reaction may be quantised only when component reactions of a non-photochemical nature are eliminated from consideration in the complete reaction. Under these conditions, the equivalence law for the primary photochemical reaction is expressed in the form $q=Nh\nu$, q being the energy absorbed in the primary process. Alternatively, the law may be expressed in the form $q=\Sigma nh\nu$, where $N=\Sigma n$. The mode of deduction of the result does not differentiate between equilibrium in a photochemical or thermodynamic system, and it is concluded, therefore, that N energy quanta are absorbed in any molecular chemical or photochemical process. The fundamental equation $u_{\nu,T}=8\pi h\nu^3 \cdot e^{-Nh\nu/RT} \cdot /c^3$ of the radiation hypothesis is deduced, and it is pointed out that the correlation by Arrhenius and others of the activating energy q with the thermochemical and optical properties of the system is not in agreement with the completely non-specific nature of the equation $q=Nh\nu$. The primary process in all chemical processes is conceived as consisting of the ejection of an electron from a quantised orbit accompanied by quanta of energy. Experiments indicate that absorption of radiation occurs in such a case only when the electron does not return to its original orbit, but enters a higher quantised orbit or becomes attached to another particle.

J. S. G. T.

Photo-chemistry of Potassium Permanganate. I. Application of the Potentiometer to the Study of Photochemical Change. E. K. RIDEAL and R. G. W. NORRISH (*Proc. Roy. Soc.*, 1923, [A], 103, 342—366).—Potassium permanganate solutions, when illuminated by ultra-violet light, undergo a marked change of electrode potential, which reverts slowly to its original value when the light is extinguished. The authors show that this change is due to an alteration in the hydrogen-ion concentration of the solution brought about by photochemical decomposition of the potassium permanganate, thus: $2\text{KMnO}_4=\text{K}_2\text{O}_2\cdot 2\text{MnO}_2+3\text{O}$. The compound $\text{K}_2\text{O}_2\cdot 2\text{MnO}_2$ is precipitated and a red sol of manganese dioxide and potassium manganite is formed. The decomposition is unimolecular over the range of concentration studied, and it is shown how the velocity constant can be calculated either from the changes of electrode potential during illumination or from the dark-recovery curve. Values of K determined by either of these methods are in very close agreement with the results of a spectrophotometric determination ($K=0\cdot00149$). A photochemical stationary state is produced in the solution owing to removal of potassium hydroxide by combination with hydrated manganese dioxide. The rate of decomposition of potassium permanganate is increased by the addition of sulphuric acid to the solution. In such solutions,

the reaction, throughout almost the whole of its course, is of zero order, the constant velocity indicating continuous complete absorption of the photoactive radiation. This change in the type of decomposition is connected with the non-formation of colloid in the acid solution. Ammonium nitrate, uranyl nitrate, and potassium hypochlorite solutions afford photoactive effects similar to those observed with potassium permanganate. A photolytic cell containing potassium permanganate and yielding an *E.M.F.* equal to 0.215 volt is described.

J. S. G. T.

The Photochemistry of Unstable Substances. EDMUND JOHN BOWEN (T., 1923, **123**, 1199—1206).

The Applications of Photography to Chemistry. PIERRE JOLIBOIS (*Bull. Soc. chim.*, 1923, [iv], **33**, 229—245).—A lecture delivered before the Strasbourg-Mulhouse section of the Société Chimique de France.

G. F. M.

Variation of the Photoelectric Activity of a Potassium Ferrocyanide Solution with Concentration. J. H. J. POOLE (*Phil. Mag.*, 1923, [vi], **45**, 895—906).—The effect of changes in the concentration of ferrocyanide solutions has been studied with the view of throwing light on the possible source of the photoelectron. The activity of the solution increases in a linear manner with increase in concentration, but at the higher concentrations the activity increases more rapidly than the concentration. This fact favours the view that the undissociated molecule is responsible for the photoelectric properties of the solution. Since potassium ferrocyanide was found to be nearly inactive in solution, the effect cannot have been due to the positive ion. When the activity is plotted along the ordinate against the number of undissociated molecules in the solution, a straight line is obtained for the lower concentrations, but the curve bends upwards, as before, for the higher values. Surface concentration effects do not appear to account for the phenomenon. An alternative explanation is suggested, which ascribes the increased photoelectric effect in concentrated solutions to association of the undissociated molecules. This is in agreement with the high photoelectric activity of the solid salt.

W. E. G.

Tracks of α -Particles in Helium. D. M. BOSE and S. K. GHOSH (*Nature*, 1923, **111**, 463—464).—Photographs have been obtained of the ionisation tracks of α -particles from polonium in helium. Both electrons are ejected on the same side of the α -particle track. Tracks indicating the collision of an α -particle with an atom more complex than hydrogen or helium may possibly originate from the breaking up of a nitrogen nucleus with the expulsion of a hydrogen nucleus.

A. A. E.

The Continuous Röntgen Spectrum. HELMUTH KULEN-KAMPFF (*Ann. Physik*, 1922, **69**, 548—595).—An investigation into the dependance of the intensities and spectral distribution of the continuous Röntgen rays on the atomic number of the metal forming the anticathode, and on the voltage of the cathode rays.

The Röntgen rays from the eight metals, aluminium, iron, cobalt, nickel, copper, silver, tin, and platinum, have been examined at the constant voltage, 10470 volts, over a wave-length $\lambda=1\cdot0$ to $\lambda=2\cdot8$ Å., and for two metals, silver and platinum, for the voltage interval, 7000 to 12,000 volts. Corrections were made to the observed intensities for the absorption in the aluminium window of the tube and in the adjoining air space, and for the absorption inside the anticathode material. The dependence of the reflecting power of the crystal on the wave-length of the Röntgen rays and the length of the ionisation chamber were also taken into account. The intensity maximum of the Röntgen rays is displaced slightly towards the shorter wave-lengths with increase in atomic weight. The intensity maximum and the total intensity is directly proportional to the atomic number of the element. The measurement of the intensity maxima and the total intensities for iron, cobalt, and nickel are made difficult by the presence of strong spectral lines, and by selective absorption on the short wave-length side of the maximum. When the specific intensity $J\gamma$ is plotted against $\gamma_0-\gamma$, the curves show a linear trend throughout the larger part of their course. The tangent to these curves is directly proportional to the atomic number, and on changing the potential (atomic number constant) a parallel series of curves is obtained. Thus, $J\gamma=\text{const.}(\gamma_0-\gamma)$, where the constant is dependent on the atomic number, and not on the potential. In the neighbourhood of the limiting frequency, a striking break in the curve occurs.

W. E. G.

Characteristic L Absorption of X-Rays for Elements of Atomic Numbers 62 to 77. J. M. CORK (*Physical Rev.*, 1923, [ii], 21, 326—333).—Compounds of samarium (62), gadolinium (64), dysprosium (66), erbium (68), ytterbium (70), tantalum (73), tungsten (74), osmium (76), or iridium (77) were uniformly distributed over a filter-paper and interposed between a Coolidge tube with a tungsten target and a calcite crystal. The emission lines of tungsten were used as reference lines for the measurement of the wave-lengths of the absorption edges. The following are tabulated: (a) The X-ray spectrum of tungsten, together with a proposed notation, based on the use for each emission line of a symbol designating the initial and final energy levels, e.g. $\lambda 1\cdot0596$, γ_3 (Siegbahn), x (Sommerfeld), is $L_3\gamma_5$. (b) The mean values of the observed wave-lengths, with values of ν/N and $\sqrt{\nu/N}$. (c) The L_2-L_1 regular doublet frequency differences expressed as $\Delta\nu/N$, exhibiting good agreement with values computed from Sommerfeld's formula, and the frequency differences of the L_β and L_α emission lines. (d) The energy levels of the various electronic orbits expressed in terms of ν/N . The expression $\sqrt{\nu/N}$ for L_1 , L_2 , and L_3 has been plotted as a function of the atomic number, and it is pointed out that the deviation of the curves from Moseley's linear relation may be qualitatively explained by taking into account the nuclear defect due to other electrons and the relativity correction. The observed results are in approximate agreement

with the empirical expression $\Delta(\nu/N) = KZ^5$, where Z is the atomic number, and K has the values 4.44×10^{-8} for L_2-L_1 , 1.97×10^{-9} for M_2-M_1 , and 9.60×10^{-9} for M_4-M_3 . A. A. E.

X-Ray Absorption Coefficients of Carbon, Hydrogen, and Oxygen. A. R. OLSON, ELMER DERSHEM, and H. H. STORCH (*Physical Rev.*, 1923, [ii], 21, 30—37).—The work of Aurén (A., 1919, ii, 89), in so far as it appeared to disclose a large discrepancy between the absorption coefficients for non-homogeneous X -rays of graphite and carbon in organic combination, would likewise suggest a difference in the case of aromatic and aliphatic carbon; it has therefore been repeated for the cases of water, benzene, toluene, xylene, mesitylene, heptane, and cyclohexanol. The variation with wave-length between 0.35 and 0.98 Å. is in all cases in accordance with the equation $\mu = A + B\lambda^3$, where (for a gram-molecule in a cell of 1 cm.² cross-section) the values for A are 3.5, 15.3, 19.0, 21.7, 24.2, 21.5, and 20.5, respectively, and for B , 44.5, 74.9, 85.3, 98.3, 113.6, 87.3, and 121.0, respectively. The mass absorption coefficients of hydrogen, carbon, and oxygen for X -rays of wave-lengths from 0.25 to 0.98 Å. are computed as follows: $\mu_H = 0.37 + 0.28\lambda^3$; $\mu_C = 0.18 + 1.01\lambda^3$; $\mu_O = 0.16 + 2.785\lambda^3$. These results are in direct contradiction to those of Aurén (*loc. cit.*), and constitute a proof of the additive law. The identity of the constants for the group CH_2 when involving carbon in the aliphatic or aromatic condition, or both, lead to the conclusion that the absorption coefficients of aliphatic carbon, aromatic carbon, and graphitic carbon are the same for wave-lengths less than 1 Å.

A. A. E.

Absorption Coefficients for Homogeneous X-Rays. E. G. TAYLOR (*Physical Rev.*, 1922, 20, 709—714).—The effect of the interposition of a cell containing a known thickness of various liquids before lead slits and a calcite crystal, by means of which only slightly divergent K_α rays from the molybdenum target of a Coolidge tube were reflected into an ionisation chamber, was measured. The following results were obtained for the molecular absorption: pinene, 1.209×10^{-24} ; limonene, 1.206×10^{-24} ; benzene, 0.707×10^{-24} ; toluene, 0.834×10^{-24} ; isopropyl alcohol, 0.683×10^{-22} ; methyl propionate, 1.089×10^{-22} ; ethyl acetate, 1.099×10^{-22} ; acetone, 0.679×10^{-22} ; ethyl formate, 0.970×10^{-22} ; trimethylene glycol, 0.986×10^{-22} . Atomic absorption coefficients for X -rays $\lambda 0.715$ Å. are computed as follows on the assumption that absorption is an additive atomic property: carbon, 0.1134×10^{-22} ; oxygen, 0.304×10^{-22} ; hydrogen (calculated from hydrocarbons), 0.0048×10^{-22} . There are, however, indications that the assumption may not be accurately true. Moreover, when the atomic absorption of oxygen is subtracted from the molecular absorption of water, 0.322×10^{-22} , a value is found for the absorption of hydrogen approximately twice that determined from the hydrocarbons; the cause may possibly lie in a difference in the strength of the bond uniting the hydrogen to the other elements of the

compound. The atomic absorption of aluminium is found to be 2.29×10^{-22} .
A. A. E.

The Adsorption of the -B and -C Members of the Radium and Thorium Series by Ferric Hydroxide. JOHN ARNOLD CRANSTON and ROBERT HUTTON (T., 1923, 123, 1318—1324).

Origin of Radioactive Disintegration. S. ROSSELAND (*Nature*, 1923, 111, 357; cf. Pease, A., 1922, ii, 757).—In view of the fact that the life-periods of the elements at the beginning of the disintegration series are large, it is possible that the nuclei may be intrinsically stable, the radioactivity of these elements being due to the action of an external field of force originating in the surrounding electrons. In the case of rubidium and potassium, radioactivity might be due to an enhanced efficiency of the perturbations due to resonance in the interaction between nuclear and electronic motion. Consideration of the relative order of magnitude of the diameter of the nucleus and the shortest distance from the nucleus attained by electrons does not appear to exclude the possibility that the existence of radioactivity among elements of high atomic number, and the non-existence of elements of atomic number greater than that of uranium, may be connected with some kind of interaction between the nuclear and external electrons. It is suggested that the nucleus as a whole will rotate, and that this rotational frequency may be comparable with some electronic frequency, the case in which the nucleus rotates with an angular momentum of $\hbar/2\pi$ (when the rotational frequency,

$$w = (\hbar/4\pi^2)(1/Ma^2),$$

where M and a are, respectively, the nuclear mass and radius of gyration about the axis of rotation) being specially considered.

A. A. E.

Ionisation by Collision in Helium. J. S. TOWNSEND (*Phil. Mag.*, 1923, [vi], 45, 1071—1079).—The ionisation of argon and helium by the collisions of electrons and positive ions with molecules of the gas was investigated by Gill and Pidduck by measurements of conductivity between parallel plates (cf. A., 1912, ii, 515). It was found that the processes of ionisation follow the same general laws as had been found previously for other gases. These experiments are not in agreement with modern views on the mode of development of currents in monatomic gases, or with the determination of resonance or ionisation potentials by the valve method. The conductivity between parallel plates should change in a well defined series of steps as the potential increases. In experiments, repeating the earlier work, no such effects have been observed. It is shown that the energy required to ionise a molecule of helium is approximately 12 volts, and the sum of the energies of the electron which ionises the molecule and the electron which is set free is 16.6 volts, after the collision. On the other hand, from the valve experiments, ionisation of a molecule of helium takes place on collision with an electron provided the energy of the electron exceeds a minimum value 21 and 25 volts, and it has been con-

cluded that this number of volts represents the loss of energy of an electron when it ionises a molecule. This is not supported by the evidence from the parallel plate experiments. W. E. G.

Thermionic Effects Caused by Alkali Vapours in Vacuum Tubes. IRVING LANGMUIR and K. H. KINGDON (*Science*, 1923, 57, 58—60).—Metallic caesium in a vacuum tube forms an adsorbed film consisting of a single layer of atoms completely covering the tungsten filament even at filament temperatures of 600° K. or more, the electron affinity of a tungsten surface being greater than that of caesium-ions (4.52 and 3.90 volts, respectively). The presence of minute traces of certain electro-negative gases increases the tendency of caesium to be held by such a surface, so that the film then remains intact up to about 900° K.; at higher temperatures the film partly evaporates and the electron emission falls rapidly. When a tungsten filament is heated above 1000° K. in caesium vapour at room temperature, the electron emission falls to negligible values, since there is a linear relation between the fraction of the surface covered by caesium and the logarithm of the saturation current. Caesium evaporates from the film at 1000° K. in the form of neutral atoms, since the electron affinity of a surface partly covered by caesium may be less than that of a caesium atom. The measurement of the ion generation may be applied to the accurate determination of the vapour pressures of alkali metals. When a thoriated tungsten filament is used in experiments with caesium vapour, both the electron emission and the ion generation disappear if the filament is first given a heat treatment by which an adsorbed film of thorium is brought to the surface, the electron affinity of a fully active thoriated filament being only 2.94 volts. Rubidium vapour is similar to caesium in its effects. A. A. E.

Rate of Evaporation of Electrons from Hot Filaments. WORTH H. RODEBUSH (*J. Amer. Chem. Soc.*, 1923, 45, 997—998).—In a previous paper (this vol., ii, 303) the author derived an equation from statistical mechanics for the rate of evaporation. This equation had the form $\bar{N} = N\sqrt{RT/E_0\pi} \cdot e^{-E_0/RT}$, and was tested for the rate of evaporation of electrons from a hot filament by placing $E_0 = \phi$, where ϕ is the thermionic work function. Further consideration has shown that E_0 should be set equal to $\phi + 2RT$. In the present paper, this has been done, and the equation tested for the cases of tungsten, tantalum, and molybdenum, using data obtained by Langmuir. The calculated value of A is very close to the experimental value. If this equation is generally true, it furnishes a relation between the thermionic work function and the thermoelectric force. The thermionic work function being known, the contact potential between metals can be calculated from the thermoelectric data. J. F. S.

New Evidence regarding the Interpretation of Critical Potentials in Hydrogen. P. S. OLMSTEAD (*Physical Rev.*, 1922, 20, 613—630).—An experimental separation of the effects due to the atom and those due to the molecule has been effected. Bohr's

atom has been closely verified, both the first and second radiation potentials (10.1 and 12.2 volts, respectively), corresponding with the first two terms of the Lyman series having been obtained. Ionisation of the molecule is observed at 11.5 volts, and of the atom at 13.6 volts; dissociation of the molecule and radiation at 12.9 volts; and dissociation of the molecule with ionisation of one of its parts at 16.0 volts. The existence of two ionising potentials of the molecule has thus been conclusively proved, and the energy required for the dissociation of the molecule is shown to be equivalent to about 2.8 volts. A. A. E.

The Dielectric Constants of some Aqueous Solutions and their Explanation by the Dipole Theory of Debye. REINHOLD FÜRTH (*Ann. Physik*, 1923, 70, 63—80).—The Drude method is employed, with aqueous alcohol and benzene as the calibrating liquids. The values for dextrose, lævulose, sucrose, carbamide, glycine, "saccharin," gelatin, albumin, and a number of substances of technical and biological importance are given. The Debye theory has been applied to correlate these results. If the dielectric constant of the solute is greater than that of the solvent, the increase in viscosity which occurs with increasing concentration should lead to three types of curves, and only one type would be anticipated if the dipole moment of the solute is smaller than that of the solvent. All three types of curves have been realised in this work. For colloidal solutions, the Debye viscosity formula is in good agreement with the results. For crystalline substances, it is not possible to derive the dielectric constant of the solute from the "mixture law." The dielectric constant of dilute solutions of electrolytes should be the same as for water, but should increase with increase in concentration. W. E. G.

The Conductivity of Highly Dissociated Binary Electrolytes. W. MUND (*Bull. Soc. chim. Belg.*, 1923, 32, 156—178).—The Ghosh theory of electrolytes (T., 1918, 115, 449, 627, 707; 1920, 117, 823, 1390), although applicable to salts, does not appear to be sufficiently trustworthy in the case of acids and bases. The author's development of the theory leads to somewhat different results which are claimed to be more in accordance with the experimental facts; his final equation expresses as a function of the observed conductivity of an electrolyte, the ions of which have different mobilities, the work done in completely dissociating a gram-molecule of a symmetrical electrolyte at the same concentration. The general equation thus obtained closely resembles that of Ghosh (T., 1918, 115, 455). An alternative equation is obtained by modifying the Ghosh equation by the factor 0.84. The latter is in close accord with many of the experimental cases studied, but scarcely applies to the case of acids and bases. The former gives results for these substances which agree with the experimental results. H. J. E.

Dissociation of Strong Electrolytes in Very Dilute Solutions. PHILIPP GROSS and OTTO REDLICH (*Z. physikal. Chem.*, 1923, 104, 315—322).—A theoretical paper in which the validity of the law

of mass action in connexion with solutions of strong electrolytes is discussed along with the measurements of Washburn and his formulation of a dilution law (A., 1918, ii, 55, 56). The authors are of the opinion that whilst the measurements of the electrical conductivity of dilute solutions of potassium chloride by Washburn are not likely to be improved, yet they nevertheless do not give an unequivocal confirmation of his assumption $\lim_{c \rightarrow 0} dk/dc = 0$. On the other hand, these measurements do not disprove this assumption. It is thought to be unlikely that the validity or otherwise of Washburn's assumption can be furnished by direct experimental proof, but it may be furnished by the establishment of a theoretically deduced dilution law. J. F. S.

The Polarisation of Electrodes. II. J. E. VERSCHAFFELT (*Rec. trav. chim.*, 1923, 42, 332—336; cf. this vol., ii, 115).—A theoretical paper in which it is shown mathematically that there is, in electrolysis, no proportionality between the current density and the effective *E.M.F.* The author points out that, if his equation does not hold, the current density increases in smaller and smaller proportion to the increase of electromotive force, as if the resistance were increasing and finally tends towards a limiting value. In practice, this would only be observed in the case of electromotive forces much greater than those usually applied. H. J. E.

Ghosh's Theory of Strong Electrolytes. ADA PRINS (*Chem. Weekblad*, 1923, 20, 237—242).—A critical discussion of the theory, comparing actual experimental results with figures deduced from Ghosh's postulates. Agreement is good, but the theory needs extension and modification. S. I. L.

Electrometric Investigation of the Action of Normal Salts on the Potential of the Hydrogen Electrode. V. A. ARKADÉEV (*Z. physikal. Chem.*, 1923, 104, 192—202).—The influence of normal salts on the potential of the hydrogen electrode has been investigated at ordinary temperatures (16—18°) by measuring the *E.M.F.* of the following elements: $H_2|0.1N, HBr, KNO_3(c)||KCl||NKCl, Hg_2Cl_2|Hg$; $H_2|0.1NHBr, KCl(c)||KCl||NKCl, Hg_2Cl_2|Hg$; $H_2|0.1NHBr, KBr(c)||KCl||NKCl, Hg_2Cl_2|Hg$; $H_2|0.1NHBr, NaCl(c)||KCl||NKCl, Hg_2Cl_2|Hg$; $H_2|0.1NHBr, LiCl(c)||KCl||NKCl, Hg_2Cl_2|Hg$, and $H_2|0.1NHBr, LiBr||KCl||NKCl, Hg_2Cl_2|Hg$. The influence of the normal salt is shown chiefly to consist in bringing about an increase in the potential of the hydrogen electrode which increases parallel with the concentration *c* of the normal salt. Only in the case of potassium nitrate and chloride is a slight change of potential observed in the opposite direction, and this is only when the concentration of the normal salt is small, (0.4—0.75*N*). For equivalent concentrations, the effect increases parallel with the ability of the normal salt to form hydrates (NaCl, LiCl, LiBr). Salts with the same anion as the acid of the electrode have a stronger influence than the corresponding salts of another anion, thus KBr and LiBr have a stronger effect than KCl and LiCl, respectively. The liquid contact potential in all the above measurements has been eliminated by

Bjerrum's method (A., 1905, ii, 793) which consists in using a bridge containing potassium chloride of concentrations $3.5N$, $1.75N$, and N and from the three values extrapolating the correction necessary to eliminate this value entirely. J. F. S.

The Slope of Current-Tension Curves in Electrolysis. A. H. W. ATEN (*Rec. trav. chim.*, 1923, 42, 337—354).—A theoretical paper in which are represented curves showing the limiting current as a function of the concentration of an added indifferent electrolyte, the current density as a function of potential under different conditions, and ionic concentration as a function of current density. H. J. E.

Electrolysis of Bromine Solutions of Phosphorus Pentabromide. V. A. PLOTNIKOV (*J. Russ. Phys. Chem. Soc.*, 1917, 49, 76—81; cf. A., 1915, ii, 508).—When electrolysed in bromine solution, phosphorus pentabromide gives rise to the ions P^{++++} and Br' .

A 20% solution placed in an *E.M.F.* apparatus with platinum electrodes shows a steady current of about 97 milliamperes, the nature of the liquid remains unchanged, and there is no polarisation. When a current of 570 milliamperes is passed through the same solution, the temperature rises considerably, owing to the reaction between the liberated phosphorus kations and the solvent.

When a saturated solution is similarly electrolysed, the current, at first equal to 130 milliamperes, quickly drops down to 4 milliamperes; on reversing the current, it again becomes 130, but begins to drop in the same way; this is due to the formation round the cathode of a crust of phosphorus pentabromide which cannot dissolve in the already saturated solution.

The formation of Br' anions is shown by means of Bruner and Bekier's silver electrodes (cf. A., 1912, ii, 732) when it is found that the cathode does not change in weight while the anode increases roughly in accordance with Faraday's law. G. A. R. K.

Electrolysis in Liquid Sulphur Dioxide. M. CENTNERSZWER and J. DRUCKER (*Z. Elektrochem.*, 1923, 29, 210—214).—In continuation of the work of Walden and Centnerszwer (A., 1902, ii, 245), the authors have investigated the electrolysis of solutions of various iodides in liquid sulphur dioxide, employing a platinum gauze cathode. In the cases of a 5% solution of potassium iodide and a 2% solution of sodium iodide, electrolysed at about -20° , unstable products were formed at the cathode. Potassium or sodium, respectively, was probably first deposited, and combined with the solvent to form hyposulphite which then decomposed, forming thiosulphate and pyrosulphite. Whilst no deposition of sulphur at the cathode was observed in the case of these two solutions, such deposition did occur when pure dry liquid sulphur dioxide was electrolysed by means of a high tension current, confirming Walden's contention that positive sulphur-ions are formed by the electrolytic dissociation of liquid sulphur dioxide.

J. S. G. T.

Electrolytic Processes in the Presence of Colloids. I. The Electrolysis of Zinc Sulphate. NIKOLAI ALEXEIEVITSCH IZGARYSCHEV and P. S. TITOV (*J. Russ. Phys. Chem. Soc.*, 1917—1918, 49, 573—595).—The electrolysis of normal solutions of zinc sulphate was studied in the presence of varying amounts of gelatin or gum arabic, 1% of boric acid being added in all cases to prevent the formation of basic zinc sulphate; different current densities were used and the electrode (cathode) potentials were measured before and during the passage of the current, the results being expressed in the form of polarisation curves (cf. Izgaryshev, A., 1916, ii, 7); the viscosity and electrical conductivity of the solutions were noted at the same time. It is shown that a certain concentration of colloid corresponds with a maximum cathode polarisation and a minimum equilibrium potential; the same concentration corresponds with a break in the viscosity curves of the solutions, the viscosity increasing more rapidly with rise of concentration after that point. It is suggested that the colloid forms complexes with the kations of the electrolyte, a small amount of gelatin being associated with a large amount of zinc-ions, the proportions being about 1:100—200 by weight; the SO_4^{--} -ions do not appear to form such adsorption compounds, probably because they are negatively charged like the particles of the colloid. The maximum polarisation corresponds with a point when all the zinc-ions present are adsorbed by the colloid to form the adsorption compound; further addition of gelatin to such a saturated solution produces little change. Similar results are obtained with gum arabic, with the exception that the viscosity curve shows no definite break. The effect of the colloid on the physical nature of the zinc deposited is discussed. G. A. R. K.

Electrolytic Processes in the Presence of Colloids. II. The Nature of the Metal-Colloid Complexes. N. A. IZGARYSCHEV (*J. Russ. Phys. Chem. Soc.*, 1918, 50, 225—229).—The nature of the colloidal metal complexes formed during the electrolysis of zinc sulphate, in the presence of gelatin or of gum arabic, is discussed. It is shown that in the case of gelatin these complexes must be formed by adsorption of zinc-ions by the gelatin molecules, since in a normal solution of zinc sulphate containing 0.25 g. of gelatin per litre each molecule of the latter must have attached to it about 12,500 ions of zinc, whereas only 780 ions per molecule could be accounted for by chemical combination. In the case of gum arabic, however, in similar circumstances, only 21 zinc-ions are attached to each colloid molecule, this being probably less than the number of ions with which it could combine chemically, although, at the same time, adsorptive influences also play some part in the formation of the complex. R. T.

Electrolytic Processes in the Presence of Colloids. III. The Heats of Formation of Zinc-Gelatin Complexes. N. A. IZGARYSCHEV and P. C. TITOV (*J. Russ. Phys. Chem. Soc.*, 1918, 50, 230—236).—The heats of formation of zinc-gelatin complexes, formed during the electrolysis in an atmosphere of hydrogen of zinc

sulphate solutions containing gelatin, are measured. These heats are calculated from the Helmholtz equation connecting heats of formation with *E.M.F.* It is hence found that the heat of formation of such complexes is -2150 cal., this value being obtained with solutions containing equivalent quantities of the colloid, i.e., with 0.025% solutions, whilst at greater concentrations greater heats of formation are found, due probably to heat of adsorption. The rate of adsorption of oxygen by solutions containing zinc dust is more than doubled by the addition of gelatin. R. T.

Electrolytic Processes in the Presence of Sugar. N. A. IZGARYSCHEV and D. V. STEPANOV (*J. Russ. Phys. Chem. Soc.*, 1918, **50**, 236—244).—The *E.M.F.* and anodal and cathodal polarisations obtained with zinc sulphate solutions containing various percentages of sugar are measured, and curves drawn showing the variations in these quantities as the proportion of sugar in the solutions varies. A maximum of polarisation is found, as when colloidal substances are used, but is much less distinct, and occurs with a 30% solution of sugar, whereas the same point is reached with a concentration of 2% of gum arabic or of 0.025% of gelatin. The curves for cathodal and anodal polarisation are symmetrical, and the values obtained are very close to each other. This is probably due to the action of the sugar being the same for both processes. From the curves, it is concluded that cathode process consists of the following: $(\text{Zn, sugar})'' \rightleftharpoons \text{Zn}'' + \text{sugar}$, $\text{Zn}'' \rightarrow \text{Zn}$, whilst the anodal process is $(\text{SO}_4, \text{sugar})'' \rightleftharpoons \text{SO}_4'' + \text{sugar}$, $\text{SO}_4'' \rightarrow \text{SO}_4$, $\text{SO}_4 + \text{Zn} \rightarrow \text{ZnSO}_4$. The zinc sulphate forms a molecular compound with sugar in the ratio of $1:1$. The conductivity of the solutions decreases rapidly with increasing concentration of sugar, and the presence of this substance does not affect the appearance of the metallic deposit obtained on the cathode. Similar measurements are made for zinc sulphate solutions containing brucine in place of sugar. This causes considerable polarisation, and the metal is deposited as a black sludge. R. T.

Electrolytic Processes in the Presence of Colloids. V. The Ultra-microscopical Examination of Metal-Colloid Complexes. N. A. IZGARYSCHEV and (MLLE) K. S. PONOMAREVA (*J. Russ. Phys. Chem. Soc.*, 1918, **50**, 245—254).—Colloid-metal complexes, formed by the addition of gelatin or of gum arabic to zinc or copper sulphate solutions, are examined ultramicroscopically, and the number of particles and of aggregations of particles per square centimetre of the field of vision determined. The number of aggregations is found to increase with increasing concentration of the colloids, up to their characteristic concentration (0.025% for gelatin, and 2% for gum arabic), and then remains stationary, whilst the number of separate particles either remains the same, as in the case of gelatin, or decreases, as in the case of gum arabic. The gelatin particles are not visible under the ultra-microscope, but become plainly visible on the addition of the metallic salt, indicating that each particle must have increased in

magnitude as a result of adsorption of zinc- or copper-ions. Such particles exhibit cataphoresis on the passage of a current. R. T.

Action of Colloidal Gelatin on Electrolytic Cadmium. E. MILLIAU (*Bull. Soc. chim. Belg.*, 1923, **32**, 143—150).—Electrolysis of a solution containing cadmium as compared with a similar solution to which gelatin has been added shows that the addition renders the metallic deposit brighter and increases its hardness. H. J. E.

Low Voltage Arcs in Diatomic Gases. I. Hydrogen, Nitrogen, and Iodine. O. S. DUFFENDACK (*Physical Rev.*, 1922, **20**, 665—687).—The current-voltage curves which have been obtained show that the breaking potential was always the ionising potential of the gas, namely, 16·3, 16·2, and 14·6 volts, respectively, the striking potential being greater. In the case of dissociated hydrogen and iodine, the arc could be maintained in normal and favourable circumstances, respectively, at 13·7, 10·0, and 12·1, 10·2 volts. The critical potentials agree with accepted results, and those associated with the atom and the molecule are experimentally distinguished. Spectroscopic investigations indicate that in the case of hydrogen the line spectrum is due to the atom and the band spectrum to the molecule. In the case of nitrogen, a flare was obtained which showed a strong spectrum of tungsten besides that of nitrogen (cf. Strutt, A., 1911, ii, 482); probably active nitrogen was formed. The positive bands appear to be due to the neutral molecule, the negative bands to the ionised molecule, and the lines to the atom. New negative bands were observed at 5075, 5018, and 4961 Å. In the case of iodine, the line spectrum only appeared in the arc. A. A. E.

The Evolution of the Molecule of Chromium Hydroxide in Contact with Water. (Mlle) SUZANNE VEIL (*Compt. rend.*, 1923, **176**, 1304—1305; cf. this vol., ii, 122).—The molecular coefficient of magnetisation of chromium hydroxide depends on the method of preparation. Variations in the value occur in the inverse sense to those obtained in the case of ferric hydroxide, but are smaller. H. J. E.

Photographic Registration of Critical Points and Irregularities in the Expansion of Liquids. C. MONTEMARTINI and L. LOSANA (*Gazzetta*, 1923, **53**, i, 89—94).—The authors describe an apparatus which, when adapted to the photographic registering device of Le Chatelier and Broniewski (*Rev. metall.*, 1912, **9**, 3, 134), permits of the accurate registration of singularities in the thermal expansion of liquids or solids and, hence, of rendering evident transformation points. A float suspended from one end of a balance beam is immersed in a liquid which can be gradually heated electrically. An adjustable counterpoise is attached to the other end of the beam, the oscillations of which are checked by means of a spiral spring. By means of a system of mirrors a ray of light is reflected from the beam on to a photographic plate, any irregularity in the expansion either of the material of the float or of the liquid being thus indicated. The apparatus has been applied

to the investigation of the maximum density of water, the expansion of sodium sulphate solution and of mixtures of quinine and cinchonine hydrogen sulphates, the allotropic transformation of sulphur, and the transformation of ammonium nitrate. T. H. P.

The Specific Heat of Carbon, Silicon, and Silicon Carbide at High Temperatures. A. MAGNUS (*Ann. Physik*, 1923, 70, 303—331).—The copper block calorimeter has been employed for the determination of specific heats between room temperature and 900°. The specific heats of graphite, silicon, and silicon carbide, the heat of adsorption of graphite in air and water, and the coefficient of expansion of silicon carbide have been measured. The atomic heats of the diamond, silicon, and silicon carbide can be represented over a wide range of temperatures by means of a Debye function, in which only one value of the characteristic temperature Θ occurs, whereas for graphite an equation with two values of Θ must be employed. A comparison of the atomic heats of diamond and graphite shows that C_v for both modifications is identical at high temperatures. The measurements for silicon and carbon give a good example of the applicability of the Kopp-Neumann rule. The differences for $\text{SiC}-(\text{C}+\text{Si})$ are always positive between 350° and 1000°, reaching a maximum at 550°. At the ordinary temperature, the rule holds fairly well.

W. E. G.

Specific Heats of Polyatomic Gases at Low Temperatures. RUSSELL W. MILLAR (*J. Amer. Chem. Soc.*, 1923, 45, 874—881).—The specific heats of methane, methyl chloride, boron trifluoride, and hydrogen sulphide have been determined from temperatures in the neighbourhood of the boiling point of the respective substances, to 5°. It is shown that the heat capacities of gases do not depend on the number of atoms in the molecule alone, but on the masses of the atoms, the constraints, and the temperature. In the case of hydrogen sulphide, the heat capacity increases with decreasing temperature, due to the heat of polymerisation and other causes. The following values of the ratio c_p/c_v and c_p/c_v° are recorded: methane, 278°, $\gamma=1.32$, $\gamma_0=1.32$, 199°, $\gamma=1.35$, $\gamma_0=1.34$, 158°, $\gamma=1.41$, $\gamma_0=1.39$, 142°, $\gamma=1.42$, $\gamma_0=1.40$; methyl chloride, 278°, $\gamma=1.32$, $\gamma_0=1.30$, 260°, 1.34, 1.31; hydrogen sulphide, 278°, $\gamma=1.31$, $\gamma_0=1.30$, 229°, 1.30, $\gamma_0=1.28$, 224°, $\gamma=1.29$, $\gamma_0=1.27$, 216°, $\gamma=1.29$, $\gamma_0=1.26$. The temperatures are absolute values. In the case of boron trifluoride, $c_p=11.70$ at 278° and 10.00 at 189°.

J. F. S.

Chemical Constants of Saturation Equations. E. WERTHEIMER (*Z. physikal. Chem.*, 1923, 104, 203—232).—A theoretical paper in which the two chemical constants, α the entropy constant, and b , the energy constant, of thermodynamic functions have been investigated. The constant α is investigated by means of the vapour-pressure formula in which it appears in the form $\alpha = Ri$, where R is the gas constant and i the Nernst chemical constant. When the vapour pressure is written in the usual form $\log_e p = f(T)$, it becomes necessary, on account of the different dimensions of

the variables, to specify exactly in what units (atm., mm. of mercury, etc.) the pressure is to be measured. The conventional chemical constant, i , is the numerical value with opposite sign, which the sum of the T containing quantities of the Nernst function assumes for any suitable pressure unit, $p=1$, $\log_e p=0$. For an ideal monatomic gas, the theoretical constant is the limiting value which the quantity i approaches asymptotically, when the pressure unit is chosen increasingly smaller, and in consequence the temperature integral of the specific heat of the solid substance vanishes. For the investigation of the energy constant, b , an isolated saturated vapour phase is considered by means of the equation $L=\varphi(b, v)$, in which a quantity of the same dimensions as energy also appears on the left-hand side; this is the energy of translatory motion of the molecules. In keeping with Bohr's hypothesis, the intramolecular energy of the molecule is introduced for b ; $W=Nh\nu/2=-b$, and it is shown that in the case of a saturated vapour an equilibrium condition must exist between W and L . From this follow the well-known phenomena of spontaneous condensation and evaporation. The dependence of the value W on the temperature is briefly discussed.

J. F. S.

Absolute Entropies and Chemical Constants. KARL F. HERZFELD (*Ann. Physik*, 1922, [iv], 69, 54—58).—A theoretical paper on the relationship between the methods of derivation of the entropy constants. The condition integral ϕ is recommended as the correct basis for the calculation of the entropies, which can then be obtained correctly from the classical theory for high temperatures, the introduction of the quantum theory being necessary for low temperatures. In order to obtain the same formula from the classical theory and the quantum theory, the phase volume must be measured, not in absolute units, but in cubes with content h^3 . In the methods due to Sackur, Tetrode, and Brody, the phase volume is measured more or less correctly, in unit cubes h^3 , but in other methods, due to Stern and Tetrode, the phase volume is measured in cm.-g.-sec. and then divided by the phase volume of the "frozen" solid body, Nh^3 .

W. E. G.

The Equation of State for Methane Gas Phase. F. G. KEYES, L. B. SMITH, and D. B. JOUBERT (*J. Math. Phys. Mass. Inst. Tech.*, 1922, 1, 191—210).—A new apparatus is described for the measurement, by the isometric method, of the properties involving pressure, volume, and temperature of a gas the critical temperature of which is below 0° . The isometrics of methane are linear within the limits of experimental error between 0° and 200° up to 300 atm. Keyes's equation accurately represents the relations in question, as follows: $p=[4.1175/(v-\delta)]T-[9802/(v+0.565)^2]$, where T represents degrees Abs., and $\log \delta=0.56195-(1.05/v)$. The weight of 1 litre of methane calculated by the equation of state is 0.7718 at 0° and 760 mm. The coefficients of expansion at 1 atm. are calculated to be 0.0036796 at constant volume and 0.0036834 at constant pressure.

CHEMICAL ABSTRACTS.

The Thermodynamic Properties of Methane. F. G. KEYES, R. S. TAYLOR, and L. B. SMITH (*J. Math. Phys. Mass. Inst. Tech.*, 1922, **1**, 211—242).—From the experimental values of the vapour pressures and densities of liquid methane, determined over the entire liquid phase region by precision methods described in detail, a number of equations and thermodynamic constants are derived: (1) an equation for the vapour pressure as a function of the absolute temperature, $\log_{10} p(\text{atm.}) = -(595.546/T) + 8.09938 - (4.04175 \times 10^{-2}/T) + (1.68655 \times 10^{-4}/T^2) - 2.51715 \times 10^{-7}/T^3$; (2) a mean density equation for calculating vapour densities near the critical point, $D_m = 0.16134 + 0.00065723(T_c - T)$; (3) critical temperature 191.03° Abs., critical pressure 45.8 atm., critical volume 6.2 c.c./g.; (4) an equation for the heat of evaporation λ , from 100 to 150° Abs., $\log_{10} \lambda = 1.65214 + 2.0076 \times 10^{-4}(T_c - T) + 0.22225 \log_{10}(T_c - T)$; (5) a linear relationship involving the internal energy change and the specific volume of liquid methane; (6) an equation for the specific heat of the vapour as a function of temperature and low pressure, $C_{p1} = 0.4288 + 1.12 \times 10^{-3}T - 6.45 \times 10^{-6}T^2 + 13.04 \times 10^{-9}T^3 + (93/T^2)p$; (7) the calculation from (6) and the usual thermodynamic equations of the specific heat of the liquid near the b. p. as 0.82 cal./g.

CHEMICAL ABSTRACTS.

A New Form of Melting-point Apparatus. H. A. BELL (*Ind. Eng. Chem.*, 1923, **15**, 375).—The apparatus is a modification of that of Thiele, and is made of pyrex glass. The thermometer, stirrer, and melting-point tube are inserted in a wide test-tube containing sulphuric acid, which itself rests in the heating apparatus. This consists of a bath of sulphuric acid with three vertical tubes. The middle and wider tube leads out of the bottom of the bath, and the two side tubes out of the top. The middle tube is heated by means of a coil of nichrome wire wound round it, the current being controlled by means of an electrolytic resistance. The heated acid ascends the middle tube and spreads out evenly over the walls of the test-tube containing the thermometer and the melting-point tube. The displaced liquid flows down the two outer tubes and a circulation is set up similar to that in Thiele's apparatus.

H. C. R.

Determination of Freezing Points of Substances. F. G. KEYES, B. TOWNSHEND, and L. H. YOUNG (*J. Math. Phys. Mass. Inst. Tech.*, 1922, **1**, 243—312).—The following freezing points are established: carbon tetrachloride, -22.87° ; mercury, -38.90° ; chlorobenzene, -45.58° ; chloroform, -64.19° ; ammonia, -77.80° ; toluene, -95.70° ; methyl chloride, -98.39° ; methyl alcohol, -98.54° ; carbon disulphide, -112.97° ; ethyl ether (modification I), -123.40° ; (modification II), -115.9° . Carbon dioxide has b. p. -78.53° , and oxygen has b. p. -182.94° .

CHEMICAL ABSTRACTS.

Vapour-pressure Measurements in Pure Argon. FRITZ BORN (*Ann. Physik*, 1922, [iv], **69**, 473—504).—The vapour pressure of solid and liquid argon have been measured from 65° K. to 90° K.

Considerable deviations between these values and those of Crommelin were found. The vapour-pressure curve agreed with the Nernst approximation formula. The heat of evaporation at the melting and boiling point and the conventional and true chemical constant were calculated from these results. The chemical constant for argon is $C=0.79 \pm 0.04$.
W. E. G.

Reduction of the Vapour Pressure of some Metallic Salts in Aqueous Solution at 0°. C. DIETERICI (*Ann. Physik*, 1923, [iv], 70, 617—621).—The lowering of the vapour pressure of water by the solution of sulphates of lithium, manganese, cadmium, zinc, magnesium, and nickel, and the nitrates and chlorides of zinc, nickel, and cadmium, respectively, has been measured directly at 0° by enclosing the pure solvent on one side of an aneroid box and the solution on the other side. The measurements show that aqueous solutions of sulphates of low concentrations have a larger vapour pressure than corresponding concentrations of non-electrolytes such as carbamide and sucrose; at concentrations about 2*N* the two sets of solutions have about the same vapour pressure, and above this concentration the lowering of the vapour pressure by the sulphates is greater than in the case of the non-electrolytes. Solutions of nitrates give uniformly lower values for the vapour pressure than solutions of non-electrolytes. Chloride solutions behave in the same way as nitrate solutions, except that the deviation from the normal value is not so great. The present results are in keeping with the values found by Tammann for 100°.

J. F. S.

Calculations on Fractionating Columns from Theoretical Data. W. A. PETERS, jun. (*Ind. Eng. Chem.*, 1923, 15, 402—403).—An equation is derived giving the relationship between the composition of the vapour and of the liquid in equilibrium with it for binary mixtures of homologues, isomerides, and other similar liquids. With the aid of this equation, the distillation equation giving the compositions of a binary mixture of liquids before and after a certain portion has been distilled, in terms of the weights of material at the beginning and end of the distillation, can be integrated. An equation is also derived which gives the height of a fractionating column required to make any given separation of a binary mixture of liquids under given conditions of heat expenditure, composition of distillate, etc.

H. C. R.

Relations concerning the Internal Heat of Vaporisation. J. E. MILLS and P. K. SMITH (*J. Physical Chem.*, 1923, 27, 301—321).—In a previous paper (A., 1909, ii, 861) Mills discussed the internal heat of vaporisation in connexion with the equations (1) $\lambda=0.000031833 \left(\frac{dP}{dT} \cdot T - P \right) (V - v)$ cal., (2) $\lambda = \mu' \left(\sqrt[3]{d} - \sqrt[3]{D} \right)$ cal., and (3) $\lambda = CRT \log_e V/v = C \times 4.577/m \times T \log d/D$ cal. In these equations, $\lambda = L - 29E = L - 0.00003183P(V - v)$ cal., L is the total heat of vaporisation of 1 g. of the liquid, λ the internal heat of vaporisation of 1 g. of the liquid, T the absolute temperature, P the vapour pressure in mm. of mercury V , the volume of 1 g. of saturated

vapour, v the volume of 1 g. of liquid, d the density of the liquid, D the density of the vapour, and μ' and C are specific constants. Equations 2 and 3 on combination give $\mu'(\sqrt[3]{d}-\sqrt[3]{D})=CRT \log d/D=CRT \log_e V/v$, and this has been transformed into $\mu' \sqrt[3]{d}+CRT \log_e v=\mu' \sqrt[3]{D}+CRT \log_e V$. The last equation has been examined by means of the existing data, which are tabulated, for diethyl ether, diisopropyl, diisobutyl, isopentane, n -pentane, n -hexane, n -heptane, n -octane, benzene, iodobenzene, carbon tetrachloride, and stannic chloride. The values for both sides of the equation have been calculated for a number of temperatures between 0° and the critical temperature and compared. It is shown that there is a remarkably exact agreement between the two quantities when the factor $\mu' \sqrt[3]{D}$ is greater than $3/2RT$.

J. F. S.

Some Properties of Ideal Gases. PAVEL N. PAVLOV (*J. Russ. Phys. Chem. Soc.*, 1917, 49, 322—327; this vol., ii, 380).—It is proved that for ideal gases, in corresponding conditions, the pressure is proportional to the absolute temperature. A formula shown previously to hold for normal liquids is applicable also to ideal gases, the critical temperature of which is given by the expression $T_c=1.6167M\sqrt{n}$, where M is the molecular weight of the gas and n the number of atoms in its molecule; whilst the critical pressure, p_c , is $0.13076M\sqrt{n}$. The expression $(p/T)_{\text{corr.}}$ is found to be equal to 0.003663 for all gases examined. From this, and since $pv=RT$, it follows that the corresponding volumes of gases must be equal, i.e., that a mole of any ideal gas must occupy the same volume, at 0° and 760 mm., as well as at corresponding temperatures and pressures. Nitrogen, oxygen, nitric oxide, and hydrogen give values in close agreement with this rule, whilst carbon dioxide and hydrogen chloride give deviations of up to 1.6%.

R. T.

The Molecular Condition of Pure Liquids. NIKOLAI ALEXANDROVITSCH KOLOSOVSKI (*J. Russ. Phys. Chem. Soc.*, 1917—1918, 49, 613—616; cf. Pavlov, A., 1917, ii, 125, 293, 358).—Pavlov's conclusion that in corresponding states all normal liquids have the same molecular volume is shown to be due to mathematical error. His criticism of Kistiakovski's rule (A., 1906, ii, 655; 1913, ii, 831), which has a theoretical basis, is also shown to be unfounded.

G. A. R. K.

The Molecular Condition of Pure Liquids. PAVEL NIKOLAEVITSCH PAVLOV (*J. Russ. Phys. Chem. Soc.*, 1918, 50, 463—464).—It is shown that Kolosovski's objections to the formulation of the molar surface of a liquid as v^n , where $v = m/d$, and m is the molecular weight of the liquid, d its density, and n is a constant, are devoid of foundation.

R. T.

Einstein's Formula ($\eta/\eta_0=1+2.5\phi$) and the Viscosity of Tannin Solutions. A. V. DUMANSKI and B. K. TARASOV (*J. Russ. Phys. Chem. Soc.*, 1917, 49, 186—192).—A formula deduced by Einstein, $\eta/\eta_0 = 1 + 2.5\phi$, where η is the internal friction of the solution, η_0 that of the solvent, and ϕ is the volume occupied by the

solute per c.c. of the solution (*Ann. Phys.*, 1911, [iv], 34, 391), is tested for the case of sols, tannin sol being selected for this purpose. A new symbol, φ_1 , the volume of 1 g. of solute, is introduced, φ being equal to $\varphi_1 c$. The relative viscosities, η/η_0 , of tannin solutions are measured at 20°, 40°, 60°, and 80°, and φ , hence, and also from the density of tannin alone, calculated for various concentrations, ranging from 0.0025 g. to 0.25 g. of solute per c.c. of solution. φ_1 is found not to be constant, but to increase with the concentration of tannin, and is greater, in general, than the corresponding value calculated from the density alone. At higher temperatures, the values of φ_1 obtained are much closer to one another than at lower temperatures. The varying values obtained are due, partly to the formulæ used in their calculation being only approximate, and partly to adsorption of solvent on the particles, causing an increase in their size. A further cause is probably the retardation of the free movement of the particles by the solution, so that when they move they carry a portion of the solution with them, producing a so-called hydrodynamic volume of the particles. This envelope of solvent becomes smaller at higher temperatures, and the values of φ_1 become correspondingly smaller. A modified form of the Einstein formula, $\eta/\eta_0(1 + Kc^2) = 1 + 2.5 \varphi_1 c$, is proposed, where K and c are constants, and in this form the equation agrees well with experimental results.

R. T.

Stalagmometry and Viscosimetry. F. V. VON HAHN (*Chem. Ztg.*, 1923, 47, 402).—A description is given of a new type of viscosistalagmometer. The instrument, by means of which two immediately consecutive measurements can be made of the rate of flow through the capillary, and of the number of drops from the end of the capillary, consists of a modification of Ostwald's viscosimeter in which the capillary tube with a carefully ground dropping surface fits into the U-shaped reservoir by means of a ground glass joint, and a second tube filled with a glass cock at its upper end is fused into the reservoir close to the lower exit of the capillary. In use, the liquid is forced up into the bulb in the upper part of the capillary, the cock in the second tube being closed, and the rate of flow through the capillary is then measured. On opening the cock, the level of the liquid falls below the capillary exit, and the contents of bulb and capillary then drop from the prepared surface of the latter, and the number of drops can be ascertained without having to remove the liquid from the apparatus or subject it to any change of temperature. An example of the use of the apparatus is given in a determination of the viscosity and stalagmometric curves of a paraldehyde-water mixture at different temperatures, and of an albumin-water mixture.

G. F. M.

Adsorption from the Gas Phase at a Liquid-Gas Interface. THOMAS IREDALE (*Phil. Mag.*, 1923, [vi], 45, 1088—1100).—A critical résumé of the drop-weight method of determining surface tension is given, and from the results of Harkins and Brown (cf. A., 1919, ii, 221) the ratio of the radius of the drop to the radius of the tube from which it falls have been calculated, and a method is

given for ascertaining, from these ratios, the surface tension of any liquid. The surface tension of mercury in contact with methyl acetate vapour at varying partial pressures has been measured by the drop-weight method. The surface tension is depressed rapidly at first and then more slowly as the partial pressure is increased, until at 62 mm. it becomes practically constant. Beyond 227 mm., the value of the surface tension suddenly falls off to that of the interfacial tension of mercury in contact with liquid methyl acetate. The horizontal portion of the curve corresponds with complete saturation of the surface with an adsorbed film. This film contains 4.5×10^{-8} g. of methyl acetate per sq. cm., and each molecule occupies 27×10^{-16} sq. cm., which is nearly the space occupied by a molecule of fatty acid on the surface of water.

W. E. G.

The Molecular State of Pure Liquids. IV.—VII. PAVEL NIKOLAEVICH PAVLOV (*J. Russ. Phys. Chem. Soc.*, 1917, **49**, 304—322; cf. A., 1917, ii, 125, 293, 358).—For normal liquids the surface tension, at corresponding absolute temperatures, *i.e.*, at temperatures which give equal values on division by the corresponding critical temperature, is deduced to be a function of the product of the molecular weight into the square root of the number of atoms in the molecule. This is formulated as follows: $M\sqrt{n}/\gamma_{\text{corr.}} = a$ a universal constant. This law is shown to hold for ethyl ether and carbon tetrachloride, over a range of temperatures in which no dissociation or association is known to take place. Propyl formate gives values very close to those calculated on the above law, showing that it deviates little from the normal, whilst water, *n*-octane, benzene, methyl formate, methyl alcohol, and acetic acid vary more widely. For associated liquids, the function $M\sqrt{n}/\gamma_{\text{corr.}}$ is smaller than for normal liquids, whilst with dissociated liquids it is greater. This function gives, therefore, an indication of the degree of association or dissociation of liquids. A formula for the calculation of the density of liquids or their saturated vapours is deduced, as follows: $d_{\text{corr.}}\sqrt{n}/T_{\text{corr.}} = a$ a universal constant, where $T_{\text{corr.}}$ is the corresponding absolute temperature, $d_{\text{corr.}}$ the density at this temperature, and n is the number of atoms in the molecule. This law holds for ethyl ether and carbon tetrachloride, and deviates little in the cases of ethyl acetate, propyl formate, and methyl propionate, whilst for water and *n*-octane greater deviations exist. The expression $M\sqrt{n}/T_{\text{corr.}}$ is shown to be equal to a constant for normal liquids, and hence it follows that $T_{\text{corr.}}$ must increase with association and decrease with dissociation. At the critical absolute temperature, the above expression is for normal liquids equal to 0.6185, and the critical temperature of such liquids is therefore given by the expression $T_c = M\sqrt{n}/0.6185$. The critical temperatures of carbon tetrachloride, ethyl ether, and some esters agree well with those calculated from this formula, whilst the critical temperature of water, actually 647° Abs., is calculated to be 50.4° Abs., showing that a high degree of association exists. Normal liquids are

shown to have, at corresponding temperatures, the same molar volume.

R. T.

Adsorption at Liquid-Vapour, and Liquid-Liquid Interfaces and some Related Phenomena. H. H. KING (*Kansas Agr. Exp. Sta. Tech. Bull.*, 1922, 9, 1—39; cf. King and Wampler, A., 1922, ii, 741).—The adsorption was calculated by plotting the surface tension at various concentrations against the logarithm of the concentration and applying Gibbs's equation. In the determination of surface tension by the drop-weight method, the weight of a hanging drop was found to depend on its time of formation, the explanation being found in the application of Fick's law. The adsorption in the liquid-vapour interface in mols. per sq. cm., the number of mols., the area occupied by each, and their diameters are given for the first ten acids of the aliphatic series, and certain alcohols, amines, and esters. The alcohols exhibit a greater adsorption than the acids, possessing also a constant degree of adsorption through a greater range of change of concentration, a difference which may be explained by the difference in electrolytic character. C_4 and C_5 alcohols and acids reach zero adsorption at the same respective concentration, whilst C_1 , C_2 , and C_3 alcohols show adsorption at lower concentrations than do the corresponding acids. The curves for the esters lie in nearly the same position as those of the alcohols with the same number of carbon atoms, and on the whole they correspond closely with those of the acids. Ethyl propionate requires a higher concentration than propyl acetate to produce the same adsorption. The more symmetrical is the ester, the smaller is the adsorption after it has once become constant. Experiments with butyric acid solutions show that the fugacity of the molecules in the interface water-benzene is three times as high as that on the surface of water when both films have the same concentration of about 10^{14} mols. per sq. cm. The adsorption of substances of the type of organic acids, alcohols, and esters is always greater at the surface of water than at the interface between water and an organic solvent of the type of benzene or a paraffin hydrocarbon. Single molecules of butyric acid appear to be more soluble in water than in benzene, whilst for double molecules the reverse is the case. The presence of benzene as an upper layer does not change the number of butyric acid molecules in this unimolecular layer.

CHEMICAL ABSTRACTS.

Adsorption of Carbon Monoxide and Hydrogen by Platinised Asbestos. FRANK HOWELL POLLARD (*J. Physical Chem.*, 1923, 27, 356—375).—The adsorption of hydrogen, carbon monoxide, and mixtures of the two gases by platinised asbestos has been determined at 0° for pressures up to 1 atm. The determination of the actual adsorption isotherms is made difficult by the fact that minute quantities of impurities, such as may be entrained by passing the gases through stopcocks lubricated by grease, decrease greatly the adsorptive power of the platinum. The observations of Berliner in this respect have been fully confirmed (*Ann. Phys. Chem.*, 1888, [ii], 35, 791). It appears probable that

all determinations of the adsorption of gases by platinum are untrustworthy unless scrupulous care be taken to eliminate all possible contamination of the adsorbent. The adsorption process is a reversible one, provided that sufficient time is allowed to elapse for the establishment of equilibrium. The adsorbed gas may be removed completely from the platinum by long-continued pumping at 0°. No evidence has been obtained supporting the contention that the gases under investigation form definite solid compounds with platinum at this temperature. When contamination of the adsorbent is most effectively prevented, platinised asbestos is able to adsorb two hundred volumes of hydrogen or three hundred volumes of carbon monoxide at 0° and atmospheric pressure, the volumes of gas being expressed in terms of the volume of platinum present. Carbon monoxide, added in relatively small amounts to the system hydrogen-platinised asbestos in equilibrium, is able to displace completely the adsorbed hydrogen from the platinum. This fact supports directly Bancroft's hypothesis of catalytic poisoning (A., 1917, ii, 566), and accounts for the fact that carbon monoxide is known to be a poison toward platinum in certain catalytic hydrogenations. The adsorption coefficient of two hundred volumes of hydrogen is greater than that obtained by previous investigators, who used platinum black instead of platinised asbestos. The greater value now obtained is doubtless the result, at least partly, of the greater precautions taken to prevent contamination of the catalyst, but it may indicate also that platinum in the form of platinised asbestos has a greater specific surface than platinum as platinum black.

J. F. S.

Adsorption of Gases by Oxide Catalysts. ARTHUR F. BENTON (*J. Amer. Chem. Soc.*, 1923, 45, 887—899).—The adsorption of carbon dioxide, oxygen, hydrogen, and carbon monoxide by copper oxide, manganese dioxide, cobalt sesquioxide, ferric oxide, vanadium pentoxide, silica, and Hopcalite (60% manganese dioxide and 40% cupric oxide) has been measured at 1 atm. pressure and at temperatures from -79° to 184°. The catalysts were prepared under conditions which were as nearly as possible analogous in the different cases. A method was devised whereby a correction could be obtained for the absorption which occurs in some cases and for the progressive chemical reaction which occurs with hydrogen and carbon monoxide, and in this way the true adsorptions were obtained. Two different types of adsorption, termed "primary" and "secondary" adsorptions, are discussed in connexion with these and other measurements. Secondary adsorption is the type which occurs with inert adsorbents, and depends on secondary valency. The melting points of the adsorbent and the adsorbed substances are a measure of the forces involved. Primary adsorption, on the other hand, occurs with active adsorbents, and depends on primary valency forces. In common with other manifestations of chemical affinity, primary adsorption is specific. The form of the adsorption isotherms and isobars is very different for the two types. In certain of the present measurements, both kinds of

adsorption occur simultaneously. A method is devised for distinguishing between the two types and estimating the extent of each, in such cases. The experiments allow the following general statements to be made: the secondary adsorption of different gases is in the order of their melting points; the secondary adsorption by different adsorbents is also in the order of their melting points, and the primary adsorption of carbon monoxide is approximately in the order of the relative reducibility of the different oxides.

J. F. S.

Adsorption and Catalysis in Carbon Monoxide Oxidation.

ARTHUR F. BENTON (*J. Amer. Chem. Soc.*, 1923, **45**, 900—907; cf. preceding abstract).—The connexion between adsorption and catalytic activity of a number of oxides for carbon monoxide has been investigated in view of the results previously published (*loc. cit.*). It is shown that neither the secondary adsorptions nor the total adsorptions by different oxide catalysts bear any relation to their relative catalytic activities. The primary adsorption of carbon monoxide is, however, in exactly the same order as the catalytic activity. The mechanism of reduction of an oxide by a reducing gas is discussed as a three-stage process involving adsorption, isomeric change, and evaporation of the product from the surface of the oxide. Several possible methods are discussed in which the catalytic oxidation of carbon monoxide in contact with active metallic oxides might occur, and it is shown that only the mechanism based on alternate reduction and reoxidation is in satisfactory agreement with adsorption data. Bone and Wheeler's experiments on the catalytic combination of hydrogen and oxygen in the presence of metallic oxides, from which they drew the conclusion that this process does not depend on alternate reduction and reoxidation (A., 1906, ii, 434), are considered in connexion with the present results and are shown to support the present view rather than to discredit it.

J. F. S.

Some Factors Governing the Complete Sorption of Iodine by Carbon from Chloroform Solution. JAMES BRIERLEY FIRTH and FRED SHEASBY WATSON (T., 1923, **123**, 1219—1222).

Adsorption. XIII. Hysteresis of the Degree of Hydration of Vegetable and Animal Charcoals. ADAM VLADISLAVOVITSCH RAKOVSKI (*J. Russ. Phys. Chem. Soc.*, 1917, **49**, 371—380).—Various kinds of vegetable and animal charcoals are dried to constant weight by keeping in a desiccator over concentrated sulphuric acid. The charcoal is then allowed to absorb water vapour, and curves are drawn of which the abscissæ are pressure of water vapour and percentage weight of water adsorbed. If such hydrated charcoals are dried in an analogous way, by gradually reducing the pressure, the whole of the water cannot be removed, 2% remaining in the charcoal after drying to constant weight. The dehydration curve exhibits, therefore, a certain constant lag behind the hydration curve. If now sugar charcoal thus treated is again allowed to adsorb water, and again dried, no further hysteresis is noticeable,

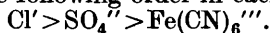
the last three curves being almost identical. In the case of animal charcoal, the second hydration curve occupies a position intermediate between the first hydration and dehydration curves. The water thus retained by the charcoal is only to a small extent given up by heating at 110° . Since the original samples used are only comparatively dry, such hydrated charcoal may contain up to 17% of water, which is not entirely expelled even by heating to redness in a current of nitrogen, and probably is chemically combined with the carbon. Charcoals are not, therefore, appropriate substances for the study of the phenomena of adsorption, as their exact action varies with the nature of the charcoal used, and with its past history.

R. T.

Anomalous Osmosis of Solutions of Electrolytes with Colloidal Membranes. II. Effect of Stirring the Solutions.

F. E. BARTELL and D. C. CARPENTER (*J. Physical Chem.*, 1923, **27**, 346—355; cf. this vol., ii, 221).—The effect of stirring or rocking on the osmosis of solutions of potassium ferricyanide, sulphate, and chloride, aluminium and calcium chlorides with collodion membranes has been investigated and the osmosis-concentration curves have been compared with those obtained when the solution is not stirred. It is shown that the shape of the initial osmosis-concentration curves and the maximum osmosis-concentration curves was of the *N*-type throughout for potassium salts and was more strongly accentuated than when the solutions were not stirred. With dilute solutions, stirring increased both the initial and the maximum osmotic effects in the case of potassium chloride, calcium chloride, and potassium sulphate, but decreased the effect with aluminium chloride and the maximum effect with potassium ferricyanide. With concentrations of electrolytes greater than $0.1M$, stirring has but little influence on either the initial or maximum osmosis. Stirring produced a tendency towards the *N*-shaped curve even in the case of aluminium chloride, a tendency which had not hitherto been observed. With sucrose solutions, stirring increased the rate of the initial osmosis, but decreased the maximum osmosis. The whole of the above results are in keeping with the view that the passage of the solute through the membrane is largely responsible for the appearance of the *N*-shaped curve in osmosis through collodion membranes. Stirring increases the rate of passage of all electrolytes through a collodion membrane at all concentrations. The rate of passage of solutes into water is greater for concentrated solutions than for dilute solutions, but it is not proportional to the concentration except in two cases with calcium chloride. In the region of $0.01M$, the percentage increase in g.-mols. of salt passing through the membrane in two hours, due to stirring, is as follows: potassium chloride, 140; potassium sulphate, 13; potassium ferricyanide, 63; calcium chloride, 72; aluminium chloride, 95. The ratio of the concentrations of solute in the two compartments decreased in magnitude as the osmosis progressed. In concentrated solutions, this ratio approached 1:1 at the maximum osmosis period, but for more dilute solutions the

ratio remained much greater. With potassium salts, the relation of anion valency to the rate of passage of electrolyte through the membrane showed the following order in each case :



This order was the same at all concentrations, and was the inverse of the order of magnitude of maximum osmosis. With chlorides, the kation order was $\text{K}' > \text{Ca}'' > \text{Al}'''$ at all concentrations. The above series are the same as those obtained when the solutions are not stirred.

J. F. S.

Diffusion of Dyes into Gels. I. TRAUBE and M. SHIKATA (*Kolloid Z.*, 1923, **32**, 313—316).—The distance which 0·1% solutions of azo-blue, Congo-red, water-blue, naphthol-green, Bordeaux-R, acid-violet, acid-green, eosin, azorubin, naphthol-yellow, tannin-heliotrope, night-blue, methylene-blue, and rhodamine diffuse into gelatin gels (2·5, 5, 7·5, 10·0, 12·5, 15·0, 17·5, and 20%), agar-agar gels (0·5, 0·75, 1·0, 1·25, 1·5, 1·75, and 2·0%), and soap gels (2·5, 5, 7·5, and 10%) in forty-eight hours has been measured. The results show that $C^{1/3}D = K$, where $C^{1/3}$ is the mean distance between two gelatin particles, D the distance travelled by the diffusing solution, and K is a constant. Put into words, this means that the mean distance travelled by a dye particle, in a given time, in gelatin gels of various concentrations is proportional to the mean distance between the gelatin particles. This rule does not hold for agar-agar or soap gels.

J. F. S.

Velocity of Diffusion in Jellies during a Simultaneous Chemical Change. MANJIRO WATANABE (*Kolloid Z.*, 1923, **32**, 320—328).—During experiments on the formation of precipitates in jellies, the distance, x , which a substance, diffusing from a limited quantity of a solution, travels in a time z into a jelly was measured, when at the same time a limited amount of chemical change is taking place with another substance dispersed throughout the jelly. In the case of diffusion from an unlimited amount of solution when no chemical change is taking place, the velocity coefficient $x/z^{1/2}$ is constant for a given preparation; in the present case, this factor is not constant, but changes with the time. On plotting the value, it is shown to change according to a regular curve, which in most cases is almost a straight line. As a first approximation, this line may be represented by $x/z^{1/2} = (Z - z)Z \cdot k$, where k is the velocity coefficient for the commencement of the process and Z a constant for a given preparation. If the formula were strictly true, Z would be the time which had elapsed from the commencement of the process to the "critical time" where the direction of the precipitate formation reverses. The equation has been examined for various concentrations of the jellies (gelatin) which contained various quantities of lead nitrate and sodium sulphide, the diffusing solutions being ammonia, ferrous sulphate, and copper sulphate.

J. F. S.

An Apparent Deviation from Henry's Law for the System, Ammonia-Water. G. CALINGAERT and F. E. HUGGINS, jun. (*J. Amer. Chem. Soc.*, 1923, **45**, 915—920).—The ratio of the

composition of vapour and liquid phase has been determined for ammonia-water solutions at the boiling point for concentrations from 0.005 g. to 1.250 g. of ammonia per litre. A deviation from Henry's law has been observed which might be attributed to the electrolytic dissociation of the ammonia. It has been shown that a solution of maximum boiling point must exist for the system ammonia-water, the composition of which is 0.000010 g. of ammonia per litre, and that the distillation curve of this system must be similar to that of hydrochloric acid and hydrobromic acid solutions, the only difference being that, on account of the high degree of dissociation of the acids, the maximum boiling point of their solutions corresponds with a much higher concentration than in the system ammonia-water where the degree of dissociation is very small.

J. F. S.

Piezo-chemical Studies. XVIII. A General Direct Process for the Determination of Solubility at High Pressures.

ERNST COHEN, D. H. PEEREBOOM VOLLER, and A. L. TH. MOESVELD (*Z. physikal. Chem.*, 1923, **104**, 323—331).—A process is described whereby the solubility of solids may be determined at high pressures with the same accuracy as is possible at ordinary pressure. The method consists in placing a supersaturated solution of the salt under investigation in one half of a double pipette, the other half being filled with benzene; this is placed in one limb of a steel U-tube and the pressure generated in the steel tube as previously described (*A.*, 1919, ii, 321). The U-tube is then fixed on an axis horizontally in an oil thermostat and given a rocking motion whereby a small quantity of mercury rolls backward and forward, producing an efficient mixing of the solution. After shaking for about twenty hours, the rocking is stopped and the U-tube brought into the vertical position, so that the undissolved solid falls to the bottom of the lower pipette; the solution is then forced under pressure into the upper pipette, which until now had been filled with benzene. The pressure is then rapidly reduced to atmospheric and the pipette removed. Its contents are weighed and analysed as in ordinary determinations. Full manipulative directions are given in the paper. The method has been applied to the determination of the solubility of thallous sulphate in water at 30° and at pressures of 500, 1000, and 1500 atm. The following results are recorded in grams per 100 g. of saturated solution: 1 atm., 5.83; 500 atm., 7.48; 1000 atm., 9.03, and 1500 atm., 10.50, each value being the mean of two very close determinations. The influence of pressure on the solubility of thallous sulphate is given by either of the equations $C = 5.831 + 0.003377p - 0.000000175p^2$ and $C = 5.831 + 0.003295p - 0.000000109p^2$. The present experiments show that increase in pressure has a considerable influence on solubility (cf. Cohen, *loc. cit.*).

J. F. S.

The Distribution of Solvent between Solutes. VI. The Optical Rotation of Solutions of Sugar with Salts. ANTON GRIGOREVITSCH DOROSCHEVSKI (*J. Russ. Phys. Chem. Soc.*, 1917, **49**, 408—413; cf. *A.*, 1913, ii, 1014; 1914, ii, 419, 610; 1916, ii, 121).—The

relative densities and optical rotations of solutions containing sugar and various salts of alkali and alkaline-earth metals are calculated from a formula put forward by the author in his preceding articles, and found to agree well with experimental results for dilute solutions. It is shown that the theory previously mentioned, as to the distribution of a solvent between substances dissolved in it, explains why the addition of such salts to sugar solutions increases the angle of optical rotation to an extent which increases with increasing molecular weight of the salt.

R. T.

The Distribution of Solvents between Solutes. V. The Specific Gravities and Refractive Indices of Mixed Solutions.

A. G. DOROSHEVSKI and E. N. EKAREVA (*J. Russ. Phys. Chem. Soc.*, 1917, **49**, 64—76; cf. A., 1915, ii, 408; 1916, ii, 121).—The deviations of the conductivities from the calculated additive values which are observed on mixing aqueous solutions of two electrolytes have been accounted for on the assumption that the solvent is divided between these electrolytes in proportion to their chemical masses.

It is now shown that specific gravities and refractive indices of mixed solutions obey the same law, and that these properties can be readily calculated for a given solution, provided, of course, there is no chemical interaction between the dissolved substances. The formula used for calculating the density d_0 of the mixed solution is $d_0 = \{100(am'd + a'md') - aa'(d - d')(m' - m)\} / (am' + a'm)$, where a and a' are the weights of the two solutes in 100 g. of mixed solution, m and m' their gram-equivalents, and d and d' the "partial" densities of their respective solutions. The same formula, substituting n_0 , n , and n' for d_0 , d , and d' , applies to refractive indices. The calculated values are shown to be in good agreement with experimental data for a number of mixed solutions such as potassium and sodium chlorides, methyl and ethyl alcohols, etc.

G. A. R. K.

Eutectic Points in Salt Solutions. PAUL MONDAIN MONVAL (*Compt. rend.*, 1923, **176**, 1313—1316).—An attempt to verify experimentally the generalisation of Le Chatelier, that at the eutectic point the trigonometrical tangents to the two curves are in the ratio of the latent heats of solutions of weights of the two substances equal to those present in the saturated solution, showed that its validity is approximate. Certain discrepancies observed probably correspond with experimental errors. The author has used for this work the heats of solution previously determined by him (this vol., ii, 295) and his observations extend to the nitrate, chloride, and sulphate of potassium, nitrate of sodium, and the nitrate and chloride of ammonium.

H. J. E.

The Factors Influencing Compound Formation and Solubility in Fused Salt Mixtures. JAMES KENDALL, E. D. CRITTENDEN, and H. K. MILLER (*J. Amer. Chem. Soc.*, 1923, **45**, 963—996; cf. Kendall and Booge, A., 1918, ii, 37; Kendall and Gross, A., 1922, ii, 33, and Kendall, Davidson, and Adler, A., 1922, ii, 34).—The freezing-point curves of fifty binary fused salt mixtures

have been investigated and the existence of forty-nine new additive compounds has been established. The binary mixtures examined were, aluminium bromide with the bromides of lithium, sodium, potassium, ammonium, silver, calcium, barium, magnesium, zinc, cadmium, mercury, thallium, carbon, tin, lead, phosphorus, arsenic, antimony, bismuth, chromium, manganese, nickel, and iron, respectively; aluminium chloride with the chlorides of lithium, sodium, potassium, ammonium, copper, silver, barium, magnesium, mercury, thallium, tin, antimony, chromium, and manganese, respectively; and antimony trichloride with the chlorides of lithium, sodium, potassium, ammonium, copper, silver, barium, tin, and mercury, respectively. The factors effecting compound formation in the above systems have been critically examined. As in the previous work (*loc. cit.*), the diversity of the constituent radicles of the components has been found to be the main influence. Other factors discussed are valency, unsaturation, position in the electrode potential series, temperature, internal pressure, atomic volume, atomic number, and association. Very unusual curves are encountered in the systems sodium bromide-aluminium bromide and stannic chloride-antimony trichloride. In the former of these, a compound breaks up into two partly miscible layers when heated, and its true melting point cannot be ascertained. In the latter, an exceedingly small change in the temperature of fusion over a wide composition range is induced by the existence of a two-liquid layer region just below the freezing-point curve.

J. F. S.

Molecular and Crystal Symmetry. T. V. BARKER (*Nature*, 1923, **111**, 632—633; cf. Shearer, this vol., ii, 223; Fedorov, A., 1913, ii, 305).—A discussion of the Fedorov-Shearer principle of the conservation of symmetry. It is pointed out that for the expression $n/m=p$, where n is the "symmetry number" of the structural unit (the number of identical or enantiomorphously related asymmetric parts into which it is subdivisible), m the number of molecules it contains, and p the symmetry number of each molecule, arbitrary and unanticipated values of p must be chosen in order to apply the principle. The case of tartaric acid is discussed in detail, and it is suggested that the structure is not simply built up of a single space-lattice arrangement, with the molecular axes uniting to create the symmetry axis of the crystal, but is formed of a pair of molecular lattices, mutually interpenetrating. The second is held to restore the symmetry lost by a refusal of the crystal to recognise molecular symmetry; if this is so, the Fedorov-Shearer principle is infringed. It is admitted, however, that the crystals of tartaric acid are too complicated to be of effective use in testing the principle; carbon tetrabromide, carbon tetraiodide, hexachloro- and hexabromo-ethane and stannic iodide would be preferable.

A. A. E.

Dielectric Constants of Colloidal Solutions. III. J. ERRERA (*Kolloid Z.*, 1923, **32**, 240—246).—A continuation of previously

published work (A., 1922, ii, 694; this vol., ii, 225). The time required for the coagulation of alcosols of mercuric sulphide, cupric sulphide, and platinum by the addition of liquids of varying dielectric constant has been determined, with the liquids benzene (2.26), carbon tetrachloride (2.25), toluene (2.51), *iso*amyl alcohol (5.7), *isobutyl* alcohol, (18.6), ethyl alcohol (25), methyl alcohol (33), nitrobenzene (35.5), water (81), chlorobenzene (5.5), xylene (2.32), hexane (1.85), acetone (21), chloroform (4.95), and ethyl ether (4.36). The figures in brackets are the dielectric constants of the liquids. Further experiments with mixtures of the liquids named with varying quantities of ethyl alcohol were also carried out. The experiments show that the addition of liquids of dielectric constant greater than that of the dispersion medium has no coagulating influence on the sol. Liquids with a dielectric constant smaller than that of the dispersion medium coagulate the sols, and in most cases the smaller the dielectric constant the greater is the coagulating power of the added liquid. Cupric sulphide alcosol, both alone and when mixed with ten times its volume of benzene, is shown by migration experiments to be negatively charged. Cupric sulphide alcosol on coagulation changes its colour from dark brown to an intense olive-green. The dielectric constant of colloidal solutions, where solvation has taken place to only a slight extent, is the same as that of the dispersion medium. Vanadium pentoxide sol is, however, exceptional; here the dielectric constant is 1280 as against 81, the value of the dispersion medium water. The effect in this case is probably connected with the well-known optical anisotropy. In certain cases, the dielectric constant has an effect on the preparation and swelling of colloidal systems.

J. F. S.

Attempt to Formulate a Theory of the Kinetics of the Process of the Solution of Colloids. N. P. PESKOV (*Kolloid Z.*, 1923, 32, 232—238).—An attempt is made to formulate a mathematical hypothesis of the kinetics of the solution of colloids. Two formulæ have been developed from theoretical considerations, and these have been tested in connexion with a series of gold sols. These expressions have the form $K = 1/t \cdot \delta/\pi r_0 C^{2/3} \cdot \{1 - (1 - \alpha)^{1/3}\}/(1 - \alpha)^{1/3}$, and $K = 1/4 \cdot \delta/\pi r_0 C^{2/3} [q \cdot 2.3 \log \{1 + q(1 - \alpha)^{1/3}/(1 + q)(1 - \alpha)^{1/3}\}]$, where K is the velocity constant of the solution process, r_0 the radius of the colloidal particles at the commencement of the process, δ the density of the colloid, C the colloid concentration, that is, the number of colloidal particles in the unit volume, t the time, α the degree of solution at the time t , and $rq = r_0$, where r is the radius of the molecule. Preliminary experiments showed that the kinetics of the solution of colloids is very different from that of macro-heterogeneous solutions, and also from that of molecular disperse processes. The experiments show, however, that the hypothesis put forward represents the actual relationships of the process of dissolution of colloids. The process is definitely heterogeneous, and, on account of the smallness of the particles of the solid phase and the Brownian movement, it is so modified that

it shows wide divergences from the process observed in the usual heterogeneous systems. J. F. S.

Metal Sols in Non-dissociating Liquids. I. Nickel in Toluene and Benzene. EMIL HATSCHKE and PERCY CYRIL LESLEY THORNE (*Proc. Roy. Soc.*, 1923, [A], **103**, 276—284).—Details are given of the preparation of very stable sols containing 1.0484 g. of nickel per litre of sol by decomposing nickel carbonyl in mixtures of benzene and toluene containing a small amount of caoutchouc as protective colloid. Sols so prepared can be concentrated considerably without coagulation by evaporating the dispersing medium. In an electric field, the particles of disperse phase move to and are deposited on both electrodes. In electric fields of different strengths, the amounts deposited on the electrodes are proportional to the first or a lower power of the potential gradient of the field. It is concluded, therefore, that positively and negatively charged particles are originally present in the sol, and that the charges do not originate owing to induction. The sol is coagulated by liquids, *e.g.*, acetone, which are not solvents for the protective colloid, and the coagulum is only very imperfectly peptised again by caoutchouc solvents such as toluene or benzene. J. S. G. T.

Sensitisation of the Process of Coagulation of Colloids. N. P. PESKOV (*Kolloid Z.*, 1923, **32**, 238—240).—When alcosols of arsenic trisulphide, platinum, and carbon are mixed with an equal volume of 0.063% solution of anthracene in ethyl alcohol and exposed at the ordinary temperature to the north light, coagulation of the sols is complete in six, five, and eight hours, respectively, whereas similar mixtures kept in the dark have not commenced to coagulate in seventeen days. The author explains the action as follows. The anthracene molecule, under the influence of light, loses an electron and thereby becomes positively charged. The positively charged anthracene molecule is adsorbed by the negatively charged colloid, and thereby brings about coagulation. J. F. S.

Borax Fusions with Gold Particles of Various Sizes and their Application to the Proof of von Smoluchowski's Coagulation Theory. A. EHRLINGHAUS and R. WINTGEN (*Z. physikal. Chem.*, 1923, **104**, 301—314; cf. A., 1917, ii, 297).—Borax beads containing various quantities of gold from 0.1% to 0.0001% have been prepared by fusing together borax and auric chloride at 925° for periods varying from one minute to five hundred minutes. The beads show various colours, pale red, rose, violet, greyish-blue, mauve, light blue, blue, and deep blue, depending on the size of the suspended particles, but the authors were unable to produce colourless beads by rapid cooling of the melt, as is the case in the preparation of ruby glass. The number of particles per c.c. has been determined ultramicroscopically in all cases. It is shown that the gold particles increase in number with the concentration of gold, but decrease with the time of heating.

An increase in the concentration leads to larger particles more rapidly than a prolongation of the time of heating. The experimental results have been examined by means of an equation which is obtained by combining Smoluchowski's equation $\Sigma_v = v_0/(1+t/T)$ with Einstein's equation $D = H\theta/N \cdot 16\pi\eta\alpha$, where Σ_v is the number of particles present at the time t , v_0 the number of particles present originally, T the time of coagulation, which is given by $T = 1/4\pi \cdot DRv_0$, in which R is the radius of activity, D is the diffusion coefficient, H the gas constant (83.19×10^6), θ the absolute temperature (1198°), N the Avogadro number (60.6×10^{22}), η the internal friction, and α the radius of the particles. The final equation has the form $1/\Sigma_v = 1/v_0 + (2H\theta R/3N\eta\alpha)t$. It is shown that the decrease in the number of particles with the time of heating is fully in keeping with von Smoluchowski's hypothesis. The gold particles combine together to form larger particles only when, in consequence of the Brownian movement, they are so close together as to be almost in contact. The results indicate that the von Smoluchowski hypothesis, which is true for hydrosols at the ordinary temperature, is also valid for fusions at 1000° . At 1000° , borax has a viscosity 3.38 at 890° , 13.61; and $d^{1000} = 2.04$.

J. F. S.

Adsorption. IV. Charge Reversal of some Colloids.

N. R. DHAR and K. C. SEN (*J. Physical Chem.*, 1923, 27, 376—383; cf. this vol., ii, 58).—Freshly precipitated ferric hydroxide, when shaken with solutions of arsenious acid, boric acid, meconic acid, tartaric acid, and molybdic acid, passes into a negatively charged colloid. Transport experiments show that the hydroxides of copper, aluminium, chromium, zinc, and cobalt, peptised by alkali hydroxides, are negatively charged, due to the adsorption of hydroxyl-ions. The ammoniacal solutions of the hydroxides of copper, cadmium, zinc, and nickel contain negatively charged hydroxides of the respective metals, owing to the adsorption of the hydroxyl-ion from ammonium hydroxide. Positively charged arsenic sulphide sol may be obtained by the adsorption of thorium-ions by the negatively charged sol. In the presence of gelatin, as protective colloid, positively charged antimony sulphide sol may be obtained, due to the adsorption of thorium-, uranyl-, aluminium-, barium-, and hydrogen-ions by the negatively charged sol. A reversal of the charge of antimony sulphide sol in the presence of gelatin may be brought about by the addition of electrolytes such as thorium nitrate, uranium nitrate, potassium alum, barium chloride, hydrochloric acid, and ferric chloride. Reversal of the charge is primarily due to the amount of adsorption of ions. A univalent ion may, if it is highly adsorbed, reverse the sign of the charge on a colloid. The blue colour in ammoniacal solutions of cupric salts, Fehling's solution, a solution of cupric hydroxide in sodium hydroxide and in mixtures containing alkali, cupric salts, and glycerol or sugars, is most likely due to peptised negatively charged cupric hydroxide. Ferric hydroxide is found to be a good adsorbent for ferric salts. The adsorption of the basic portion

from salt solutions by hydrated manganese dioxide probably furnishes a reason for the acidity of soil. J. F. S.

The Question of Colloid Protection. N. P. PESKOV (*J. Russ. Phys. Chem. Soc.*, 1917, **49**, 1—63).—The existing theories dealing with the protection and “astabilisation” of lyophobic colloids are reviewed and criticised. The erratic results recorded by a number of authors are mostly due to the fact that the solutions used by them are too concentrated; also to the fact that the protective colloid (gelatin) is not sufficiently free from electrolytes.

Working with a sol of arsenic trisulphide and specially purified gelatin in very dilute solution (As_2S_3 : 0.3, 0.05%; gelatin: 0.04, 0.02, and 0.004%), and using sodium chloride as the coagulating agent, the author shows that protection and astabilisation are separate and independent processes. Gelatin alone is unable to cause coagulation of colloids unless it is used in very concentrated solution containing very large particles; it is probable that in this case the lyophobic colloid is adsorbed by the large gelatin particles and these are then precipitated (Menz, A., 1909, i, 343). The protective action of gelatin is probably due to the formation of a film of gelatin particles around the particles of the lyophobic colloid, thus preventing their coalescence, in accordance with the view first put forward by Zsigmondy in 1901 (cf. “Kolloidchemie,” Leipzig, 1922) and Freundlich (“Capillarchemie,” Leipzig, 1909).

Billiter's electrical theory of “astabilisation” (A., 1904, ii, 18; 1905, ii, 305) is shown to be untenable for a number of reasons but chiefly because it presupposes that the particles of the lyophobic and the protective colloid must have opposite electrical charges, which is not always the case. It is suggested that the phenomenon is due to the interaction of the protective colloid with the traces of stabilisers always present in the particles of the lyophobic, either by the formation of a new system in which the stabiliser is partly adsorbed by the gelatin and thus removed from the lyophobic; or, conversely, by the precipitating action of the stabiliser on the gelatin which diminishes the concentration of the latter. It appears possible, however, that, concurrently with this main factor, the neutralisation of the electrical charges of the lyophobic particles by ions of an electrolyte may be accelerated by the adsorption of the latter by the protective colloid.

G. A. R. K.

The Question of Colloid Protection. The Phenomenon of “Reverse” Protection. NIKOLAI PETROVITSCH PESKOV and V. V. TRETIKOV (*J. Russ. Phys. Chem. Soc.*, 1917—1918, **49**, 547—566; cf. preceding abstract).—Colloidal solutions of albumin purified by prolonged dialysis are readily coagulated on heating, although the presence of even minute quantities of electrolytes prevents coagulation (Pauli, A., 1907, i, 803; 1909, i, 618; 1913, ii, 558); these therefore act as “stabilisers.” Now the phenomenon of “astabilisation” of lyophobic colloids by the addition of small quantities of a lyophilic colloid (gelatin) was explained by one of the authors (preceding abstract) by the transference of the

"stabiliser" to the particles of the lyophile colloid. It would therefore be expected that an unstable albumin solution might be able to acquire the required stabiliser on mixing with a colloidal solution of a lyophobic substance, by depriving the particles of the latter of the stabiliser adsorbed by them. This was found to be the case, and hydrosols of gold, silver, platinum, stannic acid, and ferric hydroxide were found to protect the albumin solution from heat coagulation, although they were very carefully freed from electrolytes. It is an interesting fact that such a protected solution was coagulated if, after boiling and cooling, it was subjected to dialysis. This is taken to indicate that, although no coagulation occurs on boiling the protected solution, the albumin undergoes some chemical change, and is no longer able to retain the stabilising substances; this is confirmed by the fact that coagulation is also caused by adding some fresh albumin solution to the boiled protected solution; the loosely held stabiliser is removed by the fresh albumin. The phenomenon of reverse protection is also shown to occur in solutions of gelatin, which can be made temporarily resistant to the coagulating action of tannic acid by the addition of metallic sols.

G. A. R. K.

Protective Colloids. V. The Seed of *Plantago psyllium*, L., as Protective Colloid. II. Colloidal Selenium. A. GUTBIER, J. HUBER, and P. ECKERT (*Kolloid Z.*, 1923, **32**, 255—262; cf. A., 1916, ii, 556).—Very stable solutions of colloidal selenium may be prepared by reducing selenium dioxide in the presence of the chloroform-water extract of the seeds of *Plantago psyllium*, L., by hydrazine hydrate at the ordinary temperature. Systems coloured yellow, yellowish-red, vermilion, blood-red, and bluish-red can be obtained, but if the faintest blue flickering is observed in the sols, coagulation follows almost immediately. Evaporation of the colloidal solutions gives reversible residues containing up to 65% of selenium.

J. F. S.

Protective Colloids. V. Seeds of *Plantago psyllium*, L., as Protective Colloid. III. Colloidal Tellurium. K. GUTBIER, J. HUBER, and P. ECKERT (*Kolloid Z.*, 1923, **32**, 329—330; cf. preceding abstract).—The extract of the seeds of *Plantago psyllium*, L., has been examined as a protective colloid for colloidal tellurium. It is shown that highly dialysed sols of tellurium prepared by the action of hydrazine hydrate on telluric acid in the presence of the extract are extremely stable, but the amount of the protective colloid ought not to exceed 0.3%. The colloidal tellurium prepared under the above-named conditions is negatively charged. Concentration of the sol solutions furnishes solid residues containing up to 30% of tellurium, but these are completely irreversible except in those cases where the tellurium concentration is very small.

J. F. S.

Protective Colloids. III. Gum Tragacanth as Protective Colloid. II. Colloidal Silver. A. GUTBIER and W. WÜTERICH (*Kolloid Z.*, 1923, **32**, 331—333; cf. *ibid.*, 1916, **18**, 145).—Silver

nitrate may be reduced to colloidal silver by suspensions of gum tragacanth in ammoniacal solutions, the colloidal system being coloured various shades of brown. On keeping, the solutions become coated with a thin silver mirror and deposit a brown reversible precipitate. The colloidal system is not very stable toward electrolytes; 0.1*N*-ammonium chloride produces complete coagulation in twenty-four hours. Evaporation gives reversible residues which contain up to 79.24% of silver. J. F. S.

Flame as an Example of a Stationary Disperse System. P. P. VON WEIMARN (*Kolloid Z.*, 1923, **32**, 253—255).—A theoretical note in which flame is discussed as a disperse system. J. F. S.

Determination of the Distribution of Size of Particles in Disperse Systems. THE SVEDBERG and HERMAN RINDE (*J. Amer. Chem. Soc.*, 1923, **45**, 943—954).—The principles for the determination of the distribution of size of particles in a disperse system are discussed, and an improved form of Odén's method (*A.*, 1916, ii, 301) is described. This makes use of a self-recording sedimentation balance, which permits of the recording of quantities as small as 0.02 g. with an accuracy of 0.00001 g. This method depends on the compensation of the increasing weight of sediment by means of an electric current passing through a coil acting on an iron cylinder, recorded on a sensitive recording milliammeter. The compensation apparatus works automatically by means of a system of relays and a drum resistance rotated by a motor. From the relation between time and current, the sedimentation curve can be found, and from this curve the distribution curve can be calculated. To illustrate the process, the sedimentation and distribution curves of a mercury hydrosol and a gold hydrosol have been determined and are given in the paper. A method is described for determining the distribution of size of particles, depending on the variation of concentration with height in a sedimenting system. As an example, a gold hydrosol was studied, the concentration at different heights being measured by means of the light absorption. The theory for the development of an analogous method depending on the use of centrifugal force has been discussed. J. F. S.

The Validity of the Partition Law in the Equilibrium between Mixed Crystals and their Solutions. G. MEYER (*Rec. trav. chim.*, 1923, **42**, 301—316).—A study of the potassium chromate-potassium sulphate-water, lead chloride-lead bromide-water and *p*-dichlorobenzene-*p*-dibromobenzene-water systems shows that in the two former cases the partition law probably holds, and in the latter it can be demonstrated with certainty. The lack of agreement of the author's observations in the latter case with those of Würfel (*Thesis*, Marburg, 1896) is ascribed to the non-attainment of equilibrium in that worker's experiments. The validity of the results obtained is dependent on the assumption that the substances used have the same molecular constitution in solution as in the solid phase, H. J. E.

Two Cases of Binary Eutectic Cycles. ALEXEI MICHAÏLOVITSCH VASILIEV (*J. Russ. Phys. Chem. Soc.*, 1917, **49**, 428—431).—Flavitski's rule (A., 1906, ii, 152) for cycles of three binary fusion diagrams is shown to hold for the systems antimony chloride- α -nitronaphthalene, and antimony chloride- β -chloronaphthalene. In both these systems, compound formation occurs, but it is also possible to realise the unstable eutectic points of the components. Each system may therefore be regarded as being composed of three systems, e.g., antimony chloride-compound, compound- α -nitronaphthalene, and α -nitronaphthalene-antimony chloride. R. T.

The Probable Composition of the Eutectics of some Volatile Substances. ALEXEI M. VASILIEV (*J. Russ. Phys. Chem. Soc.*, 1917, **49**, 432—441).—Flavitski's rule (A., 1906, ii, 152) is applied to sixteen binary systems of volatile components, namely, methyl ether and methyl alcohol with sulphur dioxide, hydrogen chloride, methyl chloride, carbon dioxide, hydrogen sulphide, and ammonia; methyl alcohol with water; hydrogen chloride with methyl chloride and sulphur dioxide; and ammonia with water (Baume and co-workers, A., 1914, ii, 446, 635, 636). The compositions of the eutectic mixtures calculated on the above rule in most cases agree within 6 mol. % with those obtained by Baume and his collaborators. R. T.

Rhythmic Precipitation Processes. K. NOTBOOM (*Kolloid Z.*, 1923, **32**, 247—252).—The author describes a new method for the production of Liesegang rings which allows the formation of the rings being followed microscopically. Observations are made which, in the author's opinion, supports Ostwald's hypothesis of the formation of rhythmic precipitates, namely, that the precipitates are due to a metastable boundary of the supersaturated solution ("Lehrbuch allg. Chemie," 1899, II, 2, 778). J. F. S.

Rhythmic Banded Films of Precipitates on the Surface of Liquids. I. A. JANEK (*Kolloid Z.*, 1923, **32**, 252—253).—A banded film precipitate may be prepared by pouring a solution of 1.0 g. of gelatin and 0.21 g. of potassium dichromate in 30 c.c. of water on to a glass plate so that a thin film is formed. This is allowed to solidify and then a small crystal of silver nitrate is placed on the film and moistened with a drop of water. Bands 0.08—0.15 mm. broad are produced. J. F. S.

Action of Heat on the Formation of Precipitates in Jellies. R. ED. LIESEGANG (*Kolloid Z.*, 1923, **32**, 263—264).—Hatschek has shown (*Proc. Roy. Soc.*, 1921, [A], **99**, 496) that light has a marked influence in the rhythmic precipitation of lead acetate by potassium dichromate. The author now shows that when silver nitrate is allowed to diffuse into dialysed gelatin solutions in the dark a marked turbidity is produced, but when the turbidity is exposed to electric light for an hour and then preserved in the dark for twenty-four hours it is found to have disappeared. This is not due, as the experiment would appear to indicate, to the

effect of light, but to the fact that the lighted room was 10° warmer than the dark room. J. F. S.

The Propagation of the Explosion-Wave. I. Hydrogen and Carbon Monoxide Mixtures. HAROLD BAILY DIXON and NOEL STANLEY WALLS (T., 1923, 123, 1025—1037).

The Combustion of Complex Gaseous Mixtures. II. Mixtures of Carbon Monoxide and Hydrogen with Air. WILLIAM PAYMAN and RICHARD VERNON WHEELER (T., 1923, 123, 1251—1259).

The So-called Pre-pressure Interval in Gaseous Explosions. JOHN DAVID MORGAN (T., 1923, 123, 1304—1308).

The Energy of Activation in Heterogeneous Gas Reactions with Relation to the Thermal Decomposition of Formic Acid Vapour. CYRIL NORMAN HINSHELWOOD and BRYAN TOPLEY (T., 1923, 123, 1014—1025).

The Velocity of Reaction in Mixed Solvents. V. a. The Velocity of Formation of Quaternary Ammonium Salts. b. The Study of an Intramolecular Change. JOHN DEXTER, HAMILTON MCCOMBIE, and HAROLD ARCHIBALD SCARBOROUGH (T., 1923, 123, 1229—1241).

The Speed of Chemical Reaction through a Solid. C. D. NIVEN (*Chem. News*, 1923, 126, 183—186).—Making the assumptions that the time taken to complete the chemical reaction within a small area in the solid is proportional to the distance of the area from the surface, inversely proportional to the average width of passage, and proportional to the amount of chemical reagent required, calculations are made for the relative speeds of penetration into cylinders, and spheres of varying dimensions, and these checked by experimental measurements on the speed of penetration of casein by formaldehyde. In view of the difficulties in arriving at the exact end-point, the agreement between theory and experimental is satisfactory. W. E. G.

The Mode of Reaction of Highly Insoluble or Undissociated Salts. BENJAMIN S. NEUHAUSEN (*Science*, 1923, 57, 26).—In support of Haber's contention (A., 1904, ii, 607, 808) that molecules and complex ions take part in reactions between highly insoluble or slightly dissociated substances, attention is directed to the rapid dissolution of mercuric sulphide by a solution of iodine in aqueous potassium iodide and to the precipitation of mercuric sulphide by addition of sodium sulphide to a solution containing the mercuricyanide-ion. In the latter case, precipitation takes place rapidly in a solution through which, it may be calculated, one mercury-ion flashes at minimum intervals of ten seconds (cf. Smith, A., 1922, ii, 626). A. A. E.

Hydration of Meta- and Pyro-phosphoric Acids. LEOPOLD PESSEL (*Monatsh.*, 1923, 43, 601—614).—The velocity of hydration

of metaphosphoric acid in aqueous solution is increased by addition of hydrochloric acid, the velocity being roughly proportional to the hydron concentration. The velocity constant in half the experiments increased with time, probably owing to the presence of polymerised metaphosphoric acids. Pyrophosphoric acid is not formed as an intermediate compound in this process. As stated by Sabatier (A., 1888, 404; 1889, 671), the conversion of sodium metaphosphate into orthophosphate is accelerated by adding excess of alkali, in rough proportion, to the excess added.

The hydration of pyrophosphoric acid, which may be prepared in a few days from the lead salt (cf. Giran, A., 1903, ii, 139), is also accelerated by adding hydron, the effect again being only roughly proportional to the concentration of the latter, however. The rate of hydration is smaller than in the case of the meta-acid (cf. Montemartini and Egidi, A., 1902, ii, 451). Mixtures of pyro-acid and hydrochloric acid show an abnormally low electrical conductivity, probably owing to the formation of a feebly dissociating compound between the two acids.

Sodium pyrophosphate does not change into the ortho-salt during six months in aqueous solution at 25°, even in the presence of alkali.

E. E. T.

Mechanism of Catalytic Reactions. Decomposition of Hydrogen Peroxide by Metallic Oxides. J. CLARENS (*Bull. Soc. chim.*, 1923, [iv], 33, 280—293).—A study was made of the catalytic decomposition of hydrogen peroxide in the presence of metallic oxides or hydrated oxides precipitated in the peroxide solution by the addition of sodium hydroxide to the corresponding metallic salt. Under these conditions, the decomposition was essentially a physical phenomenon, depending primarily on the physical state of the catalyst. The possibility of a chemical type of catalysis was excluded by reason of the fact that the decomposition was retarded or altogether inhibited when the metallic oxide was in colloidal or actual solution. Thus in the case of manganese, a colloidal manganese dioxide is first formed, and exactly coincident with its flocculation there is a considerable increase in the velocity of the peroxide decomposition. Conversely, in the case of lead, the peroxide precipitated by the addition of the first few drops of sodium hydroxide to a mixture of hydrogen peroxide and a solution of a lead salt, causes a decomposition which ceases on the addition of a further quantity of sodium hydroxide sufficient to redissolve the whole of the precipitated lead peroxide. The stabilisation of hydrogen peroxide by acids is thus apparently due to their solvent action on traces of metallic oxides which would otherwise cause slow decomposition. The decomposition of hydrogen peroxide being the result of its adsorption by the catalyst, and the amount adsorbed being a variable fraction of the total quantity present, the reaction only becomes unimolecular at the limit at which all that present is adsorbed. The activity of the catalyst does not depend only on its mass and physical state, but also on the concentration of the hydrogen peroxide on which it acts.

G. F. M.

The Contact Action of Charcoal in Reactions of Oxidation.

ANTONI GRIGOREVICH DOROSCHEVSKI and G. S. PAVLOV (*J. Russ. Phys. Chem. Soc.*, 1917, **49**, 169—175).—Sulphur is mixed with birch or sugar charcoal containing a little sodium carbonate, and the mixture heated at 100°. Moist air is then passed over it for some time, and the mixture is analysed for sulphuric acid, the yields of which were variable, and small in quantity. Charcoal is saturated with hydrogen sulphide, aqueous sodium carbonate is added, the hydrogen sulphide removed, and the charcoal carefully dried. Examination of the product shows that a certain amount of the hydrogen sulphide has decomposed, liberating sulphur, the sulphur content being such that from 1 g. of the mixture 0.5376 g. of barium sulphate could be obtained. A portion of the mixture is then treated as before, and it is found that after thirty hours no further oxidation takes place, and that 0.1296 g. of barium sulphate can be obtained per 1 g. of mixture. This amount corresponds with the production of an amount of sulphuric acid just sufficient to neutralise the alkali present, and if more of the latter is added, and the process repeated, further sulphur can be oxidised. Birch or sugar charcoal is shown to be a quite efficient catalyst for the oxidation of sulphur dioxide to sulphur trioxide. R. T.

Influence of Temperature, Pressure, and Supporting Material for the Catalyst on the Adsorption of Gases by Nickel. ALFRED WILLIAM GAUGER and HUGH S. TAYLOR (*J. Amer. Chem. Soc.*, 1923, **45**, 920—928).—The adsorption of hydrogen by nickel has been investigated at various temperatures between 25° and 305°, with the nickel supported on diatomaceous earth, diatomite brick, or entirely unsupported. Adsorption isotherms of hydrogen on nickel have been constructed, using nitrogen as reference gas. A definite saturation capacity of nickel for hydrogen exists which depends on the temperature. From the variation of the saturation pressure with temperature, the heat of adsorption of hydrogen on nickel has been calculated to be approximately 2,500 cal. Other methods of calculation give a value of 12,000 cal. The effect of using an inert material for catalyst support has been found to increase greatly the adsorptive capacity per gram of nickel and to yield a catalyst which will withstand much more severe heat treatment without diminution of its adsorbing power.

J. F. S.

Velocity of Catalytic Reactions. J. ZALKIND (*Z. physikal. Chem.*, 1923, **104**, 177—191).—The rate of reaction between hydrogen and solutions of $\beta\epsilon$ -dimethyl- Δ^7 -butinene- $\beta\epsilon$ -diol, $\alpha\alpha\delta\delta$ -tetraphenylbutinene- $\alpha\delta$ -diol, $\gamma\zeta$ -dimethyl- Δ^6 -octinene- $\gamma\zeta$ -diol, and phenylacetylene in ethyl alcohol has been measured in the presence of either palladium or platinum black at the ordinary temperature. The results show that the addition of hydrogen by acetylene derivatives does not in general follow the equation for a reaction of the first order and that the mechanism of the reaction is complicated as in the case of reactions catalysed by biological catalysts. In both cases, the formation of an intermediate product must be assumed,

which may be a definite compound or an adsorption complex. Probably in heterogeneous catalysis an adsorption constitutes the first stage and this is followed by the formation of an unstable chemical compound; otherwise it would be difficult to understand why the hydrogenation of different types of acetylene derivatives takes place so differently. The chemical nature of the catalyst plays an important rôle in the reaction, palladium having a markedly different action from platinum.

J. F. S.

Problem of Negative Catalysis. I. HUGH S. TAYLOR (*J. Physical Chem.*, 1923, 27, 322—341).—A theoretical paper in which a new hypothesis of negative catalysis is proposed to supplement the hypotheses hitherto held to explain the mechanism of special cases. The present hypothesis accounts for the inhibitory power of the negative catalyst by assuming an interaction between one of the reacting substances and the inhibitor, with the formation of a molecular compound, as an alternative to reaction between two or more of the reacting substances. The extent of the inhibition is determined by the degree and the velocity of compound formation. It is shown that the inhibitory power of water and the alkali sulphates in the decomposition of oxalic acid in solutions of sulphuric acid, that of water in various reactions in sulphuric acid and acetone solutions, and that of a large number of organic and inorganic compounds of widely varying character in the inhibition of autoxidation processes, can be readily explained on the basis of the present hypothesis. The experimental evidence obtained in all these cases is readily explained by the hypothesis, and various predictions have been made on this basis which have already been to some extent verified. The whole subject of negative catalysis is discussed, and many references to the literature of the subject are included in the paper.

J. F. S.

Change of Properties of Substances on Drying. II. HERBERT BRERETON BAKER (*T.*, 1923, 123, 1223—1224).

A Static or Dynamic Atom? NORMAN R. CAMPBELL (*Nature*, 1923, 111, 569).—It is pointed out that if the sharing of an electron means the sharing of an orbit, compounds being formed when some of the electronic orbits surround both nuclei, the Lewis-Langmuir theory can be expressed in terms of Bohr's conceptions, although the question whether such shared orbits are possible is one for the quantum theory to decide.

A. A. E.

The Spectrum of the Semi-circular Helium Model. H. O. NEWBOULT (*Phil. Mag.*, 1923, [vi], 45, 1085—1087).—A theoretical examination of the Langmuir model of the helium atom (cf. A., 1921, ii, 656). Since the ordinary Sommerfeld-Wilson quantum condition when applied to this model gives a negative value for the ionisation potential, Langmuir suggested that the maximum angular momentum of a single electron be set equal to $\hbar/2\pi$, and deduced a value for the ionisation potential which agreed with the experimental value. This quantum condition is

shown to lead to a spectrum for the helium atom which does not agree with that of any known series. W. E. G.

The Crossed-orbit Model of Helium, its Ionisation Potential and Lyman Series. L. SILBERSTEIN (*Nature*, 1923, 111, 567).—Mathematical. The ionisation potential is calculated for Bohr's model to be 24.35 volts, in close agreement with Lyman's latest observed value, 24.5 volts. A formula has been developed which, regardless of its significance or deduction, gives the correct ionisation potential for a number of simple rational values of $-\cos i$. A. A. E.

The Dimensions of Atomic Nuclei, and the α -, H^+ , β -, and γ -Rays. MAXIMILLIAN CAMILLO NEUBERGER (*Ann. Physik*, 1923, 70, 139—152).—A theoretical paper in which the upper and lower limits for the radii of the atomic nuclei are calculated. From the ranges of H^+ rays (Rutherford and Chadwick, A., 1921, ii, 293), and the ranges of α - and β -rays of radioactive elements, deductions are made with regard to the nuclear dimensions of all the elements. The radioactive isotopes possess widely different nuclear radii, and, on the other hand, elements with different atomic numbers give almost identical values for the lower limit of the radius of the nucleus. Periodic changes in the atomic dimensions of the elements in the radium, actinium, and thorium families are found as the atomic number decreases. Thus from uranium I to radium-A a decrease in the radius takes place, followed by a large increase at radium-C, a rapid fall at radium-C', and finally a rise to radium-F. This periodicity shows little resemblance to the periodic course of the atomic volume curve of these elements. W. E. G.

An Explanation of the Theory of the Rotation of the Atomic Nucleus. I. HERBERT HENSTOCK (*Chem. News*, 1923, 126, 262—266).—The theory advanced in a previous paper is further elaborated (cf. this vol., ii, 233). Some of the edges of the cubic atom of the Lewis-Langmuir theory will be negatively and some positively charged. Union between atoms will take place through juxtaposition of oppositely charged edges. This will lead to opposite orientation of the nuclei of adjacent atoms, resulting in alternate polarity. Double and treble bonds between carbon atoms are considered. E. H. R.

Experiments with a Model to Illustrate the Combination of Two Atoms consisting of Magnetons round a Positive Nucleus. A. P. LAURIE (*Proc. Roy. Soc. Edin.*, 1923, 43, 72—84).—A mechanical model designed to investigate the probable behaviour and disposition of magnetons in a magnetic field is described. The arrangements of magnetons and nucleus in molecules of oxygen, water, marsh gas, acetylene, ethylene, ethane, benzene, and carbon chain compounds are detailed, and it is suggested that chemical combination consists, in the first place, of addition. Thus in the combination of hydrogen and oxygen to form water, two molecules of hydrogen attach themselves to a

molecule of oxygen by means of secondary valencies to form H_4O_2 , which tends to cleave into two groups H_2O , this rearrangement reducing the total electrostatic and magnetic potential energy of the system.

J. S. G. T.

The Quantum Theory and Isotopes. J. W. NICHOLSON (*Phil. Mag.*, 1923, [vi], 45, 801—817).—A theoretical paper dealing with the quantum theory of spectra and atomic structure. Since the energy of an atom is independent of the system of co-ordinates used in its calculation, the pendulum paths of the electrons should yield the same values as those from other orbits. The energy of a hydrogen atom in which the electron is traversing a pendulum path about the nucleus is shown to be given by $W = 2\pi^2 me^4 v^2 / n^2 h^2$. It is suggested that in the nucleus an interpenetration of the electric charges may possibly occur. A double mesh structure of the ether would admit of this possibility, so that two strain systems in the same region would not annihilate each other and might pass through each other. Assuming that the quantising relation can be applied to the nucleus, it is shown that the possible hydrogen isotope, the "inverted Bohr model" of Lenz, in which two nuclei rotate symmetrically around an electron, has a spectrum which shows detectable differences from the ordinary hydrogen spectrum. The differences between the spectra of the lithium isotopes should be much smaller than those found recently by McLennan and ascribed to these isotopes. The effect for lead is comparable with that already known to occur. From a study of the structure of ionised helium, it is considered that the hypothesis of nuclei made entirely of hydrogen is unsound.

W. E. G.

The Separation of Elements and Isotopes by Diffusion. ERNST MURMANN (*Oesterr. Chem. Ztg.*, 1923, 26, 14—15).—The diffusion method has been applied to uranium, chlorine, and lithium, and in no case was any separation effected, although the same method was successful when employed in the separation of nickel from cobalt. Several attempts were made to isolate the isotopes of uranium by diffusion, fractionation, and precipitation. Thus it was precipitated many hundreds of times as tetroxide, crystallised, and fractionally precipitated in the form of its double salts, and uranyl nitrate was fractionated by a diffusion process. Sodium and lithium chlorides were also subjected to diffusion processes, but in no case was any separation observed within the experimental error of the analyses. It is considered that ionic mobility is dependent only on the atomic volume, and not on the atomic weight. This provides an explanation of the differences between the behaviour of mixtures of elements and of isotopes during diffusion processes.

W. E. G.

Valency. WILLIAM R. FIELDING (*Chem. News*, 1923, 126, 177—180, 193—197, 209—214, 226—229).—A discussion of the variability of valency. The effect of temperature on polymerisation and on valency is considered in detail.

W. E. G.

Supposed Relationships between Atomic Constants and the Valency Number of the Atoms. WALTER HÜCKEL (*Z. physikal. Chem.*, 1923, 104, 262—268).—A theoretical paper in which the author shows that the relationship between atomic constants and the physical properties (heat of combustion, molecular volume, molecular refraction, molecular cohesion, and other additive properties) as put forward by Le Bas (P., 1907, 22, 322; A., 1918, ii, 667), Traube (A., 1907, i, 145; ii, 205), and Walden (A., 1909, ii, 119) are without meaning. They do not follow from the experimental data, but are due to the use of an inexact method of calculation. It is shown that the function $\varphi = \text{additive molecular property} / \text{sum of the valencies}$ is generally, within wide limits, almost independent of the numerical relationships of the atomic constants of the particular property, just as it is almost independent of the chemical nature of the compound. If φ should prove to be rigidly constant, then it would follow that the atomic constants are proportional to the valency number, but an approximate constancy of φ does not allow of any definite conclusion being drawn, not even the statement of an approximate rule. Consequently, the relationships, quoted in the literature, between atomic volume, atomic refraction, and atomic cohesion, on the one hand, and the valency number, on the other, which are based entirely on an approximately constant value of φ , do not in reality exist. J. F. S.

Other Factors Influencing Co-ordination. T. MARTIN LOWRY (*Chemistry and Industry*, 1923, 42, 412—415).—In continuation of previous work (this vol., ii, 313), the author considers the transfer of electric charges and ring formation, respectively, as influencing co-ordination. The sharing of electrons between atoms which accompanies co-ordination causes a transfer from the radicles to the metal, and these latter components also become united by covalencies. The effects are illustrated by reference to methyl-ethylaniline oxide, the chloroplatinates, the cobaltammines, and the metallic carbonyls. Co-ordination can be effected, often under very adverse conditions, by making the co-ordinated groups part of a conjugated system. A conjugated ring-system containing three positively-charged and three negatively-charged atoms, as in benzene, is particularly favourable to co-ordination.

J. S. G. T.

Apparatus for the Measurement of the Rate of Flow of Gases. V. ARKADIEV (*J. Russ. Phys. Chem. Soc.*, 1918, 50, 210—220).—An apparatus for measuring the rate of flow of gases, for which the name rheometer is proposed, is described. The gas is made to pass through a narrow tube, the ends of which are in connexion with the limbs of a manometer. The difference of pressure recorded in the manometer is then a measure of the speed at which the gas passes through the tube. Instead of this tube, a diaphragm pierced with a small aperture may be used. An arrangement is also described for regulating the rate of flow of gases, this consisting of a diaphragm provided with an aperture, the rate of flow being proportional, with any given pressure, to the diameter

of the aperture. A rheometer constructed on a different principle is described, for use with higher velocities, in which the velocity of the gas is proportional to the height to which a small ebonite floater in a glass tube can be raised by it. Such an apparatus may also be used for the measurement of quantities of gases, by passing them at a known speed, for a definite interval of time, through a tube of known diameter, and its possible use in reactions involving gaseous combination is pointed out.

R. T.

An Apparatus for Continuous Extraction with Boiling Solvents. O. P. A. H. SCHAAAP (*Pharm. Weekblad*, 1923, 60, 375—376).—A slight modification of the apparatus used for extraction with boiling chloroform (A., 1922, ii, 797) to render it safe for use with low-boiling, inflammable solvents.

S. I. L.

Chemistry in Mediæval Islam. E. J. HOLMYARD (*Chemistry and Industry*, 1923, 42, 387—390).—In emphasising the importance of more detailed study of the Arabic chemical manuscripts, the author briefly discusses the position of certain individuals, and maintains that the first successful efforts to place chemistry on a scientific basis and apply scientific method originated in Islam.

A. A. E.

Inorganic Chemistry.

Active Hydrogen by the Action of an Acid on a Metal. A. C. GRUBB (*Nature*, 1923, 111, 600; cf. Wendt and Landauer, A., 1920, ii, 425).—Active hydrogen can be readily detected even in presence of moisture by direct combination with nitrogen to yield ammonia. When hydrochloric or sulphuric acid is dropped on to magnesium suspended so as to avoid immersion, and the hydrogen rapidly evolved is passed through a glass-wool plug, its activity is demonstrated by the formation of ammonia with pure nitrogen. It is concluded that the activity is not due to ions or to atomic gas. Langmuir (A., 1912, ii, 1162) has shown that monatomic hydrogen does not react with nitrogen to form ammonia, yet if nitrogen is allowed to impinge on the surface of magnesium at which evolution of hydrogen is taking place, a maximum quantity of ammonia is formed. Moreover, slow evolution of hydrogen, with subsequent passage through glass wool and admixture with nitrogen, does not result in the production of ammonia. The life of the active gas, about two minutes, is in agreement with that of triatomic hydrogen formed by other methods. The results are considered to substantiate the view of Wendt and Landauer (A., 1922, ii, 369) that triatomic hydrogen should be produced wherever atomic hydrogen is evolved. A. A. E.

Active Hydrogen by Electrolysis. A. C. GRUBB (*Nature*, 1923, 111, 671).—By using a method corresponding with that for

the electrolytic production of ozone, namely, by electrolysis of a solution of sulphuric acid with a high current density at the cathode, active hydrogen is produced, and will combine with pure nitrogen to form ammonia. The ozone form of hydrogen is also produced by the electrolysis of a solution of potassium hydroxide, when a high cathode current density is employed. A. A. E.

The Aëration of Quiescent Columns of Distilled Water and of Solutions of Sodium Chloride. W. E. ADENEY, A. G. G. LEONARD, and A. RICHARDSON (*Phil. Mag.*, 1923, [vi], 45, 835—845).—The aëration of water under natural conditions is effected by mixing of the exposed layer with the unexposed portions of the water to depths of at least 10 feet. The mixing is brought about by the downward "streaming" of the constantly changing layer of water exposed to the air. This process is more rapid in salt than in fresh water. The rate of "streaming" is dependent on the rate of cooling and concentration of the surface layers, which is brought about by evaporation, and is more rapid at temperatures above 10° than below it. A 1% solution of sodium chloride gives the optimum conditions for the streaming process. W. E. G.

The Formation of Hydrogen Peroxide during the Combustion of Hydrogen. MAX HAUSER (*Ber.*, 1923, 56, [B], 888—894).—The combustion of hydrogen in oxygen has been shown to be a termolecular reaction in accordance with the equation $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$, which occurs mainly at the walls of the containing vessel, but evidence has also been adduced (cf. von Wartenberg and Sieg, A., 1921, ii, 107) that hydrogen peroxide is intermediately produced and that changes represented by the appended equations take place: $\text{H}_2 + \text{O}_2 = \text{H}_2\text{O}_2$, $\text{H}_2\text{O}_2 = \text{H}_2\text{O} + \frac{1}{2}\text{O}_2$, $\text{H}_2 + \frac{1}{2}\text{O}_2 = \text{H}_2\text{O}$. Attempts are now described to catalyse the first reaction to such an extent that it occurs at temperatures below that at which rapid decomposition of hydrogen peroxide sets in, and also to effect the reaction in such a manner that the products are very rapidly cooled and thus shielded from speedy decomposition. The results, however, are negative.

Inexplosive mixtures of hydrogen and oxygen containing a large excess of one or other gas are passed over porous earthenware impregnated with platinum, palladium, silver, copper, iron, cobalt, or nickel at temperatures varying between 100° and 500°. Copper or iron-wire gauze, glass fragments, or glass wool are also suitable catalyst carriers, but asbestos, platinised or palladised asbestos, pumice, or aluminium powder causes immediate decomposition of hydrogen peroxide. Combustion of the hydrogen occurs invariably, but the presence of hydrogen peroxide in the condensates could not be detected in any instance by means of titanous acid with which a concentration of 0.00001% H_2O_2 can be readily detected. It appears probable that the contact agent catalyses both the formation and decomposition of hydrogen peroxide (cf. Hofmann, A., 1922, ii, 490).

In a second series of experiments, the rapid heating and cooling

of the mixture of gases are effected by its momentary adiabatic compression in a steel cylinder containing a small quantity of water. Partial combustion invariably occurs, but the presence of hydrogen peroxide in the water could not be detected in any instance. The supposition that the heating is sufficiently prolonged to cause the decomposition of any hydrogen peroxide which is produced is not in accord with the known properties of the substance, and under these conditions it appears probable that the formation of water is a true termolecular change.

Repetition of the experiments of von Wartenberg and Sieg on the passage of mixtures of hydrogen and oxygen through a "hot-cold" tube (*loc. cit.*) have confirmed the results of these workers and shown that the yields of hydrogen peroxide are not appreciably affected by change in the chemical nature of the walls of the tube. The effect of the introduction of quartz, copper gauze, platinum foil, and silver foil into the tube is described, but does not appear to be simply explicable. The comparatively large production of hydrogen peroxide in the "hot-cold" tube is due to the catalytic action of the glowing wall; the high temperature of the latter involves a low adsorptive power, and the hydrogen peroxide is therefore shielded from immediate reduction unless the hydrogen is in great excess.

H. W.

The Solubility of Chlorine in Water. V. ARKADIEV (*J. Russ. Phys. Chem. Soc.*, 1918, 50, 205—209).—The solubility of chlorine at various temperatures and pressures is calculated from a formula deduced by Jakovkin (*ibid.*, 1900, 32, 673), namely, $x = r + 7.94 \sqrt[3]{kr(1 + \omega t/c)^2}$, where x is the ratio of the concentration, in millimoles per litre, of chlorine in the water to that in the atmosphere, r the ratio of unhydrolysed to total chlorine in the water, k the hydrolysis constant for chlorine in water, ω the coefficient of expansion of chlorine, $=0.00371$, t the temperature, and c the volume concentration of chlorine in the atmosphere. The values thus obtained agree satisfactorily with those obtained experimentally.

R. T.

Solubility of Selenium in Alkali Hydroxides. G. CALCAGNI (*Gazzetta*, 1923, 53, i, 114—119; cf. A., 1921, ii, 195).—Powdered selenium dissolves readily in the cold in 66% sodium or potassium hydroxide solution, more slowly in saturated barium hydroxide solution on a boiling water-bath, and only slowly and in very small proportion in ammonia solution ($d\ 0.888$). The solutions thus obtained contain selenides, selenites, and, possibly, a compound analogous to the thiosulphate, formed by the action of atmospheric oxygen on the selenides; it may be, also, that a small part of the selenium is present as such in the solutions. The reactions taking place are gradual and highly complicated, the first products consisting of selenides, which subsequently undergo transformation into polyselenides and selenites. The solutions formed are at first brown, but are gradually decolorised by the combined action of the oxygen and carbon dioxide of the air.

T. H. P.

Preparation of Hydrazine by Raschig's Method. REGINALD ARTHUR JOYNER (T., 1923, 123, 1114—1121).

Reactions of Chlorites with Salts of Hydrazine and of Hydroxylamine. GIORGIO RENATO LEVI (*Gazzetta*, 1923, 53, i, 105—108).—Treatment of a solution of freshly prepared alkali chlorite with commercial hydrazine hydrate results in immediate liberation of nitrogen and gradual heating of the liquid, whereas if pure hydrazine hydrate is used neither evolution of gas nor heating is observed. The decomposition is thus accelerated by the presence of extraneous substances, and in neutral boiling solution proceeds quantitatively according to the equation $\text{N}_2\text{H}_4 \cdot 2\text{HCl} + \text{NaClO}_2 = \text{N}_2 + \text{NaCl} + 2\text{H}_2\text{O} + 2\text{HCl}$. The decomposition is slower in alkaline solution, and is accelerated by traces of iron or copper salt.

Hydrazine chlorite, $\text{N}_2\text{H}_4 \cdot \text{HClO}_2$, obtained as white crystals by the reaction $(\text{N}_2\text{H}_4)_2 \cdot \text{H}_2\text{SO}_4 + \text{Ba}(\text{ClO}_2)_2 = \text{BaSO}_4 + 2\text{N}_2\text{H}_4 \cdot \text{HClO}_2$, inflames spontaneously when dry.

The reaction of hydroxylamine hydrochloride (1 mol.) with a neutral solution of a chlorite (1 mol.), expressed by the equation $\text{NH}_2 \cdot \text{OH} \cdot \text{HCl} + \text{NaClO}_2 = \text{NaCl} + \text{Cl} + \text{NO} + 2\text{H}_2\text{O}$, occurs rapidly and with development of a considerable amount of heat. With excess of the hydroxylamine salt, however, the reaction takes place in accordance with the equation $2\text{NH}_2 \cdot \text{OH} \cdot \text{HCl} + \text{NaClO}_2 = \text{NaCl} + \text{N}_2\text{O} + 3\text{H}_2\text{O} + 2\text{HCl}$.
T. H. P.

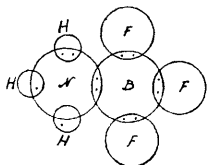
The Preparation of Hydrazine Sulphate and Sodium Azide. B. P. ORELKIN, V. G. CHLOPIN, and I. I. TSCHERNIAEV (*J. Russ. Phys. Chem. Soc.*, 1917, 49, 82—87).—The authors give full details for the preparation of hydrazine sulphate by Raschig's method (A., 1908, ii, 1029), and of sodium azide by Thiele's method (A., 1908, ii, 940). The hydrazine hydrate for the latter process is prepared by means of alcoholic sodium hydroxide instead of by the sodium methoxide used by Thiele.
G. A. R. K.

The Discovery of Red Phosphorus. R. WINDERLICH (*Chem. Ztg.*, 1923, 47, 297).—In the year 1813, Vogel published a paper on the action of sunlight on phosphorus (*Schweigger's J.*, 1813, 7, 95—121), and stated that the red powder formed was insoluble in carbon disulphide. Many years later, Berzelius (*Ann. Phys. Chem.*, 1843, 59, 77) investigated the formation and properties of red phosphorus, and recognised that it was an allotropic modification of the element. Schrötter (*Denkschr. K. Akad. Wiss. Wien Math. Naturw. Klasse*, 1850, 1, 1—12) used carbon disulphide for the separation of red phosphorus from yellow phosphorus, claiming that he was the first to effect the separation by this means.
W. P. S.

The Valency of Boron. J. BÖESEKEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1923, 26, 97—111).—It has been shown by Hermans (this vol., i, 557) that pyrocatecholboric acid, which is a considerably stronger acid than boric acid, must in all probability contain quinquevalent boron. This new type of boron compound

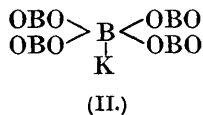
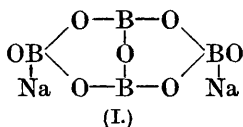
can readily be explained by, and lends considerable support to, the Lewis-Langmuir theory of valency. The quinquevalency of boron in these compounds is explained on the same lines as that of the ammonium compounds, but whereas the nitrogen atom has to lose an electron in order to become quinquevalent, thereby becoming an electropositive ion, the boron atom has to gain an electron, forming an electronegative ion. The oldest known type of compound in which boron is to be regarded as quinquevalent is the type HBF_4 . In boron fluoride, BF_3 , the outer electron shell of the boron atom contains six electrons, shared in pairs with the fluorine atom. When combining with another molecule of hydrogen fluoride, the boron atom completes its octet by sharing with the new fluorine atom one of the electrons of the latter and a hydrogen electron. By taking the hydrogen electron, however, it forms the negative ion, BF_4^- , and the positive ion, H^+ . It follows that when boron is functioning as a quinquevalent atom four of its valencies are non-polar and the fifth polar, as in the case of nitrogen.

Boron can also function as a quadrivalent element. This is accomplished when a normal boron compound such as BF_3 combines with a molecule containing two available electrons in the outer shell of one of its atoms, for instance, ammonia. Thus the stable compound, $\text{BF}_3 \cdot \text{NH}_3$, can be formulated as in the annexed diagram, in which the boron atom appears truly quadrivalent, as does the nitrogen.



The constitution of the strongly acid compounds formed by boric acid with organic hydroxy-compounds containing favourably situated hydroxyl groups can be explained in a similar way. Some of these are not known as free acids, but only as salts of a metal such as potassium, which readily cedes an electron. Their formation is favoured when the organic residue has an acidic character. Thus in pyrocatecholboric acid the four oxygen atoms of the two pyrocatechol residues are bound to the boron atom each by two electrons. This can only take place when one electron is ceded by a hydrogen or metal atom. The resulting complex acid must therefore be a mono-basic acid.

The unsaturated character of boric acid as a derivative of tervalent boron leads to the formation of stronger poly-boric acids, which must be derivatives of quinquevalent boron. Borax has the formula I and potassium pentaborate, KB_5O_8 , probably the formula



II. In nitrogen boride, BN , which is an extraordinarily infusible, stable substance, it may be supposed that continuous polymerisation of the simple BN molecules has taken place, so that each

element is in effect quadrivalent as in the compound NH_3BF_3 , discussed above. The structure of the compound would then be similar to that of carbon in the diamond. The valency here becomes identical with Werner's co-ordination value as expressed, for instance, in the formula $[\text{BF}_4]\text{H}$. A few other compounds of boron, including the hydrides, are discussed. E. H. R.

Boron Hydrides. VI. The Simplest Boron Hydrides.

ALFRED STOCK and ERNST KUSS (*Ber.*, 1923, 56, [B], 789—808).—An extension of previous work (A., 1915, ii, 340, and earlier abstracts). The decomposition of the so-called magnesium boride by acids has been re-examined with the help of much larger quantities of material. The isolation and characterisation of the various boron hydrides are greatly complicated by the presence of silicon hydrides, which cannot be completely avoided, as it has not been found possible to obtain magnesium completely free from silicon, which is largely converted by acids into silicon hydrides whereas, even under the most favourable conditions, boron hydrides are only produced in extremely small amount. On the other hand, the use of the authors' vacuum process and the substitution of fractional condensation for fractional distillation have greatly facilitated the investigations. Tetraborane and diborane have been examined in greater detail. A product to which the composition B_6H_{12} was previously assigned provisionally is shown to be a mixture of B_4H_{10} , B_5H_9 , B_6H_{10} , and silicon hydrides.

The decomposition of "magnesium boride" by hydrochloric acid is most advantageously effected by gradually adding it to an excess of the acid at 40—50° (the latter temperature must not be exceeded). The necessary apparatus for the automatic addition is fully figured and described in the original. The gas is washed with water, dried successively with calcium chloride and phosphoric oxide, and condensed in two vessels cooled with liquid air. The separation and purification of the components of the mixture thus obtained are chiefly effected by fractional condensation. Boron hydrides more volatile than tetraborane do not appear to be formed. Diborane is not present in the crude gas; monoborane and triborane could not be detected even in traces.

The following individual hydrides are described. Tetraborane, B_4H_{10} , has m. p. -120.0° (-119.7°), $d_{-70}^{20} 0.59$, $d_{-35}^{20} 0.56$. Its vapour tension has been measured at the following temperatures: -113.2° , 0.2 mm.; -107.9° , 0.4 mm.; -98.0° , 0.8 mm.; -91.1° , 1.0 mm.; -86.3° , 1.9 mm.; -77.8° , 3.2 mm.; -75.1° , 4.0 mm.; -72.3° , 5.0 mm.; -70.2° , 5.9 mm.; -66.0° , 8.5 mm.; -63.2° , 10.8 mm.; -57.4° , 16.7 mm.; -53.3° , 22.2 mm.; -52.2° , 24.2 mm.; -46.7° , 34.4 mm.; -43.8° , 41.4 mm.; -39.2° , 55 mm.; -36.8° , 64 mm.; -33.7° , 76 mm.; -28.7° , 101 mm.; -27.5° , 108.5 mm.; -21.4° , 150 mm.; -16.1° , 188 mm.; -10.6° , 247 mm.; -6.5° , 295 mm.; -2.0° , 369 mm.; 0° , 388 mm.; $+4.9^\circ$, 469 mm.; $+10.0^\circ$, 572 mm.; $+15.1^\circ$, 697 mm.; $+17.6^\circ$, 755 mm. Even when highly purified, tetraborane decomposes fairly rapidly at the atmospheric temperature into hydrogen, diborane, and a number

of less volatile hydrides. The hydrogen which is thus liberated is an extremely powerful reducing agent which converts disilane and the higher hydrides of silicon into monosilane. Tetraborane and ethane yield hydrogen, diborane, the hydride B_5H_9 , and a pale yellow, crystalline substance containing boron, carbon, and hydrogen.

The analysis of tetraborane and the other hydrides is effected by thermal decomposition into boron and hydrogen. The volume of the latter is measured. The boron is estimated by direct weighing and also titrimetrically after oxidation to boric acid. The necessary apparatus is figured and described.

Diborane, B_2H_6 , obtained by heating tetraborane in a sealed tube, is very stable in the absence of moisture and grease. It has m. p. -165.5° , tensions, 6.0 mm./ -148.3° , 11.3 mm./ -144.8° , 20.3 mm./ -139.0° , 30.7 mm./ -134.9° , 48 mm./ -130.5° , 52 mm./ -129.5° , 83 mm./ -124.5° , 122 mm./ -119.9° , 187 mm./ -115.2° , 272 mm./ -109.2° , 361 mm./ -104.5° , 521 mm./ -99.3° , 608 mm./ -96.4° , 637 mm./ -95.5° , 701 mm./ -93.8° , 748 mm./ -92.75° , $d^{112}_0 0.44$. Diborane does not appear to undergo dissociation at any temperature between -24° and $+155^\circ$. Diborane reacts with hydrogen bromide in the presence of aluminium bromide at $80-90^\circ$ to give hydrogen and monobromodiborane; the latter is, however, very unstable and becomes converted largely into boron tribromide and diborane: $6B_2H_5Br = 2BBr_3 + 5B_2H_6$.

The *hydride*, B_5H_9 , is present in small quantity in the higher boiling fractions of the "crude condensate," but its isolation from this source is extremely difficult and it is more readily obtained in the homogeneous condition from the products of the decomposition of tetraborane at 100° . It is a colourless, mobile, not highly refractive liquid with an extremely unpleasant odour; it is the noxious component of the crude boron hydrides. It is slowly decomposed by water, but otherwise fairly stable. It has m. p. -46.9° , tensions, 4.8 mm./ -41.3° , 7.4 mm./ -35.6° , 12 mm./ -28.9° , 15.1 mm./ -25.1° , 21.1 mm./ -20.0° , 28.5 mm./ -14.9° , 37.8 mm./ -9.9° , 49.0 mm./ -5.0° , 65 mm./ 0° , 84 mm./ $+6.0^\circ$, 111 mm./ $+11.2^\circ$, 131 mm./ $+15.1^\circ$, $d^0_0 0.61$. It is slowly hydrolysed by water at 90° into hydrogen and boric acid: $B_5H_9 + 15H_2O = 5H_3BO_3 + 12H_2$.

The *hydride*, B_6H_{10} , is isolated from the crude condensate. It is a colourless, moderately highly refractive liquid which is less mobile and not so unpleasant in odour as the other boron hydrides. It has m. p. -65.1° , tension 7.2 mm./ 0° , $d^0_0 0.70$. It is slowly hydrolysed by water at 90° into boric acid and hydrogen. It slowly decomposes when preserved in daylight at the atmospheric temperature, giving small quantities of hydrogen and diborane and mainly a yellow, crystalline solid of the possible composition $B_{26}H_{36}$.

The thermal decomposition of diborane at 300° gives mainly boron and hydrogen. At lower temperatures ($100-200^\circ$) and higher pressures, other products, chiefly $B_{10}H_{14}$, and further solid hydrides, are also formed. Tetraborane is converted at 100° into diborane,

B_5H_9 , and other substances; at 300° , it yields mainly boron and hydrogen. The hydride, B_5H_9 , is much more stable than tetraborane at 300° , and is only partly decomposed into boron and hydrogen. Under similar conditions the hydride, B_6H_{10} , also suffers decomposition less readily than tetraborane.

Diborane does not resemble disilane in its action towards sodium amalgam, which causes condensations which have not been investigated completely. Similar reactions appear to take place with tetraborane.

Diborane and tetraborane react readily with ammonia to form liquid and solid products. They do not appear to have any action on acetylene when cold, but if the mixtures are heated at 100° or rapidly compressed an explosive change occurs accompanied by the separation of a solid, brown substance. If the mixtures are warmed gently, aromatic condensation products are formed which evolve hydrogen when treated with water. H. W.

The Melting and Working Properties of Boric Oxide Glasses with Special Reference to the Sodium Borosilicates.

VIOLET DIMBLEBY, F. W. HODKIN, M. PARKIN, and W. E. S. TURNER (*J. Soc. Glass Tech.*, 1923, 7, 57—72).—Three series of sodium borosilicate glasses were prepared containing, respectively, 20, 10, and 5% of sodium oxide. In the first series, the amount of boric oxide was varied between 0 and 45%, in the second between 15 and 50%, and in the third between 20 and 45%. In every case, homogeneous glasses were obtained with no evidence of segregation. High proportions of boric oxide give unstable glasses. Those with more than 40% B_2O_3 in the first and second series or more than 35% B_2O_3 in the third series quickly developed a white film, the most readily disintegrated being those containing the smallest proportion of sodium oxide. Melting and refining proceed more rapidly with increasing proportion of boric oxide, but the fluxing action of borax or boric oxide is not so great as that of sodium carbonate. The rate of change of viscosity with temperature increases rapidly with increasing boric oxide concentration. The glasses of the first and second series showed no devitrification when worked. E. H. R.

The Influence of Boric Oxide on the Annealing Temperature of Borosilicate Glasses.

S. ENGLISH and W. E. S. TURNER (*J. Soc. Glass Tech.*, 1923, 7, 73—76).—In the case of sodium borosilicate glasses containing 20% of sodium oxide, as the proportion of boric oxide increases from 0 to 46% the annealing temperature rises steadily from 505° to a maximum of 570° at about 16—17% B_2O_3 , and then falls gradually to about 521° . In the case of glasses containing 10% of sodium oxide, the annealing temperature falls steadily from 597° with 12.45% B_2O_3 to 495° with 46.07% B_2O_3 . It is probable, however, that had glasses in this series been obtainable with 0–12% B_2O_3 , a maximum annealing temperature would have been found in the neighbourhood of 12% B_2O_3 . E. H. R.

Active Charcoal. I. Nature of the Activity. OTTO RUFF [with SUSANNE MUGDAN, ERNST HOHLFELD, and FRITZ FEIGE] (*Kolloid Z.*, 1923, 32, 225—232).—The authors describe a number of experiments designed to ascertain the cause of the activity of certain varieties of charcoal in the adsorption of gases and liquids. Charcoal prepared from ashless filter-paper, coconut, and wood were investigated with respect of their activity in connexion with the temperature of formation, ash content, and the nature of the ash. As the result of the experiments, it is shown that the activity of charcoal is due to the atoms and atom groups of foreign materials bound to the surface of the charcoal. These atoms are the cause of the specific properties of active charcoal, and they are characterised by the firmness of their linking to the carbon atoms on the surface. Other atoms can also attach themselves to the surface, but these are easily replaced by others and are not firmly bound. With every change in the nature of the surface of the charcoal the adsorptive properties are markedly changed. J. F. S.

The Molecular Complexity of Graphite at High Temperatures. A. JOUNIAUX (*Bull. Soc. chim.*, 1923, [iv], 33, 260—267).—It has already been shown by numerous investigators that the higher the temperature at which carbon is liberated by the decomposition of its compounds, the greater the percentage of graphite which it contains, until, at about 3500°, the temperature of sublimation of carbon, the product consists of pure graphite, and, further, all varieties of amorphous carbon are converted into graphite at the temperature of the electric arc. The system amorphous carbon-graphite therefore behaves as an univariant system, with a position of equilibrium corresponding with each temperature. On cooling the system, a false equilibrium may be attained, and the physical constants determined at low temperatures will be those of mixtures in proportions varying according to the temperature at which the carbon was prepared, but at high temperatures (above 3000°) the constants are those of graphite, and the specific heat, for example, is in accord with Dulong and Petit's law. The above considerations justify the result obtained in the determination of the molecular weight of graphite from cryoscopic observations on solutions of carbon in iron and cobalt, \bar{M} , the molecular weight, being given by the formula $0.02T/L(c/p_1 - p_2)_0$, where T is the absolute temperature and L the latent heat of fusion of the solvent. At the temperatures in question, about 1500°, \bar{M} was 15.4 in the one case and 15.1 in the other, values in fair agreement with that obtained from the specific heat of graphite at that temperature and Dulong and Petit's law, namely, 14.5. The graphite molecule at these and higher temperatures would therefore appear to be monatomic at least when in solution in the metal. G. F. M.

Preparation of Thiocarbonyl Chloride. REMO DE FAZI (*Gazzetta*, 1923, 53, i, 175—176).—Although the action of iron on thiocarbonyl tetrachloride may result in the formation of ferrous chloride and carbon tetrachloride (cf. Frankland, Garner, Challenger, and Webster, A., 1920, ii, 753), under special conditions it proceeds

in accordance with the equation $\text{CCl}_3\cdot\text{SCl} + \text{Fe} = \text{FeCl}_2 + \text{CSCl}_2$; when certain catalysts are used, a yield of 80% of thiocarbonyl chloride is obtainable.

T. H. P.

Revision of the Atomic Weight of Silicon. The Analysis of Silicon Tetrachloride and Tetrabromide. G. P. BAXTER, P. F. WEATHERILL, and E. W. SCRIPTURE, jun. (*Proc. Amer. Acad. Arts Sci.*, 1923, **58**, 245—268; cf. A., 1920, ii, 487).—Consistent results, agreeing to about one part in two thousand, yield a value of 28.063.

CHEMICAL ABSTRACTS.

Silicon Hydrides. XIV. Trichloro- and Tetrachloromonosilanes, SiHCl_3 and SiCl_4 . ALFRED STOCK and FRIEDRICH ZEIDLER (*Ber.*, 1923, **56**, [B], 986—997).—Trichloromonosilane has been prepared from technical copper silicide and hydrogen chloride at 300° and purified by fractional distillation and condensation in the authors' vacuum apparatus. The isolation of the pure compound is very tedious, since the main impurities, hydrogen chloride and silicon tetrachloride, are very obstinately retained and the former appears to be continuously produced probably owing to the slight but unavoidable water content of the glass. The pure material has m. p. -126.6° or -126.4° , d_0^{20} 1.35, tensions 0.7 mm./ -85.0° , 1.3 mm./ -80.1° , 1.9 mm./ -75.0° , 2.8 mm./ -70.1° , 4.1 mm./ -65.2° , 6.0 mm./ -60.5° , 9.4 mm./ -54.2° , 13.0 mm./ -50.0° , 19.0 mm./ -44.9° , 25.3 mm./ -40.2° , 34.9 mm./ -35.5° , 45.5 mm./ -30.5° , 60.5 mm./ -25.3° , 80 mm./ -20.3° , 104 mm./ -15.2° , 132 mm./ -10.5° , 167 mm./ -5.9° , 218 mm./ 0° , 275 mm./ $+5.4^\circ$, 338 mm./ 10.5° , 412 mm./ 15.3° , 501 mm./ 20.2° , 598 mm./ 25.0° , 717 mm./ 30.1° , 765 mm./ 32.0° , b. p. $31.8^\circ/760$ mm. Trichloromonosilane is remarkably stable towards heat, but at 900° suffers almost quantitative decomposition into silicon, hydrogen, hydrogen chloride, silicon tetrachloride, and a trace of liquid less volatile than the latter. It is not affected by aluminium chloride at 175°. It reacts readily with sodium amalgam, obviously in accordance with the scheme $\text{SiHCl}_3 + 3\text{Na} \rightarrow 3\text{NaCl} + (\text{SiH})_x$, since volatile compounds are not produced in appreciable amount. It reacts with ammonia in the gaseous phase under diminished pressure, and at the atmospheric temperature in accordance with the equation $2\text{SiHCl}_3 + 9\text{NH}_3 = [\text{SiH}(\text{NH})_2]_2\text{NH} + 6\text{NH}_4\text{Cl}$. The same products are obtained when the components are successively condensed in the same vessel by means of liquid air, and the mixture is slowly warmed. If the product is gradually heated, the imide becomes decomposed, mainly in accordance with the scheme $[\text{NH}:\text{SiH}]_2\text{NH} \rightarrow 2\text{SiHN} + \text{NH}_3$, and at about 250° the ammonium chloride commences to sublime. A quantitative separation of the two compounds cannot, however, be effected in this manner. The action of hydrogen chloride on the compound $[\text{NH}:\text{SiH}]_2\text{NH}$, proceeds mainly according to the scheme $[\text{NH}:\text{SiH}]_2\text{NH} + 9\text{HCl} = 2\text{SiHCl}_3 + 3\text{NH}_4\text{Cl}$, but is accompanied by difficultly explicable side changes.

Even at low temperatures, silicon tetrachloride does not appear to react with more than seven molecular proportions of ammonia

in accordance with the equation $\text{SiCl}_4 + 7\text{NH}_3 = \text{Si}(\text{NH}_2)_2 \cdot \text{NH} + 4\text{NH}_4\text{Cl}$. The amide-imide is quantitatively converted when warmed to 0° or the atmospheric temperature into the di-imide, $\text{Si}(\text{NH})_2$. When the mixture of the latter with ammonium chloride is treated with hydrogen chloride, it is transformed into silicon tetrachloride and ammonium chloride, $\text{Si}(\text{NH})_2 + 6\text{HCl} = \text{SiCl}_4 + 2\text{NH}_4\text{Cl}$.

Trichloromonosilane is immediately decomposed by an excess of water into solid, non-volatile, polymerised dioxodisiloxane, $[\text{SiH}(\text{O})_2]_x$ (silicoformic anhydride), which has been isolated in the homogeneous condition and is then remarkably stable towards water. In the gaseous condition, the chloro-compound only reacts slowly with a deficiency of water vapour, without giving any indication of the formation of products intermediate between it and dioxodisiloxane. Attempts to isolate the latter in a less highly polymerised form by decomposing trichloromonosilane in the presence of benzene were unsuccessful. It gives indications of its ability to form salts in the absence of water.

The halogenated monosilanes appear to react uniformly with water and ammonia. Monochlorosilane yields the substances $(\text{SiH}_3)_2\text{O}$ and $(\text{SiH}_3)_3\text{N}$, which are unimolecular and volatile. The dichloro-compound gives the products SiH_2O and $\text{SiH}_2 \cdot \text{NH}$, which can be preserved for a short time in the volatile form with low molecular weight, but rapidly become associated to non-volatile polymerides. The trichloro-derivative gives the derivatives $[\text{SiOH}]_2\text{O}$ and $[\text{NH}:\text{SiH}]_2\text{NH}$, which do not occur in volatile modifications of low molecular weight, whereas silicon tetrachloride yields $\text{Si}(\text{OH})_2\text{O}$ and $\text{Si}(\text{NH}_2)_2 \cdot \text{NH}$, which are only known in the associated condition; the latter substances readily lose water and ammonia, respectively, and pass into silicon dioxide and di-imide.

H. W.

Positive-ray Analysis of Potassium, Calcium, and Zinc.

A. J. DEMPSTER (*Physical Rev.*, 1922, 20, 631—638; cf. A., 1921, ii, 402; 1922, ii, 417).—The charge deflected by a constant magnetic field through a fixed slit into a Faraday cylinder is measured as a function of the voltage accelerating the rays, and curves showing maxima corresponding with the various isotopes are plotted. Aston's results for potassium (39, 41) were confirmed; calcium has isotopes at 40 and 44, and zinc at 64, 66, 68, and 70. In the cases of potassium and calcium, the ratios of the intensities give average atomic weights in good agreement with the accepted values. When accurate and trustworthy results for the relative proportions of all the isotopes of an element are available, comparison of the calculated and observed atomic weights will give a measure of the packing effect, or divergence of the atomic weights of the isotopes from integral values.

A. A. E.

Precision Measurements of Crystals of the Alkali Halides.

WHEELER P. DAVEY (*Physical Rev.*, 1923, [ii], 21, 143—161).—By the use of Hull's powder method, the X-ray diffraction patterns of the alkali halides have been compared with that of sodium

chloride. The following measurements of the side of the unit cube in each case, that of sodium chloride being assumed to be 2.814 \AA. , are given; the figures within brackets represent the crystal densities, computed from the X-ray data, assuming that of sodium chloride to be 2.163 . Lithium fluoride, $2.007 \pm 0.004 \text{ \AA.}$ (2.646 ± 0.016); chloride, 2.566 ± 0.003 (2.069 ± 0.006); bromide, 2.745 ± 0.003 (3.463 ± 0.010); iodide, 3.537 ± 0.005 (2.494 ± 0.015). Sodium fluoride, 2.310 ± 0.002 (2.809 ± 0.008); bromide, 2.968 ± 0.003 (3.246 ± 0.010); iodide, 3.231 ± 0.003 (3.665 ± 0.011). Potassium fluoride, 2.664 ± 0.003 (2.534 ± 0.008); chloride, 3.138 ± 0.003 (1.990 ± 0.006); bromide, 3.285 ± 0.003 (2.768 ± 0.008); iodide, 3.525 ± 0.004 (3.125 ± 0.009). Rubidium fluoride, 3.663 ± 0.004 (3.504 ± 0.010); chloride, 3.267 ± 0.003 (2.859 ± 0.009); bromide, 3.418 ± 0.003 (3.415 ± 0.010); iodide, 3.655 ± 0.004 (3.557 ± 0.011). Cæsium fluoride, 3.004 ± 0.003 (4.617 ± 0.014); chloride, 4.118 ± 0.004 (3.973 ± 0.012); bromide, 4.287 ± 0.004 (4.453 ± 0.013); iodide, 4.558 ± 0.005 (4.523 ± 0.014). There is general, although not complete, agreement with densities determined by other methods.

A. A. E.

The Structure of Halogen Salts Based on their Compressibility. IDA WOODWARD (*Phil. Mag.*, 1923, [vi], 45, 882—895).—A theoretical paper in which calculations, based on Thomson's hypothesis (cf. A., 1922, ii, 252, 355), are made of the compressibilities of the cubic crystals, the chlorides, bromides, and iodides of sodium and potassium, and the chloride and bromide of silver. The following values were obtained: NaCl, 4.139 ; NaBr, 5.099 ; NaI, 6.990 ; KCl, 5.061 ; KBr, 6.351 ; KI, 8.660 ; AgCl, 2.30 ; AgBr, 2.68×10^{-12} . These are in good agreement with the experimental values of Richard and Jones. In addition, the specific photoelectric effect and the specific inductive capacity for the sodium and potassium salts have been calculated from the atomic diameters given by W. L. Bragg (cf. A., 1920, ii, 537). The calculated values of K , as far as there are experimental data, are seen to lie between the extreme observed values.

W. E. G.

The Solubility of Potassium Carbonate in Water. P. P. RUBCOV (*J. Russ. Phys. Chem. Soc.*, 1918, 50, 220—224).—The discrepancies between solubility curves for potassium carbonate, as obtained by Ozanne, by Poggiale (1843), by Gerlach (1862), and by Mulder (*Scheikund. Verhandel*, 1864, 96) are pointed out, and the solubility of potassium carbonate in water at 16.5° and at 19.5° found to agree with the corresponding values obtained by Mulder.

R. T.

The Crystalline Structure of Sodium Bromate and Sodium Chlorate. N. H. KOLKMEIJER, J. M. BLJVOET, and A. KARSEN (*Z. Physik*, 1923, 14, 291—295).—The relative intensities of the lines in the X-ray spectrum of sodium bromate, obtained by reflection in various planes of the crystal, as determined and calculated by the authors (A., 1921, ii, 200) and by Vegard (this vol., ii, 162) are compared, and it is concluded that the authors' values of the

parameters of the crystal are the more accurate. It is pointed out that the crystalline structure of sodium bromate and sodium chlorate, as determined by Dickenson and Goodhue (A., 1922, ii, 145), agrees with the structure found by the authors and by Vegard, and that the values of the crystalline parameters deduced therefrom are in close agreement with the values obtained by the present authors.

J. S. G. T.

Fluorophosphate and Fluorovanadate of Sodium Extracted from Bauxite. TRAVERS (*Bull. Soc. chim.*, 1923, [iv], 33, 297—306).—The octahedral crystals deposited on cooling a sodium hydroxide extract of bauxite after separation of the aluminium are composed of an isomorphous mixture in varying proportions of a double fluoride and phosphate, and a double fluoride and vanadate of sodium, having the composition $2\text{Na}_3\text{PO}_4\cdot\text{NaF}\cdot 19\text{H}_2\text{O}$ and $2\text{Na}_3\text{VO}_4\cdot\text{NaF}\cdot 19\text{H}_2\text{O}$, respectively. The crystals are usually mixed with traces of prismatic crystals of $\text{Na}_2\text{CO}_3\cdot 10\text{H}_2\text{O}$. Using a 2.5% solution of sodium hydroxide free from carbonate for the extraction, the crystals contained 76% of the fluorophosphate, 22.2% of the fluorovanadate, and 1.5% of carbonate. The proportion of the fluorovanadate increases somewhat as the concentration of the hydroxide is increased, and diminishes owing to hydrolysis if weaker hydroxide solution or water is employed in the preparation. The fluorophosphates and fluorovanadate are not complex salts, but double salts which are dissociated in solution into their constituents, at least in the neighbourhood of 100° , as on seeding a hot saturated solution with sodium phosphate or vanadate prisms are first formed, which are progressively transformed into octahedra of the double salt as the solution cools.

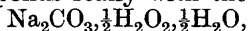
G. F. M.

The Acid Borates of Sodium. I. F. PONOMAREV (*J. Russ. Phys. Chem. Soc.*, 1917, 49, 229—240).—The difficulty of obtaining the higher borates in a crystalline form is overcome by heating strongly one end of a long platinum boat containing mixtures of borax and boric oxide, so that, in some part of the mass, cooling conditions must be favourable for the formation of crystalline nuclei. In this way, the fusion diagram for the system borax-boric oxide is constructed, and the melting points of the compounds formed are determined. The fusion diagram indicates the formation of two hitherto unknown compounds, with a composition corresponding with $\text{Na}_2\text{O}\cdot 3\text{B}_2\text{O}_3$, m. p. 694° , and $\text{Na}_2\text{O}\cdot 4\text{B}_2\text{O}_3$, m. p. 783° , capable of forming mixed crystals with each other, and with boric oxide. Pure crystalline boric oxide was not obtained, although crystals containing only 3% of sodium oxide separated from the 90% boric oxide mixture.

R. T.

Constitution of Per-salts, more especially of Percarbonates and Perborates. M. LE BLANC and R. ZELLMANN (*Z. Elektrochem.*, 1923, 29, 179—187, 192—198).—The literature of the preparation of percarbonates and perborates is briefly reviewed and

an investigation of the conditions determining the electrolytic preparation of sodium percarbonate by the electrolysis of solutions of sodium carbonate detailed. A platinum wire anode and a nickel wire cathode were employed. Experiments were made at 0° and 15° . The results indicate that the percentage yield, calculated from the current employed, fell off with time and was less for an anode- or cathode-current density of 32 amperes per sq. dcm. than for 22 amperes per sq. dcm. A maximum initial percentage efficiency equal to 74% was obtained by the electrolysis at 0° of a solution containing 60 g. of sodium carbonate per litre, employing a current density of 22 amperes per sq. dcm. of anode or cathode surface. The percentage efficiency of the process fell to 40% after two hours' electrolysis. The efficiency is initially reduced owing to the presence of sodium hydrogen carbonate, and during the electrolysis carbon dioxide is displaced from the latter by hydrogen peroxide. The increased efficiency of production of sodium perborate by the electrolysis of a solution of borax, due to the addition of sodium hydrogen carbonate to the electrolyte, as observed by Arndt and Hantge (A., 1922, ii, 569), is attributable mainly to the decreased solubility of the perborate in the resulting solution. By a modification of the process due to Wolfenstein and Peltner (A., 1908, ii, 180), the per-salts $\text{Na}_2\text{C}_2\text{O}_6$ and NaHCO_4 were prepared of a greater purity than those obtained by the latter. The salt, $\text{Na}_2\text{C}_2\text{O}_6$, is hydrolysed in the same manner as persulphates and perphosphates, with production of NaHCO_4 . It is shown that all methods of preparation of sodium perborate are based on the reaction $\text{NaBO}_2 + \text{H}_2\text{O}_2 = \text{Na}[\text{BO}_2, \text{H}_2\text{O}_2]$. This last compound is termed a ψ -perborate. Sodium perborate may be prepared in accordance with the equation $\text{NaOOH} + \text{H}_3\text{BO}_3 = \text{NaBO}_3 + 2\text{H}_2\text{O}$. Potassium ψ -perborate is prepared by adding 3% hydrogen peroxide solution to a dilute solution of potassium metaborate. The constitution and classification of per-salts are discussed. Amongst percarbonates, NaHCO_4 and $\text{Na}_2\text{C}_2\text{O}_6$ are true percarbonates. The composition of the compound $\text{Na}_2\text{CO}_4, 1\frac{1}{2}\text{H}_2\text{O}$, corresponds really with the formula



whilst the compound Na_2CO_5 prepared by Wolfenstein and Peltner is really a mixture of NaOOH and NaHCO_4 . Potassium perborate, $2\text{KBO}_3, \text{H}_2\text{O}$, prepared by von Girsawald and Wolokitinn (A., 1909, ii, 312) is a true per-salt.

J. S. G. T.

The Acid Reaction of Ammonium Salts to Litmus. CAM. GILLET (*Bull. Soc. chim. Belg.*, 1923, 32, 178—179).—The observation of Reichard (A., 1904, ii, 30) that blue litmus paper, when moistened by the solution of an ammonium salt and allowed to dry in air, turns red is confirmed. His explanation of oxidation fails, as the same phenomenon occurs in an atmosphere of hydrogen. The author shows that the reddening is due to dissociation of the ammonium salt with subsequent volatilisation of ammonia in presence of the blue potassium salt derived from litmus with which the paper is coloured.

H. J. E.

The Sulphides of Ammonium. JOHN SMEATH THOMAS and RICHARD WILLIAM RIDING (T., 1923, 123, 1181—1189).

Calcium Iodide. TOMOZÔ MIZUTANI (Japan. Pat. 40944).—Calcium iodide is prepared from calcium chloride and an alkali iodide by mixing their saturated alcoholic solutions in the ratio of 1 : 2 mols. The whole process should be carried out in the absence of air. The sodium or potassium chloride first precipitated is filtered off, and the mother-liquor is concentrated in a vacuum and placed in the dark. About 10 g. of calcium iodide are produced from 20 g. of hydrated calcium chloride. K. K.

The Dehydration of Gypsum. PIERRE JOLIBOIS and PIERRE LEFEBVRE (*Compt. rend.*, 1923, 176, 1317—1320; cf. van't Hoff, Armstrong, Hinrichsen, Weigert, and Just, A., 1904, ii, 35).—Dehydration of hydrated calcium sulphate in dry air gives no indication of the formation of $2\text{CaSO}_4 \cdot \text{H}_2\text{O}$ as an intermediate substance, but the loss of weight measured on heating gypsum in a closed vessel at temperatures ranging up to 160° shows the existence of a limit of dehydration corresponding with the hemihydrate. Above 160° , further loss of water occurs, whilst at 200° it is complete and rapid. H. J. E.

Electrometric Study of the Neutralisation of Phosphoric Acid by Calcium Hydroxide. GERALD L. WENDT and ALFRED H. CLARKE (*J. Amer. Chem. Soc.*, 1923, 45, 881—887).—The electrometric titration of phosphoric acid with solutions of calcium hydroxide and the titration of calcium hydroxide with phosphoric acid have been investigated, using the apparatus described by Hildebrand for electrometric titrations (A., 1913, ii, 721). Graphic representation of both the slow and the rapid electro-titration of phosphoric acid with calcium hydroxide shows that the existence of dicalcium phosphate is transitory, so that under equilibrium conditions only the mono- and tri-calcium salts are present. The rearrangements involved in these changes are partly responsible for the difficulty in titrating monocalcium phosphate for its "neutralising value." J. F. S.

The Reflection of Röntgen Rays from certain Remarkable Reticular Planes in Calcite. CH. MAUGUIN (*Compt. rend.*, 1923, 176, 1331—1334; cf. W. L. Bragg, A., 1914, ii, 181).—A critical discussion of the interpretation of the experimental results bearing on the spatial arrangement of atoms in calcite. The conclusions afford a new confirmation of Bragg's hypothesis. H. J. E.

Studies on the Dolomite System. I. The Nature of Dolomite. ALLAN ERNEST MITCHELL (T., 1923, 123, 1055—1069).

Diagrams of the Solidification of the System MgCl_2 - KCl - BaCl_2 . C. MATIGNON and J. VALENTIN (*Bull. Soc. chim.*, 1923, [iv], 33, 267—280).—The principal points of the diagrams of the binary systems MgCl_2 - KCl and MgCl_2 - BaCl_2 obtained by previous

workers were re-verified, and the same results obtained except for the second eutectic of the former system, which was found to be at 440° instead of 425° as given by Menge (A., 1911, ii, 982). The solidification of the ternary system was studied by means of a Le Chatelier platinum-rhodium thermoelectric couple in conjunction with a Rengade recording camera (*Bull. Soc. chim.*, 1909, [iv], 7, 934), the boiling point of sulphur and the melting point of sodium chloride being employed as points of reference on the temperature scale. The materials were melted in a platinum crucible, and the results obtained are recorded by means of triangular diagrams and tables. G. F. M.

Solubility between Cadmium and Thallium in the Solid State. CLARA DI CAPUA (*Atti R. Accad. Lincei*, 1923, [v], 32, i, 282—285; cf. Kurnakov and Pushin, A., 1902, ii, 139; Bornemann, *Metallurgie*, 1910, 7, 103).—The author has investigated the diagram of state of cadmium-thallium alloys by Plato's method (A., 1906, ii, 521; 1907, ii, 239). The eutectic corresponds with about 1.82% of thallium, and the initial solidification curve closely resembles that given by Kurnakov and Pushin, but different results are obtained in so far as the extension of the eutectic horizontal is concerned. On the cadmium side, the annulment of the eutectic arrest corresponds virtually with the pure metal, whilst on the thallium side the eutectic arrest is annulled at a concentration of about 2.5% of cadmium; thus appreciable solubility of thallium in cadmium is excluded, whereas cadmium is slightly soluble in thallium in the solid state. The results of conductivity and cryoscopic measurements are in agreement with these conclusions. T. H. P.

Electrical Conductivity and the Chemical Constitution of Alloys. I. The System Lead-Thallium. W. GUERTLER and A. SCHULZE (*Z. physikal. Chem.*, 1923, 104, 269—300).—The use of electrical conductivity measurements for determining the constitution of alloys is discussed, and it is shown to supplement the method of thermal analysis, in the following points. The determination of the commencement of a crystallisation can generally be ascertained by the thermal method, but only in rare cases by the conductivity method. The determination of the end of a crystallisation (that is, the extent of the eutectic horizontal between two saturated mixed crystals), and the determination of the exact position of the curve of the mixed crystals which are in equilibrium with the liquid phase during melting, cannot be found exactly by thermal analysis, but are obtained very sharply from conductivity measurements. The fixing of the saturation boundaries of non-continuous mixed crystal series is achieved very exactly by the conductivity method, but not by the thermal method. In the absence of mixed crystals, the existence of a compound may be overlooked by the conductivity method, because of the ill-defined inflection of the conductivity-concentration curve, but this is not likely by thermal analysis or when the temperature-resistance curve is used. In series of mixed crystals, thermal analysis does not give a clear indication when maxima or minima appear in the curves,

but conductivity measurements indicate the existence of a compound. The testing of a system with respect of its stability is often not possible by the thermal method, but this can be tested very sharply by the conductivity method. Transitions and chemical actions, on account of the small thermal effect, often remain unrecognised by the thermal method, but are definitely indicated by resistance measurements. The electrical conductivity of lead-thallium alloys has been determined over the temperature range 0—260° for the whole range of compositions by the method previously described and used for gold-iron alloys (this vol., ii, 284). Resistance-temperature curves have also been constructed which are shown to be continuous over the range 100—22·5% of lead; a small discontinuity is found between 20% and 6·5% of lead at temperatures between 130° and 150°. The curves for alloys containing less than 6% of lead show a definite discontinuity, which indicates a transition. Diagrams are shown indicating the regions in which mixed crystals of α -thallium with lead, β -thallium with lead, and lead with a form of thallium which is unknown in the free state, exist. There is no evidence of the existence of a compound PbTl_2 , since the resistance curves of the alloys with 25, 30, 33, and 40% of lead run parallel to one another. The results in general are in keeping with those deduced by other authors from thermal data. The transition of the mixed crystal series rich in thallium has been followed completely, and the diagram obtained previously from thermal data has thereby been completed. Since the conductivity curve and that of the temperature coefficient for the concentrations 30—40% of thallium are perfectly continuous, Kurnakov's contention (*A.*, 1902, ii, 139) that a maximum on the melting point-composition curve does not indicate a chemical compound, is justified.

J. F. S.

Crystallographic Transformations in Lead-Bismuth-Tin Alloys. KARL BUX (*Z. Physik*, 1923, 14, 316—327).—Crystallographic transformations similar to those first observed by Hauser (*ibid.*, 1921, 5, 220) in the case of the ternary lead-bismuth-tin eutectic are shown to occur at various temperatures in the case of all other ternary alloys of the system, the only apparent exception being the alloy Pb_3BiSn_4 . The phenomenon has been investigated by examining microscopically the surface of cooling crystals of the various alloys at various temperatures. Amongst binary alloys of the series, the phenomenon occurs probably only in the case of the lead-bismuth alloys, but thermal investigations are necessary to decide this point definitely. The transformation temperature depends on the composition of the alloy, the dependence on the proportion of lead present being very pronounced. A variation in the proportion of tin affects the transformation temperature only very slightly. The following transformation temperatures were determined: PbBi_4Sn_4 , 71°; $\text{Pb}_2\text{Bi}_4\text{Sn}_4$, 54°; $\text{Pb}_3\text{Bi}_4\text{Sn}_4$, 46°; $\text{Pb}_5\text{Bi}_4\text{Sn}_4$, $\text{Pb}_7\text{Bi}_4\text{Sn}_4$, and $\text{Pb}_9\text{Bi}_4\text{Sn}_4$, about 40°; $\text{Pb}_3\text{Bi}_4\text{Sn}_1$, 40°; $\text{Pb}_2\text{Bi}_4\text{Sn}_7$, 41°; $\text{Pb}_3\text{Bi}_4\text{Sn}_9$, 45°; Pb_3Bi_4 , 70°. The phenomena observed can be explained by assuming that the temperature of transformation of one allotropic modification of bismuth into the

other is reduced by the addition of lead and tin, the reduction being determined principally by the percentage of lead added. Approximately, eutectic mixtures may be cooled to the respective transformation temperatures without appreciable surface changes occurring. In the case of alloys containing one component largely in excess of that contained in the eutectic, crystallisation occurs before the alloy cools to the transformation temperature. Chilling the alloys causes the transformation phenomenon to be suppressed very considerably.

J. S. G. T.

Action of Alkali Hydroxides on Lead Salts. AKIRA OGATA and TAKANORI KAI'UN (*J. Pharm. Soc. Japan*, 1923, 78—81).—It is generally assumed that lead hydroxide is precipitated on adding an alkali hydroxide to lead nitrate solution. The authors have studied the action of *N*-sodium hydroxide solution on lead nitrate quantitatively and analysed the products of the reaction, the result being summarised as follows: (1) When an insufficient quantity of sodium hydroxide is used the basic nitrate, $\text{Pb}(\text{NO}_3)\cdot\text{OH}$, is precipitated. (2) By using a slight excess of the alkali, a second basic salt, $\text{NO}_3\cdot\text{Pb}\cdot\text{O}\cdot\text{Pb}\cdot\text{O}\cdot\text{Pb}\cdot\text{OH}$, is precipitated. As the solubility of $\text{NO}_3\cdot\text{Pb}\cdot\text{OH}$ is small, a comparatively long time is needed for the completion of the above reaction. (3) By adding a large excess of the alkali to the nitrate solution, lead hydroxide is never produced, more basic salts which still contain NO_3 -groups being formed. For the preparation of lead hydroxide, lead acetate must be used instead of the nitrate, but the product is $2\text{PbO}, \text{H}_2\text{O}$, not $\text{Pb}(\text{OH})_2$ (cf. Schaffner, *Annalen*, 1844, 51, 175).

K. K.

Thallous Hydroxide. R. DE FORCRAND (*Compt. rend.*, 1923, 176, 873—876).—Thallous hydroxide is readily obtained in good yield as a yellow, microcrystalline powder by adding to thallous ethoxide in the cold an equal volume of water, and drying the precipitate on porous plates out of contact with air. A determination of the heat of hydration of thallous oxide by finding the difference in the heat of solution of the oxide and hydroxide in dilute hydrofluoric acid gave a value 3.117 Cal., compared with 3.231 Cal. found by Thomsen. The heat of hydration is therefore very far removed from that of the oxides of the alkali metals, but thallous hydroxide is nevertheless an equally powerful base, and towards feeble acids, phenols, etc., shows even stronger basic properties than the alkali hydroxides. It can be estimated acidimetrically using phenolphthalein as indicator.

G. F. M.

Thallium Compounds. II. The Reduction of Thallic Compounds with Ferrous Sulphate and with Sodium Arsenite. ARTHUR JOHN BERRY (*T.*, 1923, 123, 1109—1114).

A Prehistoric Greek Axe; Its Composition by Spectral and Chemical Analysis. The Partial Reconstruction of its Metallurgy by Microscopic Metallography. H. WEISS, DAN-DURAND and DUREUIL (*Bull. Soc. chim.*, 1923, [iv], 33, 439—447).—The axe contained 96.4% of copper and 1.25% of arsenic, together with the following elements in much smaller amount: tin 0.1%,

lead 0.12%, iron 0.1%, sulphur 0.25%, oxygen (by difference) 1.78%, and traces of antimony, silver, nickel and cobalt, and zinc. Spectral analysis also showed the presence of distinct traces of chlorine, the presence of which is ascribed to the formation of an oxychloride of copper by the action of salt water on the metal in sunlight. Details are given of the analytical procedure adopted. A photomicrographic study of the metallography of the axe clearly indicated that it was not made from native copper, and that it was cast in a mould and cooled, but not so rapidly as would have occurred had cold water been used as cooling agent. The cast axe had then been subjected to hammering. The origin of the axe is uncertain, but arsenical copper ores are known to have been exploited in the earliest times in Serbia, Armenia, the Caucasus, and in the Sinai district. G. F. M.

The Action of Thiosulphates on Cupric Salts. HENRY BASSETT and REGINALD GRAHAM DURRANT (T., 1923, 123, 1279—1291).

The Interaction of Ammonium Hydroxide with Mercurous Bromide. J. G. F. DRUCE (*Chem. News*, 1923, 126, 225—226).—The black precipitate which is produced in this reaction is shown to be a mixture of $\text{NH}_2\cdot\text{HgBr}$ and metallic mercury. W. E. G.

Chlorites of Mercury and Other Metals. G. R. LEVI (*Atti R. Accad. Lincei*, 1923, [v], 32, 165—169; *Gazzetta*, 1923, 53, i, 245—249; cf. A., 1922, ii, 567).—*Mercuric chlorite*, $\text{Hg}(\text{ClO}_2)_2$ (cf. Bruni and Levi, A., 1916, ii, 27), forms a red, crystalline precipitate and, if kept dry in more than very small amount, undergoes rapid decomposition and sometimes spontaneous ignition, with formation of mercuric chloride; it explodes slightly on percussion. *Mercurous chlorite*, Hg_2ClO_2 , a canary-yellow precipitate, was not obtained quite free from mercurous oxide. *Basic mercurous chlorite*, $2\text{HgClO}_2\cdot\text{Hg}_2\text{O}\cdot 5\text{H}_2\text{O}$, forms a cream-yellow precipitate and, like the preceding compound, is readily decomposed when heated or struck. *Mercuriammonium chlorite*, $\text{NH}_2(\text{HgOHg})\text{ClO}_2$, is highly unstable and explosive and was not obtained pure. *Nickel chlorite* ($+2\text{H}_2\text{O}$) is not readily exploded on percussion but even in solution decomposes rapidly when gently heated. *Erbium chlorite*, $\text{Er}(\text{ClO}_2)_3\cdot 4\text{H}_2\text{O}$, obtained as a pink precipitate, decomposes only very slowly when its aqueous solution is boiled. T. H. P.

The Ceric Hydroxide Sol. H. R. KRUYT and (MISS) J. E. M. VAN DER MADE (*Rec. trav. chim.*, 1923, 42, 277—300).—Three ceric oxide sols, differing considerably from each other in properties, were prepared. The “peptisation sol” (so-called from its preparation by peptisation of precipitated cerous hydroxide) is strongly acid, coagulates on warming or on dialysis and also, in a very irregular manner, on addition of electrolytes. Free cerous salt is always present. The “freshly dialysed sol,” i.e., that which is viscous and is inclined to gelatinise, has in general the properties described by Fernau and Pauli (A., 1917, ii, 189). It is hydrated and con-

tains nitric acid as the peptising electrolyte; its properties are influenced by the escape of nitric acid from the dialyser and the entry of water. Addition of alcohol results in the replacement of water with formation of alcohol-gels. The "altered sol," one that has lost its viscosity by long keeping, behaves differently towards electrolytes, although no change has taken place in the proportions of ter- and quadri-valent cerium. This sol appears from a detailed study of its viscosity to be non-hydrated, yet the coagulation values indicate the influence of ion-lyotropy. From the viscosity experiments, reasons for the spontaneous congelation of the authors' sols as contrasted with the non-congelation of those prepared by Fernau and Pauli (*loc. cit.*) are adduced. H. J. E.

The Conversion of Aluminium-Zinc Alloys into a Crystalline Form. ALEXANDER SEMENOVITSCH FEDOROV (*J. Russ. Phys. Chem. Soc.*, 1917, 49, 394—407).—A binary fusion diagram is constructed for mixtures of aluminium and zinc. The diagram obtained corresponds with those of Shepherd (A., 1905, ii, 588) and of Eger (A., 1913, ii, 408), who found no evidence for the formation of the alloy Al_2Zn_3 , which Rosenhain and Archbutt (A., 1911, ii, 895) observed to occur within the limits 5—22% of aluminium. Photomicrographs of certain of the alloys also indicate that no compound formation occurs. R. T.

The Corrosion of Iron in Presence of Iron Sulphide. ROBERT STUMPER (*Compt. rend.*, 1923, 176, 1316—1317).—The effect of iron sulphide on the corrosion of iron was investigated under different conditions, the results showing that corrosion was considerably increased in the case of direct contact of iron with the sulphide, whilst in the case of galvanic contact the corrosion was more than twice as great. The general conclusion is drawn that the phenomenon is electro-chemical. H. J. E.

The Physico-chemical Investigation of Ternary Alloys of Iron, Phosphorus, and Carbon. III. -IV. Electrical Conductivity and Hardness. N. S. KONSTANTINOV (*J. Russ. Phys. Chem. Soc.*, 1918, 50, 311—334).—The electrical conductivity curve of the binary system, iron-phosphorus, corresponds with the fusion curve, and indicates the existence of solid solutions of the components up to the saturation concentration of 1.75% of phosphorus, after which a phase corresponding with an alloy, Fe_3P , separates. The hardness of the alloys increases linearly up to the saturation point for solid solution, at which a break occurs in the curve, the degree of hardness continuing to rise more slowly in the eutectic regions. With ternary iron-phosphorus-carbon alloys, the electrical conductivity depends on the carbon content, the addition of the same quantity of phosphorus to iron containing 0.7% of carbon causing a greater increase in resistance than when the carbon content is 0.4%. The hardness of the alloys varies in a parallel way to the conductivity, but to a less marked extent. The effect of the addition of phosphorus to steels is less marked when they are tempered than when they are allowed to cool slowly.

The presence of free phosphorus in the binary and ternary alloys can be shown by treating their polished surfaces with 10% sodium carbonate solution, and in this way it is shown that all eutectic alloys containing from 0—1·2% of carbon and from 0—1·9% of phosphorus are binary phosphorus-iron eutectics. R. T.

Alloys of Iron and Aluminium. N. KURNAKOV, G. URAZOV, and A. GRIGORIEV (*J. Russ. Phys. Chem. Soc.*, 1918, **50**, 270—293).—The freezing points, the micro-structure, and the electrical conductivities of alloys of iron and aluminium, ranging from 0 to 100% of each constituent, are investigated. The components of such alloys are, in general, aluminium, occurring to a preponderating extent in the aluminium eutectic mixture, an alloy called δ -alloy, and solid solutions of aluminium in α - and γ -iron. A compound, Al_3Fe_2 , crystallises from molten mixtures containing from 32·1 to 39·5 atomic % of iron, but below 1100° this is unstable, and changes into a solid solution of aluminium in α - and γ -iron, and for this reason cannot be found in the solid alloy. The δ -alloy exists within the limits of 24·2—34 atomic % of iron. This alloy is distinguished from others by its brittle nature, its hardness, this being several times greater than that of any other alloy, by its minimum values for electrical conductivity, and for its temperature coefficient of electrical resistance. The constituents of this alloy are not in any simple relation to one another, so that it appears to be, not a definite chemical compound, but probably a double compound of the Berthelot type (cf. *ibid.*, 1912, **44**, 107) in which two or more aluminium-iron compounds, themselves unstable, form a solid solution, stable within the concentration limits above mentioned. R. T.

Iron Oxide Jellies. (FRL.) E. SCHALEK and A. SZEGVARY (*Kolloid Z.*, 1923, **32**, 318—319).—Transparent, slightly elastic ferric oxide jellies may be produced by adding sodium sulphate or sodium chloride to a 6—10% ferric oxide sol. The amount of electrolyte added must be insufficient to cause coagulation. On shaking the jellies gently, they reassume the liquid form, but on keeping, the liquefied jelly sets again, producing a mass identical in every way with the original jelly. This process may be repeated indefinitely without changing the nature of the jelly ultimately obtained. J. F. S.

Nickel Sulphide. W. GLUUD and W. MÜHLENDYCK (*Ber.*, 1923, **56**, [B], 899—901).—In extension of Gluud's experiments on copper sulphide (A., 1922, ii, 446, 572), the authors have examined the behaviour of other sulphides which are soluble in ammonia, notably those of zinc, cadmium, cobalt, manganese, and nickel. Of these, only that last named shares the ability of copper sulphide to yield free sulphur when its solution is oxidised by air. The concentration of the ammonia and the age of the sulphide appear to influence the course of the change to a less extent with nickel than with copper sulphide. H. W.

Oxidation of Nickel Sulphide. JOHN STANLEY DUNN and ERIC KEIGHTLEY RIDEAL (T., 1923, 123, 1242—1251).

Theory of Smelting. III. Equilibrium between Metal Pairs and Sulphur. The System Nickel-Antimony-Sulphur. W. GUERTLER and H. SCHACK (*Metall u. Erz*, 1923, 20, 162—167).—In the ternary system nickel-antimony-sulphur there are four binary compounds, Ni_5Sb_2 , NiSb , Ni_3S_2 , and NiS , that melt unchanged and one ternary, NiSbS . All these compounds form binary eutectics among themselves, and there is also evidence of a ternary eutectic consisting principally of NiSbS and NiS . The complete ternary diagram of the system is reproduced, as well as photographs showing the characteristic structure of certain of the alloys (cf. *J.S.C.I.*, 1923, June). A. R. P.

Reduction by Hydrogen of Metallic Oxides Reducible only with Difficulty. H. VON WARTENBERG, J. BROY, and R. REINICKE (*Z. Elektrochem.*, 1923, 29, 214—217).—A simple form of electrically-heated furnace suitable for heating substances to temperatures up to 2500° , in the presence of hydrogen or nitrogen under pressures up to 10 atmospheres, is described. The substance to be heated is contained in a tube of zirconium oxide or of 80% zirconium oxide and 20% yttrium oxide, or of thorium oxide, heated by current flowing through a spiral of tungsten wire wound round the tube. In the case of the reduction of oxides in the presence of hydrogen, water formed is absorbed by means of phosphoric oxide. Chromium oxide (Cr_2O_3), vanadium oxide (V_2O_5), and columbium oxide (Nb_2O_5) were reduced in hydrogen at a pressure of about 5 atmospheres. The authors were unable to reduce tantalum oxide (Ta_2O_5), titanium oxide (TiO_2), or uranium oxide (UO_2). The oxides of yttrium, zirconium, and thorium could be similarly reduced by hydrogen in the presence of another metal, e.g., tungsten, with which the reduced metal alloyed. At 1250° , tungsten dissolved 0.07% of thorium, whilst at 2000° the saturation solubility of thorium in tungsten was 0.24%. The solubility was not much affected by the presence of iron, but was considerably reduced when zirconium was present. The question as to whether thorium contained in tungsten filaments used in electric incandescence lamps exists as metal or oxide cannot be decided by analysis alone.

J. S. G. T.

Basic Chromic Sulphate. F. S. WILLIAMSON (*J. Physical Chem.*, 1923, 27, 384—388).—The production of basic chromic sulphates has been investigated. It is found that by adding 2—5 g.-mols. of sodium hydroxide to 1 g.-mol. of potassium chromium alum a precipitate is obtained which has practically a constant composition, and it must therefore be tentatively regarded as a definite basic salt of the formula $(\text{Cr}_2\text{O}_3)_7(\text{SO}_3)_5 \cdot 25\text{H}_2\text{O}$. At the ordinary temperature, the salt is practically stable when kept over concentrated sulphuric acid. On heating the compound to 150° , it lost 36% of the total water, at 200° the loss of water was 64% of the total, and at 250° the whole of the water except about

5% was expelled. The loss of water is not reversible. These facts make it extremely unlikely that the water contained in the salt is present as water of crystallisation. Material which has been heated at 250° when moistened with water takes up only a small fraction of the water lost. The present basic salt retains its water more vigorously than the corresponding basic aluminium sulphate previously described (this vol., ii, 324). J. F. S.

The Oxidising Properties of Sulphur Dioxide. IV. Molybdenum Sulphates. WILLIAM WARDLAW and NORMAN DARBY SYLVESTER (T., 1923, 123, 969—980).

Crystal Structure of Tin Tetraiodide. ROSCOE G. DICKINSON (*J. Amer. Chem. Soc.*, 1923, 45, 958—962).—The crystal structure of stannic iodide has been investigated by means of X-ray and Laue photographs. It has been found that the unit cube contains eight molecules of stannic iodide; the value of d^{100} is found to be 12.23 Å. The iodine atoms cannot be all in equivalent positions. The space group symmetry is T_h^6 . It is shown to be probable that the tin atoms are at points equivalent to (*uuu*) and the iodine atoms at points equivalent to (*vvv*) and (*xyz*). The values $u=0.129$, $v=0.253$, $x=0.009$, $y=0.001$, and $z=0.253$ have been found to account for the intensity data, and to surround each tin atom tetrahedrally by iodine atoms. If these parameters are even approximately correct, the structure may be considered to be molecular. J. F. S.

Eutectic Mixtures of Stannic Iodide with Iodine, Arsenic Tri-iodide, and Antimony Tri-iodide. A. M. VASILIEV (*J. Russ. Phys. Chem. Soc.*, 1917, 49, 88—91; cf. A., 1912, ii, 919).—Stannic iodide shows practically no tendency to form double compounds, and it was to be expected that simple eutectics would be obtained, as already observed for stannic iodide and iodine by van Klooster (A., 1913, ii, 142) and by Reinders and de Lange (A., 1913, ii, 60). This was found to be the case.

The system stannic iodide-iodine was reinvestigated, using the freezing-point method; the eutectic point was found to be 77.8° and the composition corresponded with $\text{SnI}_4 + 3.257 \text{ I}$, in good agreement with the published values (see above).

The eutectic of stannic iodide with arsenic tri-iodide melts at 106.2° and solidifies to a brick-red, amorphous mass, its composition being $\text{AsI}_3 + 0.6936 \text{ SnI}_4$.

The eutectic of stannic iodide and antimony iodide is a dark red, crystalline solid, melting at 127° and having the composition $\text{SbI}_3 + 0.8728 \text{ SnI}_4$. G. A. R. K.

The Behaviour of Stannic Acid towards Dyes. A. M. MORLEY and J. K. WOOD (*J. Soc. Dyers and Col.*, 1923, 39, 105—106).—Samples of stannic acid obtained by precipitation from an alkaline solution adsorb basic dyes, whilst those from a slightly acid solution adsorb acid dyes. This behaviour is similar to that of different samples of titanous acid (following abstract) and may be explained in a similar manner. E. H. R.

The Behaviour of Titanic Acid towards Dyes. A. M. MORLEY and J. K. WOOD (*J. Soc. Dyers and Col.*, 1923, 39, 100—105).—It is generally supposed that meta- or β -titanic acid differs from ortho- or α -titanic acid in the greater complexity of its ultimate particles. The greater relative surface of the α -form might be expected to result in its having a greater adsorptive capacity than the β -form. Experiments on the adsorption of dyes by different forms of titanic acid have confirmed this deduction, for α -titanic acid, prepared by adding ammonia to a cold solution of titanic chloride until alkaline, had a greater adsorptive power for basic dyes than the β -acid precipitated in a similar manner at the boiling point. These preparations did not adsorb acid dyes, but samples obtained by stopping the precipitation while the solution was still acid adsorbed acid dyes readily, but not basic dyes. Finally, samples of titanic acid obtained by precipitation of a solution of titanic chloride with calcium carbonate had a very much lower adsorptive power, but took up both acid and basic dyes to a small extent. The difference in behaviour of titanic acid obtained from acid and alkaline solutions, respectively, may be attributed to the amphoteric character of titanium hydroxide, resulting in the formation in the one case of a highly basic titanium salt, and in the other of an alkali titanate; or it may be accounted for by the adsorption of hydrogen- or hydroxyl-ions, giving positively and negatively charged colloidal particles, respectively. Titanic acid obtained by precipitation with calcium carbonate would be neutral and have no preference for negative or positive ions of basic or acidic dyes. E. H. R.

Urbain's Celtium Lines. H. M. HANSEN and S. WERNER (*Nature*, 1923, 111, 461).—In view of a previous observation that the optical spectrum of hafnium does not contain any of the lines belonging to the characteristic spectrum ascribed by Urbain to a rare-earth element celtium, an examination has been made of the measurements of the spectra of rare earths published by Eder, and it is noted that the majority of Urbain's celtium lines (A., 1911, ii, 115) have been observed (Eder, A., 1916, ii, 277) in the spectrum of lutecium. The optical spectrum of a very pure preparation of lutecium has been reinvestigated, and it is found that the conditions affecting the relative intensities of the lines lead to the assumption that Urbain's preparation contained a comparatively small amount of the element with atomic number 71, and that only after further treatment of the preparation a concentration was obtained sufficient for the production of the diffuse lines which in 1911 were ascribed to the presence of a new element celtium. The X-ray spectrum of the same pure preparation gave no indication of the presence of an element with atomic number 72. A. A. E.

Celtium and Hafnium. D. COSTER and G. HEVESY (*Nature*, 1923, 111, 462—463; cf. preceding abstract, and Urbain, this vol., ii, 171).—The development of the controversy regarding the existence of an element with the properties ascribed to celtium is briefly reviewed, and it is argued that the magnetic properties

observed by Urbain in his preparations of 1911 need not be explained as being due to the presence of a new element, but may be considered to be a consequence of the gradual concentration of lutecium (Auer von Welsbach's cassiopeium) in his preparations. Moreover, hafnium can be readily separated from the rare-earth elements by means of oxalic acid, and should therefore have been absent from Urbain's preparation in which Dauvillier considered an element of atomic number 72 to be present. The claim to the identity of celtium with hafnium, and consequent priority of nomenclature, is therefore rejected.

A. A. E.

The Chemistry of Thorium. V. I. SPICIN (*J. Russ. Phys. Chem. Soc.*, 1917, **49**, 357—370).—The solubilities of various difficulty soluble thorium salts in various acids and alkalis and in water are measured by a modification of a method described by Joly (A., 1909, ii, 458), which consists of the addition of a small quantity of a strongly radioactive isotope of thorium to a solution of the latter, and precipitating them together, the solubility being then measured by boiling the salt in the given reagent, and measuring the radioactivity of the saturated solution. Joly did this by passing the emanation into a gold-leaf electroscope, obtaining results accurate to within 10%. By more carefully regulating the speed of the current of air passed over the solution for the purpose of collecting emanation, an accuracy of 1—2% is obtained. A different method based on a similar principle is also used, this consisting of the measurement of the β -radiation of isotopic mixtures of salts of thorium and of uranium- X_1 , prepared as in Joly's method. Portions of the solutions of these salts are then evaporated to dryness, and the β -radioactivity of the residue is compared with that of the original mixture. The accuracy of this method is also 1—2%. The advantages of this over Joly's method are that determinations can be carried out immediately, whilst for the latter method it is necessary to wait one month for equilibrium conditions, and further that the technique of the operations involved is not so difficult, the analysis requiring three and a half hours instead of five. This method cannot, however, be applied to the estimation of thorium in solutions containing non-volatile mineral substances, such as sodium hydroxide.

R. T.

Crystal Structures of the System : Palladium-Hydrogen. L. W. MCKEEHAN (*Physical Rev.*, 1923, [ii], **21**, 334—342).—The system : palladium-hydrogen has been studied by measuring the changes in crystal structure produced by the process of occlusion. The parameters of the face-centred cubic lattices of palladium and palladium saturated with hydrogen, as measured by the usual powder method, employing the K -radiation of molybdenum filtered through zirconium oxide, were found to be 3.900 and 4.000–4.039 $\times 10^{-8}$ cm., respectively. A value of 4.036 $\times 10^{-8}$ would correspond with a compound Pd_2H , but it is pointed out that the variability in the parameter of saturated crystals is opposed to the assumption of the formation of a definite compound in every case. Only two crystalline phases appear to coexist, namely,

palladium and a saturated solution of hydrogen in palladium; with partly saturated strips of metal, the distribution of saturated crystals over the surface was shown to be irregular. Further, the presence of atomic hydrogen, produced by electrolysis of dilute sulphuric acid with a palladium electrode, or by surface dissociation of hydrogen at high temperatures, is a necessary condition of occlusion. The paper concludes with the compilation of a number of physical assumptions concerning the nature of the system, with which the phenomena observed appear to be consistent; a bibliography of recent literature is also appended. A. A. E.

The Crystal Structure of Silver-Palladium and Silver-Gold Alloys. L. W. MCKEEHAN (*Physical Rev.*, 1922, 20, 424—423).—The *K*-radiation of molybdenum was allowed to fall on the face of a thin ribbon of silver, gold, or palladium, and of seven binary alloys in each of the series of silver-gold and silver-palladium alloys, the shadow cast by the edge of the ribbon, and the diffracted beams due to its suitably oriented crystals being detected by a strip of photographic film wrapped on a cylinder, the axis of which coincides with the edge of the ribbon. All the metals and alloys examined have their atoms arranged in face-centred cubic lattices with unit edge of cube 4.08×10^{-8} , 4.075×10^{-8} , and 3.90×10^{-8} cm. for silver, gold, and palladium, respectively. For both series of alloys (except in the case of silver-gold alloys containing 30, 40, and 60% of silver, which gave results 1% too high), the length of the edge is nearly a linear function of the atomic percentage of either component. Annealing at 830—940° in a vacuum for at least an hour increased the size of individual crystals, rendered them more homogeneous, and made their orientations more isotropic, whereas moderate cold working reduced their size and made them less isotropic. In the case of the silver-palladium alloy when repeatedly annealed at 870°, no indication of a progressive change of composition could be detected; the volatility of silver at this temperature is therefore negligible. The densities of crystals of silver, gold, and palladium are computed to be 10.49, 19.24, and 11.87, respectively. A. A. E.

Mineralogical Chemistry.

The Relative Chlorine, Bromine, and Iodine Content of the Waters of the Strait of Georgia, B.C. A. T. CAMERON (*Contrib. Canad. Biol.*, 1922, 75—80).—By the use of Winkler's methods (A., 1916, ii, 109, 184, 389), the relative proportions of chlorine, bromine, and iodine present in the water examined were 100 : 0.358 : 0.0002, as compared with 100 : 0.347 : 0.00023 found by Winkler for the Adriatic. As reported by Winkler, most of the iodine was present as iodate. CHEMICAL ABSTRACTS.

Analytical Chemistry.

Modification of Gillespie's Method for the Determination of Hydrogen-ion Concentrations. WILLIAM D. HATFIELD (*J. Amer. Chem. Soc.*, 1923, 45, 940—943).—Gillespie's method for the determination of hydrogen-ion concentration has been investigated, and a modified procedure is put forward (A., 1920, ii, 382). The modifications consist essentially in the method of preparing the indicator solutions and the buffer solutions, details of which are given in the paper. The standards prepared have been preserved from four to eight weeks or more. The method as modified is particularly suited to average technical laboratory practice because of its accuracy, simplicity of technique, and the use of ordinarily pure reagents instead of the specially purified materials recommended by Clark.
J. F. S.

The Nephelometer and its Working. HANS KLEINMANN (*Biochem. Z.*, 1923, 137, 144—156).—The criticisms of Weinberg (A., 1922, ii, 309) of the Kleinmann nephelometer (A., 1920, ii, 634) are replied to. A modified apparatus is now described suitable for small quantities of liquid, 2·6 or 1·5 c.c., and a method of producing permanent standards is described. A matt appearance is produced by coating a tube with collodion containing talc in suspension, colour variations of the turbidity being obtained by use of a separate powder containing talc, copper sulphate, and litmus powder in suitable proportions. With the Kleinmann nephelometer as now made a somewhat modified permanent standard of turbidity is used.
H. K.

The Use of the Oxy-acetylene Blowpipe in Spectral Analysis. Application to Mineralogy. A. DE GRAMONT (*Compt. rend.*, 1923, 176, 1104—1109).—A description is given of the application of the oxy-acetylene blowpipe flame in the spectral analysis of certain minerals. The method and apparatus employed are similar to those already described for the case of aluminium (A., 1914, ii, 82), and whilst the oxy-acetylene flame has not the universal applicability of the spark spectrum, it can be successfully used for the alkali and alkaline-earth metals, copper, silver, gallium, indium, thallium, chromium, manganese, iron, cobalt, nickel, tin, lead, and bismuth, and somewhat less satisfactorily for magnesium, zinc, cadmium, and mercury. A reproduction of the spectra of hæmatite, chromite, and lepidolite obtained by this method is given.
G. F. M.

Systematic Method for the Detection of the Principal Anions. L. FERNANDES and U. GATTI (*Gazzetta*, 1923, 53, i, 108—114).—According to the scheme proposed by the authors, the principal anions are precipitated by a number of successive group reagents, each precipitate being then tested for the possible anions. *Group I*: Magnesium nitrate and ammonia solution precipitate carbonic, phosphoric, phosphorous, arsenic, arsenious,

hydrofluoric, silicic, and hydroferrocyanic acids. *Group II*: Calcium and ammonium nitrates precipitate sulphurous, molybdic, tungstic, oxalic, tartaric, and citric acids. *Group III*: Barium nitrate precipitates sulphuric, chromic, and thiosulphuric acids. *Group IV*: Mercuric nitrate precipitates hydroferrocyanic and vanadic acids. *Group V*: Silver nitrate precipitates hydrochloric, hydrobromic, hydriodic, and thiocyanic acids. *Group VI*: The residual liquid is tested for hydrocyanic, boric, hypophosphoric, chloric, perchloric, nitrous, benzoic, and salicylic acids. Separate tests are made for nitric, carbonic, and acetic acids, the last two being introduced, prior to the group precipitations, by fusion of the substance with sodium carbonate and decomposition of excess of the carbonate by means of acetic acid. T. H. P.

Direct Estimation of Oxygen in the Gaseous Exchanges of Animals. K. I. GODZIKOVSKI and A. A. LICHATSHEV (*J. Russ. Physiol.*, 1918, 1, 56—60).—The method is based on that of Regnault and Reiset. The arrangement of the apparatus employed by the authors is illustrated diagrammatically in the original. E. S.

Titration of Sulphates. ERWIN BENESCH (*Chem. Ztg.*, 1923, 47, 366).—The sulphate is precipitated with excess of barium hydroxide and the excess precipitated with ammonium carbonate, which is then removed by boiling and the alkali carbonate titrated. The results obtained agree well with gravimetric determinations, and the determination can be completed in two hours. If the sulphate solution contains a kation the hydroxide or carbonate of which is insoluble, the kation is precipitated with sodium hydroxide, filtered, and the filtrate neutralised with hydrochloric acid before the barium hydroxide is added. H. C. R.

Electrometric Titration of Selenium in the Presence of Tellurium, Iron, and Copper. H. H. WILLARD and FLORENCE FENWICK (*J. Amer. Chem. Soc.*, 1923, 45, 933—939).—The volumetric estimation of selenium by means of titanous sulphate solution has been investigated. It is shown that the volumetric reduction of selenious acid to selenium by titanous sulphate in hydrochloric acid solution saturated with sodium chloride is rapid and accurate in cold solutions to 0.1 mg. Under these conditions, tellurium is not reduced, and its only effect is to modify the nature of the end-point. Moderate amounts of sulphuric acid have no deleterious effect on the determination of the end-point, and there is no volatilisation of selenium at the fuming temperature of this acid. The titration of selenium is quantitatively independent of the concentration of any iron which may be present, although ferrous iron is produced in the reaction. The reducing effect of tervalent titanium on mixtures containing copper and selenium is selective, the latter being reduced first, and consequently both elements may be determined electrometrically in a single titration. J. F. S.

Use of Hydrogen Peroxide in the Estimation of Nitrogen. ROBERT HEUSS (*Woch. Brau.*, 1923, 40, 73—74).—The use of

hydrogen peroxide, as suggested by Kleemann (*Z. angew. Chem.*, 1921, **34**, 625) in Kjeldahl's method for estimating nitrogen, is of advantage in the case of barley, the time required for the complete attack of 1.75 g. of the finely-ground grain being reduced from seventy-five to ninety minutes to forty-five minutes. The quantities of the different reagents suggested by Kleemann may be reduced to: 7—8 g. of potassium sulphate, 20 c.c. of sulphuric acid, and 15 c.c. of 30% (by weight) hydrogen peroxide solution. A blank estimation must be made with the materials alone and the results corrected accordingly.

T. H. P.

Use of Persulphate in the Estimation of Nitrogen. I, By the Arnold-Gunning Modification of Kjeldahl's Method; II, by Folin's Direct Nesslerisation Method. SAN YIN WONG (*J. Biol. Chem.*, 1923, **55**, 427—430, 431—435).—I. Considerable saving of time results if the following procedure is adopted: When the acid mixture becomes amber-coloured, heating is discontinued. Water (3 c.c.) and potassium persulphate (10 g.) are added and the mixture is again heated until oxidation is complete.

II. This modification has been adapted to Folin's direct nesslerisation method for the estimation of nitrogen in urine, blood, and milk.

E. S.

Estimation of Nitrogen in Aromatic Nitro-compounds by the Kjeldahl-Flamand-Prager Method. B. M. MARGOSCHES and W. KRISTEN (*Z. ges. Schiess.-Sprengstoffw.*, 1923, **18**, 39—40).—The Kjeldahl-Flamand-Prager method (A., 1905, ii, 201) for estimating nitrogen in azo-compounds can be applied to aromatic mono-, di-, and tri-nitro-compounds with good results, except in the cases of dinitrotoluene, dinitroxyline, trinitroresorcinol, and nitrotoluidine, which showed errors up to -3%, and nitrotoluene and nitrobenzyl chloride, which showed errors up to -12%. The error in most cases does not exceed 1%. The method has certain advantages over other modifications of the Kjeldahl method, particularly as regards rapidity.

H. C. R.

Detection of Hydroxylamine. WALDEMAR M. FISCHER (*Chem. Ztg.*, 1923, **47**, 401).—A sensitive colour reaction capable of detecting hydroxylamine in a concentration of 0.00005%, is carried out by adding 1—2 drops of 2½% yellow ammonium sulphide solution, and 1—2 c.c. of ammonia to 1—5 c.c. of the solution to be tested. In presence of hydroxylamine an unstable purple colour is developed in the solution on shaking in presence of air, and its appearance is greatly accelerated by adding 1—2 drops of N/10-manganous sulphate solution which appears to act as an oxidising catalyst. The reaction is apparently specific for hydroxylamine, and it is not disturbed by the presence of ammonium or hydrazine salts, or by any of the common anions or kations with the exception of those giving insoluble precipitates with hydrogen sulphide in acid solution, which must first be removed by filtration. The nature of the purple colour is uncertain, but it may be due to the formation of a bivalent sulphur compound or of a sulphur dispersion.

G. F. M.

New Test for Nitrates. IVOR G. NIXON (*Chem. News*, 1923, 126, 261—262).— β -Naphthol-6 : 8-disulphonic acid ("G acid"), 7-amino- α -naphthol-3-sulphonic acid ("Gamma acid"), 1 : 6- and 1 : 7-naphthylaminesulphonic acids ("Cleve's acids") all react vigorously with solutions of nitrates and nitrites, giving wine-red solutions. With "G acid" a distinct red colour was obtained with 0.02 mg. of nitrogen as nitric acid. 1 c.c. of the suspected solution is mixed with 1 c.c. of concentrated sulphuric acid and 5 c.c. of a 1% solution of "G acid" is slowly added. The test may also be applied as a ring test if the nitrate solution is mixed with the sulphonic acid, and concentrated sulphuric acid is run down the side of the test-tube. There is no need to cool the solutions during the test. H. C. R.

Gravimetric Estimation of Organic Phosphorus. WALTER JONES and M. E. PERKINS (*J. Biol. Chem.*, 1923, 55, 343—351).—The substance is oxidised as in Kjeldahl's nitrogen method, and the phosphorus precipitated from the diluted digest as ammonium phosphomolybdate. The latter is dissolved in ammonia and the solution so obtained treated at the boiling point, drop by drop, with magnesia mixture. After cooling, one-third of its volume of concentrated ammonia is added, and the mixture left overnight. Under these conditions, the precipitate of magnesium ammonium phosphate forms large, stable crystals of constant composition ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$). After filtering and drying in the air, these can be readily removed quantitatively from the filter-paper and hence may be weighed in this form without conversion into the pyrophosphate. Similar large crystals of magnesium ammonium phosphate may be obtained from solutions of phosphates if the precipitation is made in the presence of ammonium molybdate. E. S.

The Analysis of Glasses Rich in Boric Oxide. VIOLET DIMBLEBY and W. E. S. TURNER (*J. Soc. Glass Tech.*, 1923, 7, 76—79).—In the estimation of boric oxide in glass by the method described by Cauwood and Wilson (*A.*, 1919, ii, 169), boric oxide is lost by volatilisation during the sodium carbonate fusion unless the glass does not contain much more than 10% of B_2O_3 . It is therefore recommended, in the analysis of glasses rich in boric oxide, to reduce the amount of glass taken for analysis and to add pure silica to adjust the boric oxide content to about 10%. The weight of sodium carbonate for a fusion is kept constant at 3 g. and the combined weight of glass and silica is adjusted accordingly. E. H. R.

Estimation of Carbon and Hydrogen by Means of a Mixture of Sulphuric Acid and Silver Dichromate. L. J. SIMON and A. J. A. GUILLAUMIN (*Compt. rend.*, 1923, 176, 1065—1067).—Numerous substances which are not completely burnt by a chromic-sulphuric acid mixture, give satisfactory results with silver dichromate and sulphuric acid. A known weight, p , of the substance is heated at 100° with a weighed excess, P , of silver

dichromate (about 6 g.) and sulphuric acid for twenty minutes. From the volume of carbon dioxide produced, or the increase in pressure, the weight, π , is obtained and the percentage of carbon is given by $300\pi/11p$. The hydrogen is obtained by a second combustion with the residue and an excess of an easily combustible substance such as potassium methyl sulphate. If α is the weight of carbon dioxide corresponding with 1 g. of $\text{Ag}_2\text{Cr}_2\text{O}_7$, and π' the weight of carbon dioxide evolved in the second combustion, π'/α is the weight of dichromate present and the residue from the first combustion, and $P-\pi'/\alpha$ is the weight used in that combustion. The percentage of hydrogen is then given by $[9(p-\pi)+P-\pi'/\alpha]100/81p$. The value of α determined empirically is 0.108, the difference from the theoretical, 0.102, being due to the production of small amounts of carbon monoxide when the dichromate is not present in excess. The results of analyses by this method of naphthalene, strontium acetate, ethyl pyruvate, rhamnose, aspirin, thymol, etc., are quoted.

G. F. M.

Analysis of Potassium Iodide. H. MATTHES and P. SCHÜTZ (*Pharm. Ztg.*, 1923, 68, 256—257).—The following method is recommended for the estimation of potassium iodide in the presence of bromides and chlorides. One g. of the dry powdered salt is dissolved in water and the solution diluted to 100 c.c.; 10 c.c. of this solution are treated in a stoppered flask with 5 c.c. of 2% sodium nitrite solution and 2 c.c. of dilute sulphuric acid. After five minutes, 100 c.c. of 5% sodium hydrogen carbonate solution are added slowly and the liberated iodine is titrated with *N*/50-arsenic trioxide solution. Each c.c. of the latter is equivalent to 0.00332 g. of potassium iodide.

W. P. S.

Nephelometric Estimation of Small Quantities of Calcium. P. RONA and H. KLEINMANN (*Biochem. Z.*, 1923, 137, 157—182).—For the estimation of small quantities of calcium, as, for instance, in blood, the Kleinmann nephelometer or micro-nephelometer is employed. Lyman's reagent, ammonium stearate, for the production of a cloud (*A.*, 1915, ii, 700; 1917, ii, 271) is replaced by sodium sulphuricinoleate. The authors have examined the influence of time, volume, impurities, and degree of alkalinity of the reagents on the production of the cloud. Using the micro-nephelometer, the calcium in 0.25 c.c. of blood can be estimated with a probable error of 1%.

H. K.

The Influence of Phosphoric Acid on the Volumetric Estimation of Calcium. J. GROSSFELD (*Chem. Weekblad*, 1923, 20, 209—210).—A criticism of the modifications suggested by Vürtheim and van Bers (this vol., ii, 257) on the procedure of the author. In presence of a large excess of phosphoric acid, neutralisation with ammonia and precipitation with oxalate causes the carrying down of calcium phosphate, which is avoided if the neutralisation is not carried too far, the author's procedure leading to the formation of primary sodium phosphate only. The change in volume due to evaporation consequent on the heat of neutralisation is negligible.

S. I. L.

Estimation and Quantitative Separation of Barium and Strontium. RUDOLF LEO (*Monatsh.*, 1923, 43, 567—588).—A careful investigation has been made of a modification of Fresenius's fluorosilicate method for the quantitative separation of barium and strontium, consisting in using ammonium fluorosilicate in place of the free acid; in addition, a method for separating barium and strontium by means of their thiosulphates has been developed, which gives satisfactory results when there is a relatively large excess of barium.

The ammonium fluorosilicate method:—The following points were noticed: (1) the solubility of barium fluorosilicate is depressed by using ammonium fluorosilicate in place of the free acid so that precipitation is more nearly quantitative. (2) Barium fluorosilicate dried at 180° to constant weight gives results 0.2 to 0.3% too high, due to water. (3) Heating barium fluorosilicate in an electric oven for two to three hours only converts it incompletely into barium fluoride. (4) Barium precipitated by ammonium fluorosilicate in neutral or acetic acid solution always carries down some strontium; this can be counteracted by the addition of hydrochloric acid. (5) Barium precipitated from hot solution carries down more strontium than when precipitated from cold solution. (6) The decomposition of barium and strontium fluorosilicates by means of excess of warm ammonia and ammonium carbonate takes place completely in about ten minutes, and can be utilised for the complete separation of barium and strontium.

The analysis is effected in the following manner: 50—70 c.c. of a solution of 0.3 to 0.5 g. mixed barium and strontium chlorides are treated with 6—10 c.c. of *N*-hydrochloric acid per 100 c.c. and with a 10—50% excess of a 10% ammonium fluorosilicate solution. After thirty minutes, $\frac{1}{3}$ volume of alcohol is added. The washed and decanted precipitate is then warmed with excess of ammonia and ammonium carbonate. The granular precipitate of barium carbonate is dissolved in dilute hydrochloric acid and the barium fluorosilicate reprecipitated as before. The precipitate is finally converted into barium sulphate by heating with sulphuric and hydrofluoric acids. The strontium left in the filtrates is determined as sulphate.

The thiosulphate method:—The solubility of barium thiosulphate in water at 18.5° is 1 in 479.8, and in a mixture of equal volumes of acetone and water, 1 in 31,450, the solubility of strontium thiosulphate in the mixed solvent at 18.5° being 1 in 281.7. The following special points were noted: (1) A slight excess of sodium thiosulphate diminishes considerably the solubility of barium thiosulphate, which, however, carries down some sodium salts. (2) By reprecipitating the barium as barium thiosulphate, satisfactory results are obtained if there is a large excess of barium over strontium; in the converse case, the precipitated barium thiosulphate always contains some strontium. In carrying out the estimation, the solution of the mixed chlorides of barium and strontium is treated with a slight excess of sodium thiosulphate with stirring, an equal volume of acetone added, and the mixture

allowed to remain. The washed and decanted precipitate is dissolved in hydrochloric acid, the solution concentrated, and the barium reprecipitated as thiosulphate, which is then redissolved in hydrochloric acid and estimated as sulphate. The filtrates containing strontium are concentrated, and the strontium estimated as sulphate.

F. A. M.

Volumetric Estimation of Manganese as "Permanganic Phosphate" in Phosphoric Acid Solution. MATHEVET (*Ann. Chim. Analyt.*, 1923, 5, 99—108).—The substance is dissolved in a mixture of phosphoric, nitric, and sulphuric acids and silver nitrate is added as a catalyst together with ammonium persulphate. A violet-amethyst coloration appears, and the liquid is titrated with arsenious acid. The end-point is sharper in the presence of phosphoric acid, and there is less danger of precipitates being formed. The presence of iron does not disturb the titration, as the colour of the iron salts is destroyed by the phosphoric acid. The mechanism of oxidation with ammonium persulphate is discussed. The mode of action of the phosphoric acid is uncertain. The use of nitric acid alone gives higher results than a nitric-sulphuric acid mixture, some arsenious acid probably being oxidised by the nitric acid. The results are not sensitive to the amount of phosphoric acid present, unless it is in large excess. In titrating solutions rich in manganese, sufficient phosphoric acid must be present to obtain all the manganese as "permanganic phosphate" and sufficient sulphuric acid to transform the manganese reduced during the titration into sulphate. Details are given for the application of the method to the analysis of cast irons, manganese steels, and alloys containing chromium, nickel, copper, cobalt, molybdenum, and vanadium. The manganese in an ordinary steel can be determined by this method in about seven minutes.

H. C. R.

Quantitative Separation of Manganese and Chromium. H. J. TAVERNE (*Chem. Weekblad*, 1923, 20, 210—211).—The metals are precipitated with ammonium sulphide and redissolved in water after conversion into chlorides; the solution is treated with hydrogen peroxide and sodium hydroxide, and boiled for thirty minutes; manganese is collected as hydrated oxide and weighed as sulphate, the chromate in the filtrate being titrated by means of iodine.

S. I. L.

Colorimetric Estimation of Iron and Hæmoglobin in Blood. SAN YIN WONG (*J. Biol. Chem.*, 1923, 55, 421—425).—One c.c. of blood is used for the estimation. Organic material is oxidised by heating with concentrated sulphuric acid (1 c.c.) for three and a half minutes, carefully adding 1 c.c. of a 10% sodium chlorate solution and again boiling for three minutes, and finally boiling for two minutes after the further addition of 0.3 c.c. of the chlorate solution. Iron is then estimated colorimetrically by means of a solution of thiocyanate (cf. Brown, A., 1922, ii, 319).

E. S.

New Method for Estimating Nickel. W. LÖFFELBEIN and J. SCHWARZ (*Chem. Ztg.*, 1923, 47, 369—370).—Nickel may be

precipitated quantitatively from a neutral solution containing only alkali metals and a little ammonia with oxalic acid. This precipitate may either be ignited and weighed as NiO , or dissolved in hot sulphuric acid solution and titrated with permanganate. Details of each method are given, together with specimen analyses, which indicate that both methods are capable of the highest accuracy. The completeness of the precipitation of the oxalate is such that the filtrate only gives a trace of precipitate when boiled for half an hour with dimethylglyoxime; the precipitate is coarser and easier to filter if formed in the presence of ammonium nitrate. It is soluble in strong mineral acids, but not in glacial acetic acid, which, however, makes it slimy and difficult to wash. It is unaffected by excess of oxalic acid or by dilute tartaric, citric, boric, or phosphoric acids. H. C. R.

Electrometric Titration of Molybdenum with a Titanous Salt. H. H. WILLARD and FLORENCE FENWICK (*J. Amer. Chem. Soc.*, 1923, 45, 928—933).—Molybdenum in the sexavalent condition is reduced sufficiently rapidly by a titanous salt to the quinquevalent condition to allow of the process being used for the electro-titrimetric estimation of molybdenum, using a bimetallic electrode system. The titration is carried out in hydrochloric acid solution, the most suitable concentration of acid being about 5—10% of concentrated hydrochloric acid. The end-point is characterised by a slight increase in *E.M.F.* when equivalent amounts are present, followed by a decrease when an excess is added. The reaction is only complete in the presence of a small excess of titrating liquid, and this amount, which must be found for the solutions in question, must be used as a correction factor. The method has been used for alkali molybdates, and found to give results accurate to within 0.5 mg. The method furnishes an indirect method for the estimation of phosphorus. The phosphorus is converted into ammonium phosphomolybdate by any of the recognised methods. The precipitate is dissolved in ammonia, filtered to remove any iron, and the acidified solution titrated with titanous sulphate. If the precipitate is very large, it tends to reprecipitate on the addition of acid. This may be prevented by the addition of a few drops of phosphoric acid to the ammoniacal solution, but the character of the end-point is thereby altered. In the cold, there is no voltage drop with excess of the titrating solution. Just before the end-point, the normal rise begins, ceases, then continues with increased velocity just as the equivalent point is passed. If the solution is titrated hot, however, the end-point is perfectly normal and as distinct as in the absence of phosphoric acid. The presence of tungsten does not interfere with the determination, but it makes it quite unnecessary to apply the correction which is necessary in its absence. J. F. S.

Gravimetric and Volumetric Methods for the Estimation of Tin in Alloys. ANTONIN JÍLEK (*Chem. Listy*, 1923, 17, 53—56, 85—87).—The modification of Gerwek's method for the

estimation of tin, described in a previous article (cf. this vol., ii, 186), is shown to give the best results for bearing metals when for alloys containing 14–30% of tin, 0.5 g. is taken, for 30–75% of tin, 0.25 g. is taken, and for 75–100% of tin, 0.15 g. of alloy is used. If smaller quantities are used, low results are obtained owing to incomplete precipitation of the tin, whilst larger quantities give high results, due to adsorption of antimony salts on the stannic-phosphate precipitate.

Classen's electrolytic method for the estimation of tin (A. Fischer, "Electroanalytische Schnellmethoden," p. 217) is tested for bearing metals and found to give satisfactory results with a current of 0.5 ampere, for which V is 3.5. This method has the advantage over Czerwek's method and its modification of being more rapid. For type metal containing about 2% of tin, the results obtained by the modification of Czerwek's method are lower than by the iodimetric method, agreement being obtained commencing with alloys containing more than 14% of tin. Below this, better results are obtained by using the unmodified Czerwek solution. R. T.

Estimation of Tin by Means of the Molybdenum-blue Reaction. G. F. HÜTTIG (*Chem. Ztg.*, 1923, 47, 341–342).—

The colour reaction between ammonium molybdate and stannous tin is of too uncertain a nature to be of use in quantitative analysis at ordinary concentrations, as the molybdenum-blue formed is a colloidal solution and its depth of colour depends on many conditions. In very great dilution, however, the depth of colour produced is directly proportional to the amount of stannous-ions present, other conditions being kept constant. The depth of colour formed under the conditions prescribed for colorimetric estimations reaches a maximum after about thirty minutes, and thereafter remains constant for at least ninety minutes, so that there is ample time for comparison with standards previously prepared. Directions are given for the preparation of the molybdate solution, which must be used before molybdic acid begins to separate. The solution of molybdenum-blue used in the colorimeter should not contain more than 30 mg. of tin per litre, or the proportionality between depth of colour and tin content no longer holds. The depth of colour is not influenced by the presence of antimonious chloride, sodium arsenite, sodium arsenate, or zinc salts. The solution for colorimetric estimation is prepared as follows. The hydrogen sulphide in the hydrochloric acid solution containing tin and antimony is boiled off, zinc and further excess of hydrochloric acid are added to the boiling solution, and the reduction is allowed to proceed for about one minute. The solution is then slowly poured through a filter with constant stirring into a mixture of 6 c.c. of the ammonium molybdate solution prepared as described (as used for testing for phosphoric acid), 3 c.c. of 2*N*-sodium hydroxide solution, and about 1000 c.c. of water. 0.1 Mg. of tin is easily detected in the above manner. If antimony alone is present, the solution may show a faint green coloration, which cannot be confused with the blue colour of the tin reaction.

H. C. R.

Estimation and Separation of Rare Earth Metals from other Metals. I. Application of Hydrolysis to the Separation of Titanium, Iron, and Aluminium. LUDWIG MOSER and ERNST IRÁNYI (*Monatsh.*, 1923, **43**, 673—677).—Titanium and aluminium may be separated by a method based on the differential hydrolytic dissociation of their salts. At a hydrion concentration of 0.05*N*, titanic salts are completely hydrolysed to give insoluble, non-colloidal, and therefore non-adsorbing, titanic oxide, whilst no hydrolysis of aluminium salts takes place. After fusion with alkali, the mixture is dissolved in dilute hydrochloric acid, the solution neutralised with sodium hydroxide (indicator methyl-orange), treated with 20 c.c. of hydrochloric acid (1 vol. concentrated acid : 9 vols. water), and allowed to become clear. Potassium sulphate (1 g.) and bromate (1.5 g.) are added, the solution diluted to 200 c.c., and boiled for half an hour, when quantitative separation of titanic oxide occurs (cf. *J.S.C.I.*, 1923, June). E. E. T.

Estimation and Separation of Rare Earth Metals from Other Metals. II. Separation of Titanium from Iron and Aluminium by Means of Sulphosalicylic Acid. LUDWIG MOSER and ERNST IRÁNYI (*Monatsh.*, 1923, **43**, 679—684).—An aqueous solution of 4-sulphosalicylic acid, $\text{SO}_3\text{H}\cdot\text{C}_6\text{H}_3(\text{CO}_2\text{H})\cdot\text{OH}$, is prepared by diluting (etc.) the mixture obtained by heating salicylic acid with sulphuric acid. For the separation of titanium and iron, the mixture of oxides is fused with potassium hydrogen sulphate or sodium carbonate, and a solution made in dilute sulphuric acid. Sulphosalicylic acid solution is added, then ammonium carbonate until the colour changes from violet to red, and the iron precipitated by means of hydrogen sulphide.

Titanium and aluminium are separated as follows. The acid solution containing the two metals, after treating with sulphosalicylic acid, is strongly basified with ammonium carbonate, and then boiled for five minutes, when the titanium is precipitated as hydroxide.

The separation of the three metals concerned is effected as follows : (1) The mixture of oxides is weighed; (2) fused with alkali, dissolved in sulphuric acid, sulphosalicylic acid and then sufficient ammonium carbonate to give a red solution are added; the iron is precipitated as sulphide; (3) the filtrate from the ferrous sulphide saturated with ammonia, boiled, and the precipitated titanic hydroxide collected; (4) the aluminium is either estimated by difference, or the filtrate from (3) is evaporated, heated at 280° to remove sulphosalicylic acid, and the aluminium then estimated in the usual manner. E. E. T.

Estimation of Antimony by Means of Phenylthiohydantoic Acid. A. LASSIEUR and (MME) A. LASSIEUR (*Compt. rend.*, 1923, **176**, 1221—1223).—Phenylthiohydantoic acid,

$$\text{CO}_2\text{H}\cdot\text{CHPh}\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}_2,$$

prepared by boiling 95 parts of monochloroacetic acid with 75 parts of ammonium thiocyanate, 83 parts of aniline, and 450 parts of alcohol, is recommended as a precipitant for antimony. The

estimation of the metal is carried out as follows. The neutral solution diluted to 150 c.c. is acidified with 5 c.c. of *N*-acetic acid, and boiled with 0.5 g. of the reagent for five to six minutes. The precipitate is collected on a Gooch crucible and washed with water. For an approximate estimation, it can then be weighed as such after drying over sulphuric acid in a vacuum, calculating on the basis of an antimony content of 18.6%, but when accurate results are required the washed precipitate is dissolved in warm alcohol, and the antimony precipitated as sulphide by the addition of acetic acid and sodium sulphide. The precipitate is collected, washed, and dissolved in sodium sulphide solution, and the antimony is deposited electrolytically from the solution after the addition of 5 g. of potassium cyanide, and weighed. G. F. M.

The Detection of Traces of Stibine. EDWARD J. WEEKS (*Chem. News*, 1923, 126, 275).—The gas to be tested is passed through a tube the walls of which are wetted with silver nitrate solution. A brown stain indicates the presence of stibine. A. R. P.

Detection of Bismuth in Urine. III. DOMENICO GANASSINI (*Boll. Chim. Farm.*, 1923, 62, 193—195; cf. this vol., ii, 93).—The author replies further to Dezani's criticisms. As regards Dezani's method, according to which a yellow coloration is obtained when potassium iodide is added to a very dilute solution of a bismuth salt in presence of hydrochloric acid, the author suggests that the yellow liquid be shaken with its own volume of chloroform or carbon disulphide. Three cases may then present themselves: (1) If the yellow liquid becomes decolorised and the organic solvent assumes an amethyst colour, the presence of bismuth is excluded, the yellow coloration being due to free iodine. (2) If the yellow coloration is only partly lost, and the organic solvent acquires an amethyst tint, the presence of both bismuth and iodine is demonstrated. (3) If the yellow liquid retains its colour and the solvent remains colourless, bismuth is present. T. H. P.

A New Reaction for Rhodium and a Colorimetric Method for its Estimation. VASIL NIKOLAEVITSCH IVANOV (*J. Russ. Phys. Chem. Soc.*, 1917—1918, 49, 601—603; 50, 460—462).—Aqueous solutions of rhodium salts give, when mixed with stannous chloride, heated to boiling, and cooled, brown, colloidal solutions of the metal (analogous to those obtained with gold and platinum salts in the cold) which develop a fine crimson colour, doubtless owing to the gradual solution of the colloidal particles in the acid medium; the greater the amount of rhodium present the longer the colour takes to develop. In practice, the material examined is fused with potassium hydrogen sulphate, the fused mass lixiviated with a little water, and the filtered solution evaporated down to 1 c.c. To this an equal volume of a 40% solution of stannous chloride in 30% hydrochloric acid is added, the mixture heated to boiling and allowed to cool; rhodium is absent if a crimson colour does not develop in a few hours. For the quantitative estimation of the metal, the tint obtained is compared with that

of test solutions made up in the same way. The reaction will detect rhodium in a solution containing 0.0005 g. per litre.

G. A. R. K.

Detection of Benzene in Corpses. ALEXANDER O. GETTLER (*J. Pharm. Expt. Ther.*, 1923, 21, 161—164).—The ground tissue is acidified with a few drops of sulphuric acid, steam-distilled, and the benzene extracted from the distillate with carbon tetrachloride. Addition of a 2 : 1 mixture of fuming nitric-sulphuric acids, with shaking, to the carbon tetrachloride solution converts the benzene into a mixture of the dinitrobenzenes, which are extracted with ether after evaporation of the solvent and neutralisation of the acid with sodium hydroxide. Qualitative tests for dinitrobenzene may then be applied. With suitable precautions, quantitative results may be obtained.

E. S.

The Microchemical Estimation of Methyl along with Ethyl. WILLIAM KÜSTER and WILHELM MAAG (*Z. physiol. Chem.*, 1923, 127, 190—195).—The mixture of methyl and ethyl iodides is absorbed in an alcoholic solution of trimethylamine, when the sparingly soluble tetramethylammonium iodide crystallises out, and can thus be separated from the soluble trimethylethylammonium iodide. Accurate results are obtained with from 10 to 20 mg. of substance.

W. O. K.

Estimation of Dextrose in Sugar Mixtures. G. BRUHNS (*Chem. Ztg.*, 1923, 47, 333—335).—The method of Willstätter and Schudel (A., 1918, ii, 337), which depends on the oxidation of dextrose by potassium iodide and sodium hydroxide to gluconic acid, was tested on solutions of pure dextrose, sucrose, and lævulose, on invert-sugar, and on solutions containing dextrin. It was found that sucrose was oxidised so as to give an apparent content of about 1.2% of invert-sugar with quantities of 1—4 g., whilst if only 0.1 g. of sucrose was taken an apparent content of 2.4% of invert-sugar was obtained. Pure lævulose is also attacked, and gave an apparent dextrose content of 9.8%. Invert-sugar, in consequence, appeared to contain more than 1% too much dextrose. By reducing the volume of sodium hydroxide added from 14.5 c.c. to 11 c.c., the apparent excess of dextrose was reduced to 0.55%. The method can therefore not be considered accurate for the estimation of dextrose in the presence of other sugars.

H. C. R.

The Ferricyanide Method for Estimation of Blood-sugar. II. H. C. HAGEDORN and B. NORMAN JENSEN (*Biochem. Z.*, 1923, 137, 92—95).—Using the authors' micro-method, errors of sampling are less than 0.5%. The presence of acetone or β -hydroxybutyric acid in blood does not introduce an error in the dextrose estimation, but uric acid and creatinine produce an error through reduction of the ferricyanide, equal approximately to one-half of their weight expressed as dextrose.

H. K.

Estimation of Dextrose and Lactose in Blood and Urine. WM. THALHIMER and MARGARET C. PERRY (*J. Amer. Med. Assoc.*, 1922, 79, 1506—1508).—The total sugar is first estimated as dextrose

by Folin and Wu's method for blood or serous fluids, or by Folin and Berglund's method for urine. The solution (which should be adjusted to contain about 0.3% of sugar) is then heavily inoculated with *Bacillus paratyphosus B*, and after incubation for forty-eight hours the sugar remaining is estimated as lactose.

CHEMICAL ABSTRACTS.

Estimation of Yeast Glycogen and the Action of Alkali on Glycogen-formation in Yeast. PAUL MAYER (*Biochem. Z.*, 1923, **136**, 487—497).—Glycogen can only be estimated in yeast when separated from yeast gum. The following method is recommended. Ten g. of yeast (pressed) were heated for three hours with 30 c.c. of 60% potassium hydroxide at 100°, cooled, and treated with 50 c.c. of water and 200 c.c. of 96% alcohol. After a day, the precipitated glycogen was filtered, washed twice with 60% alcohol, twice with absolute alcohol and ether, and the powder dissolved in hot water, filtered, neutralised with hydrochloric acid, and exactly saturated with ammonium sulphate. After ten hours, the glycogen is filtered, dissolved in hot water, and an aliquot portion hydrolysed with hydrochloric acid (2.2%) at 100°. The cooled solution is neutralised and the dextrose estimated by the Pavy-Kumagawa-Suto process. The results show that glycogen estimation in presence of yeast gum are too high, the actual values found for various races lying between 2.5 and 5.7% on the pressed yeast. Contrary to the findings of Elias and Weiss (*A.*, 1922, i, 485), alkali does not stimulate yeast to form increased glycogen. H. K.

Improved Volumetric Method for Estimating α -, β -, and γ -Cellulose. M. W. BRAY and T. M. ANDREWS (*Ind. Eng. Chem.*, 1923, **15**, 377—378).—The method depends on the oxidation of cellulose with potassium dichromate in sulphuric acid solution. Ten c.c. of a solution of the cellulose in 72% sulphuric acid are treated with 10 c.c. of potassium dichromate solution (90 g. per l.) and 60 c.c. of 72% sulphuric acid are added. The mixture is boiled for exactly five minutes, cooled on ice, and the excess of dichromate titrated with ferrous ammonium sulphate solution, using potassium ferrieyanide as indicator. The dichromate solution is standardised in this way against 1 g. of cellulose obtained by the chlorination method of Cross and Bevan from sulphite pulp. For the estimation of α -, β - and γ -cellulose, 1 g. of the sample is triturated with 25 c.c. of the mercerising liquid (17.5% sodium hydroxide solution) and left for thirty minutes. The insoluble (α) cellulose is dried by suction on a filter pump, washed with 4% sodium hydroxide and distilled water, dissolved in 72% sulphuric acid, and estimated with dichromate as above. In one half of the filtrate, the β -+ γ -cellulose is determined in the same way. In the other half, the β -cellulose is precipitated by carefully adding 10% sulphuric acid solution until neutral to methyl-orange, and then adding 5 c.c. of acid in excess. The precipitate is allowed to coagulate and the γ -cellulose estimated in the supernatant liquid as above. The β -cellulose is obtained by difference. The method is more accurate

and rapid than the gravimetric method and difficulties of filtration and washing are practically overcome. Check determinations can be made without repeating the Cross and Bevan chlorination, as is necessary in the gravimetric method.

H. C. R.

Estimation of Formaldehyde in the Presence of Copper Sulphate. M. JAKÉŠ (*Chem. Ztg.*, 1923, 47, 386).—The usual methods of estimating formaldehyde cannot be applied directly to insecticide solutions containing copper sulphate. The copper is best removed by precipitation with potassium ferrocyanide. If the correct quantity of the latter is added, the solution will be found free from both copper- and ferrocyanide-ions after titration, as the excess of potassium ferrocyanide is removed by the formation of an insoluble potassium copper ferrocyanide. Before proceeding with the estimation of formaldehyde, the solution should be tested for the absence of both copper- and ferrocyanide-ions. The formaldehyde may then be oxidised with hydrogen peroxide, and the acid produced titrated with alkali, using azolitmin as indicator. If the excess of peroxide is boiled off, phenolphthalein may be used as indicator.

H. C. R.

The Detection and Behaviour of Formaldehyde in Corpses. A. BRÜNING (*Ber. Deut. pharm. Ges.*, 1923, 33, 99—103).—Owing to the rapidity with which formaldehyde is oxidised in the tissues, it can rarely be detected with certainty if any great length of time has elapsed before the toxicological examination, and the investigation should therefore be extended to include tests for the presence of formic acid. In the case of a body which had been some time in the water, a steam distillation of the liver with phosphoric acid revealed traces of formaldehyde by Hasse's peptone and sulphuric acid test in the first few drops of the distillate, but a negative test was given by all the other organs. The investigation of the same organs for formic acid, however, by Fincke's method gave a distillate which immediately reduced mercuric chloride, and after reduction with magnesium and hydrochloric acid with ice cooling, gave a strong formaldehyde reaction. The oxidation of formaldehyde by the oxydases in the tissues affords a possible explanation of the acid reaction of formaldehyde leather.

G. F. M.

New Reaction for Ketones. CAM. GILLET (*Bull. Soc. chim.*, 1923, [iv], 33, 465—466).—Referring to the paper by Bougault and Gros (A., 1922, ii, 666) on the use of Nessler's reagent for the characterisation of ketones, the author directs attention to his prior publication on the same subject (*Bull. Soc. chim. Belg.*, 1899, 13, 170) and to that of Marsh and Struthers (P., 1908, 24, 266).

G. F. M.

Use of Potassium or Sodium Bromide as a Source of Bromine for Urea Estimations. C. H. COLLINS (*Chem. News*, 1923, 126, 180—181).—An apparatus is described for the preparation of small quantities of sodium hypobromite solutions for urea analyses.

W. E. G.

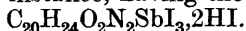
Estimation of Urea in Blood by Folin and Wu's Method. A Modified Apparatus. GEO. G. BOGGS and W. S. McELROY (*J. Lab. Clin. Med.*, 1923, 8, 254—255).—In the estimation of urea in blood by Folin and Wu's method, slight variations in pressure cause acid in the receiver to be drawn back into the receiving tube. The authors have modified the original apparatus in such a way that a slow current of air may be passed into the delivery tube so that a slight positive pressure is maintained and back suction prevented. The air current enters the delivery tube beyond the bend. It is found that no ammonia is lost even with a moderately fast current of air. CHEMICAL ABSTRACTS.

Estimation of Calcium Cyanamide. ALESSANDRO NANUSSO (*Giorn. Chim. Ind. Appl.*, 1923, 5, 168).—This method is based on the treatment of the silver salt of the cyanamide with ammonium chloride, and titration of the ammonia and guanidine thus formed with standard acid: $\text{Ag}_2\text{N}\cdot\text{CN} + 2\text{NH}_4\text{Cl} = 2\text{AgCl} + \text{N}:\text{C}\cdot\text{N}(\text{NH}_4)_2 \rightarrow \text{NH}_3 + \text{NH}:\text{C}(\text{NH}_2)_2$ (cf. *J.S.C.I.*, 1923, June). T. H. P.

The Quantitative Millon's Reaction in Blood-serum, after Removal of the Proteins. I. GEORG HAAS (*Z. physiol. Chem.*, 1923, 127, 39—51).—The tyrosine content of the blood may be estimated colorimetrically, making use of Millon's reaction. Salts influence the development of the red colour. The quantity of tyrosine in the blood is increased in acute yellow atrophy of the liver. W. O. K.

The Colorimetric Reagent of Folin and Denis and Weiss's Modification of Millon's Test [Estimation of Tyrosine]. GEORG HAAS and WILLY TRAUTMANN (*Z. physiol. Chem.*, 1923, 127, 52—66).—If the tyrosine in the blood is estimated by the Folin-Denis phenol reagent, higher values are obtained than when estimated by Millon's reagent. The difference is no doubt due to the fact that the phenol reagent reacts with substances other than tyrosine. W. O. K.

A New Alkaloidal Reagent, and the Preparation of the Iodoantimonates of Alkaloids in Crystalline Form. CAILLE and E. VIEL (*Compt. rend.*, 1923, 176, 1156—1159).—An antimony reagent composed of antimonious oxide or chloride 5 g., hydrochloric acid (*d* 1.123) 20 c.c., potassium iodide 40 g., and water to 100 c.c., is a precipitant for organic amines, the solubility of the complexes formed increasing with decrease in molecular weight. In dilutions of 1 in 500 or less, only alkaloids are precipitated, and the sensitiveness of the reagent in this respect is of a high order, for example, 1 part of quinine in 100,000 parts being capable of detection by its means. The precipitates obtained are yellow, amorphous substances containing both antimony and iodine, the quinine compound, for instance, having the composition



These iodoantimonites were also obtained in crystalline form by the method of François and Blanc (*A.*, 1922, i, 851). G. F. M.

Estimation of Choline in Blood. JOHN SMITH SHARPE (*Biochem. J.*, 1923, 17, 41—42).—The choline is extracted from the blood and tissues and is precipitated with iodine as the periodide. After washing off any free iodine, the periodide is decomposed with dilute nitric acid and the free iodine extracted with chloroform and titrated with standard sodium thiosulphate. The possibility of lecithin being formed as a degradation product is small if the estimation is carried out with reasonable speed. A recovery of 90—94% of choline added to blood was thus obtained. Normal blood to which no choline was added gave negative results. S. S. Z.

The Interconvertibility of Creatine and Creatinine. V. Estimation of Creatine in Muscle. AMANDUS HAHN and L. SCHÄFER (*Z. Biol.*, 1923, 78, 155—160; cf. this vol., ii, 195).—The muscles are extracted with boiling 5% sodium chloride solution containing acetic acid and then with boiling water. Any proteins in the combined extracts are precipitated with trichloroacetic acid, which avoids adsorption of creatine and creatinine, and the creatine is then determined colorimetrically. Results are given for various muscles, which indicate that previous methods give rather low results. W. O. K.

Estimation of Morphine and of Secondary Alkaloids in Opium and its Galenical Preparations. MARIO ALAZZI MANCINI (*Boll. Chim. farm.*, 1923, 62, 3—8, 35—39, 69—71, 101—105).—The author has investigated various methods for estimating morphine in opium, etc., including those given in the Pharmacopœias of the principal countries, and draws the conclusion that, as regards both accuracy and simplicity, the method of the U.S. Pharmacopœia is the most satisfactory. For the estimation of the secondary alkaloids, the methods of van der Wielen (A., 1903, ii, 519) and Tingle (A., 1918, ii, 87, 88, 175) are to be preferred. T. H. P.

The So-called Pyrrole Reaction. E. S. CHOTINSKI (*J. Russ. Phys. Chem. Soc.*, 1917, 49, 149—153).—The pyrrole reaction, in which a pine shaving moistened with hydrochloric acid develops a red coloration on exposure to the vapours of pyrrole, is found also to be given by shavings of fir, cypress, linden, alder, birch, deal, pear, ash, and oak. Anderson (*Annalen*, 1858, 105, 354) stated that this reaction is due to the presence of resin in pine shavings, and that an extract of the former in alcohol would also give the pyrrole reaction. This observation is repeated, and the extract found to give only a faint coloration, whilst the shaving, after extraction, gives as intense a coloration as before. The connexion between the pyrrole reaction and the coniferin reaction with phenols, whereby a blue coloration is produced, is shown, and the probability of the former reaction also being due to coniferin is pointed out. Coniferin is insoluble in alcohol, but soluble in hot water, and an aqueous extract of pine shavings gives a marked pyrrole reaction. Further, asparagus, which is rich in coniferin, but not resin, gives an intense red coloration with pyrrole vapours. R. T.

General and Physical Chemistry.

Use of Helium Light in Refractometry. N. SCHOORL (*Ber.*, 1923, **56**, [B], 1047—1048).—Corrections are given which enable the helium lines ($\lambda=6678$, 5876, and 5016) to be employed with the Pulfrich refractometer, using only the tables supplied for the *D* line of sodium. The deviation of the emergent beam is measured in the usual way, and the corresponding refractive indices are obtained from the tables for the *D* line. The following corrections are then applied to give true refractive indices. The corrections are given in units of the fifth decimal place :

Line.	Prism I ^c .	Prism II ^c .
He red (λ 6678)	— 895/(n_D)	— 1536/(n_D)
He yellow (λ 5876)	+ 23.3/(n_D)	+ 41/(n_D)
He green (λ 5016).....	+ 1582/(n_D)	+ 2775/(n_D)

where n_D in each case denotes the apparent refractive index obtained from the tables.

The refractive index of the substance for the sodium line can then be calculated with sufficient accuracy by means of the formulæ :
 $n_D = n_{5876} - 0.0255 (n_{5876} - n_{6678})$ or $n_D = n_{5876} - 0.0155 (n_{5016} - n_{5876})$.
H. H.

The Theory of Band Spectra. H. A. KRAMERS and W. PAULI, jun. (*Z. Physik*, 1923, **14**, 351—367).—An explanation of band spectra is put forward based on the assumption that the electron impulse moment makes an angle with the line joining the atomic nuclei. The infra-red bands of diatomic molecules must be ascribed to radiation processes in which the atomic vibratory movements and the rotation of the molecule play a part. Only in the case of the halogen acids is the dispersion of the ultra-red bands so great that they can be resolved into discrete lines. The line missing in the middle of the bands corresponds with the rotationless condition, and the absence of this line is in agreement with the Bohr rule, that quantum conditions for which the impulse moment disappears possess no statistical weight. According to the Bohr theory, the rare gases and halogen-ions possess a resulting impulse moment $1 \cdot h/2\pi$. If the same impulse moment be assumed for the halogen acids, then the distance between the innermost bands is three times as great instead of twice that of the distance between the other bands. This difficulty is overcome if the impulse moment makes an angle with the axis. An explanation is given of the negative group of oxygen bands described by Runge. The bands in the visible spectrum are due to strongly excited molecules in which the electron emitting light is directly influenced by the rotation of the molecule.

W. E. G.

The Mode of Excitation of the Atom and Molecule Spectrum by Electron Collisions. VICTOR VON KEUSSLER (*Z. Physik*, 1923, 14, 19—31).—Experiments have been carried out on the intensities of the two hydrogen spectra in the absence and in the presence of helium at a pressure of hydrogen of 0.01 mm. Under a potential of 16 to 17 volts, the addition of helium did not cause any material change in the relative intensities of the two spectra. At slightly higher voltages, but still lower than the resonance potential of helium, the Balmer series became relatively more intense with respect to the secondary spectrum. In the presence of much helium, only the Balmer series is observed. Concurrently, the intensities of the individual lines of the Balmer series undergo change; in the presence of helium, the lines of short wave-length become more intense. These results and those of previous workers are explained on the assumption that the excited hydrogen molecules which normally emit the secondary spectrum, on collision with helium atoms, undergo dissociation into a normal and an excited atom with the subsequent emission of the Balmer series. Thus the dissociation of hydrogen occurs in two steps. The first is the excitation of the molecule by electron collision, and the second occurs when the excited molecule is subjected to atomic collisions before the emission of the radiation. The smallest ionisation step for hydrogen is the conversion of the H_2 molecule into a normal atom, a H^+ atom, and an electron. W. E. G.

The Effect of a Probable Electric Field on the Bands of Nitrogen. SNEHAMOY DATTA (*Astrophys. J.*, 1923, 57, 114—120).—When the partial pressure of bromine vapour in a discharge tube containing air is gradually raised, the sharp bands of nitrogen become blurred until even the heads have disappeared. It is suggested that the blurring may be a Stark effect produced by the electric fields of the ionised bromine atoms, as predicted by Hettner. The similar blurring due to increased pressure in pure nitrogen may also be a Stark effect. The cyanogen band was unaffected by the bromine. The displacement observations recorded by Dufour (A., 1907, ii, 920) and by Clinkscales (*Physical Rev.*, 1910, 30, 594) may also be a Stark effect. A. A. E.

Spectra Associated with Carbon. T. R. MERTON and R. C. JOHNSON (*Proc. Roy. Soc.*, 1923, [A], 103, 383—395).—The authors have investigated the effect of the presence of helium in vacuum discharge tubes on the band and line spectra of carbon, and the conditions under which the different spectra can best be experimentally isolated. The Swan spectrum can be excited by means of uncondensed discharges in tubes with carbon electrodes and containing hydrogen, and provided with side tubes containing potassium hydroxide and phosphoric oxide. The Ångström bands appear in vacuum tubes containing carbon and oxygen when excited by uncondensed discharges and are usually accompanied by faint bands in addition to well-marked bands which are degraded to the violet. The faint bands, for the production of which hydrogen is essential, do not form part of the Ångström system, and can be

isolated as separate bands under appropriate conditions. The CH bands are observed with great brilliance in tubes provided with carbon electrodes and side tubes as described, and with a palladium regulator through which hydrogen is admitted. The high-pressure carbon monoxide bands may be isolated almost completely by employing a discharge tube containing carbon dioxide and provided with carbon electrodes and side tubes and palladium hydrogen regulator. On passing the discharge, the high-pressure bands appear after the carbon dioxide is reduced to carbon monoxide by the electrodes. "Comet-tail" bands may be isolated almost completely, the spectrum being accompanied only by a few feeble lines representing the principal lines of the helium spectrum, by employing a discharge tube provided with a palladium regulator, side tubes containing phosphoric oxide and potassium hydroxide, and containing helium at about 20 mm. pressure. The "comet-tail" bands appear suddenly after the tube has been run sufficiently long for all traces of water vapour and carbon dioxide to be absorbed and the quantity of hydrogen to be reduced very considerably. Particulars are given of the various lines observed. The measurements of wave-lengths and intensities are not in good agreement with those of Fowler (*Mon. Not. Roy. Astr. Soc.*, 1910, **70**, 484). When a small quantity of hydrogen is admitted to a vacuum tube exhibiting the comet-tail bands, these disappear almost completely, and are replaced by a spectrum consisting of well-marked triplet-bands degraded to the red, with some indication of Swan and Ångström bands. Details are given of a new spectrum of carbon excited when a condensed discharge is passed through a wide-bore tube with carbon electrodes containing helium at a pressure of about 20 mm., and such that an uncondensed discharge would excite the "comet-tail" spectrum. It is suggested that the function of helium in the discharge tubes under the conditions of the experiment is to permit the passage of a discharge, thus enabling spectra appropriate to extremely low pressures of other gases present in the tube to be excited.

J. S. G. T.

The Series Spectrum of Trebly-ionised Silicon (Si^{IV}).

A. FOWLER (*Proc. Roy. Soc.*, 1923, [A], **103**, 413—429).—Numerous new lines of silicon have been observed and have been classified in four groups, in extension of the groupings made by Lockyer in connexion with stellar spectra. The four groups represent successive stages of ionisation, and are designated Si^{I} , Si^{II} , Si^{III} , and Si^{IV} . The spectra consist alternately of triplets and doublets, and the series constant has successive values N , $4N$, $9N$, and $16N$, where N is the series constant for hydrogen. The value $16N$ for the series constant of Si^{IV} is fully established by the new data. The spectrum resembles that of neutral sodium Na^{I} , but the main series corresponding with the familiar series of Na^{I} are in the extreme ultra-violet. The secondary series which fall partly within the ordinary range of observation, correspond with series occurring in the infra-red in the case of Na^{I} . A comparison of the series spectra of the elements Si^{IV} , Al^{III} , Mg^{II} , and Na^{I} , the atoms of

which are characterised by the same number and distribution of external electrons whilst the nuclei differ in charge and mass, indicates that differences in the four spectra are to be attributed mainly to differences in the nuclear charges, or to differences in the net charges of the atoms as a whole with respect to the electron producing the spectrum by its transitions from one quantum orbit to another. The respective doublet separations in the respective series are as follows: Na^{I} , 17.18; Mg^{II} , 91.55; Al^{III} , 238; Si^{IV} , 460. These and the series terms exhibit greater regularity than those for elements of the same chemical group. The largest term in the Si^{IV} series system corresponds with the $1(\sigma)$ or $3\sigma(\text{Bohr})$ term and is equal to 364,117, corresponding with a value of the ionisation potential equal to 44.95 volts. J. S. G. T.

Regularities in the Band Spectrum of Silicon. C. PORLEZZA (*Gazzetta*, 1923, **53**, i, 215—224; cf. this vol., ii, 198).—The bands observed by the author in the arc spectrum of silicon and also those obtained by de Gramont and Watteville (A., 1908, ii, 909) by burning silicon chloride or by passing a spark between silicon electrodes may be grouped into the five series: (1) $1/\lambda = 37812 + 1185.5m + 6.25m^2 (m=0, 1, 2, 3, 4)$; (2) $1/\lambda = 36288 + 1170.6m + 5.2m^2 (m=0, 1, 2, 5, 6)$; (3) $1/\lambda = 35966 + 1152.2m + 5.95m^2 (m=0, 1, 4, 5, 6, 7)$; (4) $1/\lambda = 35632 + 1139m + 6.2m^2 (m=0, 4)$; (5) $1/\lambda = 38738 + 1170.8m + 4.4m^2 (m=0)$. As regards the grouping in series, it is shown that, just as for the line spectra, the arc spectrum of silicon is intermediate to the flame and spark spectra, as regards both the number and the intensity of the bands. T. H. P.

The Explosion Spectra of the Alkaline-earth Metals. R. A. SAWYER and A. L. BECKER (*Astrophys. J.*, 1923, **57**, 98—113; cf. A., 1922, ii, 242, 803; Anderson, *Astrophys. J.*, 1920, **51**, 37).—The explosion spectra of the chlorides of barium, calcium, magnesium, and strontium between λ 2280 and λ 4550 have been investigated, using the asbestos fibre method, and found, in agreement with the theoretical conclusions of Saha and of Sommerfeld, to be almost pure spark spectra, consisting chiefly of the doublets of the first and second subordinate series, $2p-md$ and $2p-ms$. Only the fundamental singlet arc line $1S-2P$ appears, with a relative intensity corresponding with that in the spectra of the solar chromosphere and class B stars. So small an amount of material is required to give explosion spectra that lines due to copper, zinc, aluminium, lead, carbon, and nitrogen present as impurities were prominent; lines of chlorine, hydrogen, and oxygen were not detected. A. A. E.

Röntgen Ray Spectroscopic Measurements. Röntgen Ray Spectra. ELIS HJALMAR (*Z. Physik*, 1923, **15**, 65—109).—Particulars are given of the determination of the M -series of lines in the X-ray spectra of uranium, thorium, bismuth, lead, thallium, gold, platinum, iridium, osmium, tungsten, tantalum, lutecium, ytterbium, erbium, holmium, and dysprosium, and of the N -series

of lines of uranium, thorium, and bismuth. In the case of the *M*-series, the complexity of the strong lines is established. Certain new lines are recorded and arranged in the general classification of X-ray spectra. The validity of the combination principle in the case of these lines is established. Certain *N*, *O*, and *P* levels can be calculated from them, and the values agree with those determined by Coster and Bohr. The results in the case of the *N*-series are in agreement with previous results.

The existence of differences in the calculated values of the wave-length of a line when determined by the application of Bragg's formula $n\lambda = 2d \sin \phi$ to spectra of different orders is definitely established. The experimental results in this connexion are critically examined, and it is shown that the reflection theory of the production of the lines due to Ewald (*Ann. Physik*, 1917, [iv], 54, 519), leading to the relation $\log (\sin \phi / n) = \text{const.} + A/n^2$, where *A* is a constant, is alone compatible with the determinations, and affords results according in some measure with the deviations from a constant value observed in the various orders of spectra.

J. S. G. T.

The Arc Spectrum of Cesium. JACQUES BARDET (*Compt. rend.*, 1923, 176, 1711—1712).—A complete list is given of the wave-lengths of the lines of the arc spectrum of cesium, the material employed for the research being zirconium containing besides cesium only a trace of lead. The measurements were made over the region comprised between 2300 and 3500 Å. G. F. M.

The *L*-Series of Hafnium. AUGUST ŽÁČEK (*Z. Physik*, 1923, 15, 31—32).—A hafnium preparation, a mixture of hafnium and zirconium oxides, has been used for the measurement of the *L*-series. The stronger lines have been measured by the absolute method. The values of λ were α_1 , 1566,14; α_2 , 1576,70; β_1 , 1370,17; β_2 , 1323,6; β_3 , 1349,1. W. E. G.

Absorption in Iodine and Other Vapours. K. VOGT and J. KOENIGSBURGER (*Z. Physik*, 1923, 13, 292—311).—The selective absorption, absorption bands, and lines of iodine vapour, of bromine and nitrogen peroxide vapours, have been measured over a range of temperatures, pressures, and thicknesses. The selective absorption of iodine broadens with increase in temperature, the maximum retaining its position unchanged, but the amount of absorption being smaller at the higher temperatures. The selective and band absorption become fainter above 600°, giving rise to a typical line spectrum. The selective and band absorption are to be ascribed to the molecule or to some condition peculiar to molecule formation. Beer's law holds for iodine only up to thicknesses, $5 \cdot 10^{-5}$. Experiments with bromine confirmed the limits of applicability of this law given by Ribaud. Addition of air increased the absorption slightly on the short wave-length side and to a considerable extent on the long wave-length side of the maximum. Calculation of the selective absorption and comparison with the experimental

values have been made, and better agreement is obtained on the short wave-length side than on the long wave-length side of the maximum. The number of molecules taking part in the continuous absorption at any moment is 1/100 of the total present. The band spectrum of iodine at low densities possesses a channelled appearance, which disappears on raising the density. At high densities, the single absorption lines of bromine became broadened, as did also a number of iodine, bromine, and nitrogen peroxide lines when the density was increased by the addition of foreign gases. The cause of this widening is traced to the molecular collisions. The rotation Doppler-effect does not occur to an appreciable extent.

W. E. G.

The Absorption of Near Ultra-red Radiation by Carbon Dioxide. JUNZŌ ŌKUBO (*Sci. Rep. Tōhoku Imp. Univ.*, 1923, 12, 39—43).—It is shown that in agreement with the results of Hertz (A., 1911, ii, 830) and of Bahr (A., 1913, ii, 6) the near ultra-red absorption spectrum of gaseous carbon dioxide comprises intense bands at $\lambda\lambda$ 2.71 and 2.77 μ and a somewhat weaker band at λ 2.61 μ . In addition, feebler maxima occur at $\lambda\lambda$ 3.02, 2.99, 2.97, 2.93, 2.88, 2.84, 2.81, 2.73, 2.67, 2.63, 2.57, 2.53, 2.48, 2.44, 2.40, 2.37, 2.34, and 2.29 μ . These weaker maxima are not so prominent as in the case of the spectra of diatomic molecules, e.g., hydrochloric acid.

J. S. G. T.

The Ultra-violet Absorption Spectra of Eugenol and iso-Eugenol. GARTHA THOMPSON (T., 1923, 123, 1594—1597).

Absorption Spectra of Sulphuric and Nitrated Solutions of Phenanthroxazine and Phenanthrazine. B. FORESTI and R. MARTORELLI (*Gazzetta*, 1923, 53, i, 262—264).—Examination of the absorption spectra of sulphuric acid solutions, with and without addition of a nitrate, of phenanthroxazine and phenanthrazine and of a mixture of 77.4 parts of the former with 22.6 parts of the latter, confirms the results previously obtained (A., 1922, i, 1062; ii, 524). Sulphuric acid solutions of phenanthroxazine exhibit an absorption band at about 500 $\mu\mu$ and an absorption decreasing continuously from the extreme red to about 560 $\mu\mu$; when nitrate is present, an intense absorption band is shown at about 575 $\mu\mu$ and a slight absorption in the violet. With phenanthrazine, a sharp absorption band occurs at about 620 $\mu\mu$ and a moderate absorption in the extreme violet; when nitrate is present, the absorption begins at about 600 $\mu\mu$ and increases rapidly towards the violet, culminating in a band at about 470 $\mu\mu$. Absorption curves deduced from photographs of the spectra are given.

T. H. P.

The Ultra-violet Absorption Spectra of Alkaloids of the isoQuinoline Group. Narceine. PIERRE STEINER (*Compt. rend.*, 1923, 176, 1379—1381; cf. Hartley, A., 1885, 1174; Dobbie and Lauder, T., 1903, 83, 605).—The study of the ultra-violet absorption spectrum by Henri's method shows a large band the maximum

of which lies at $\lambda=2707 \text{ \AA.}$ with a maximum absorption coefficient of $\epsilon=9800$, the minimum values being $\lambda=2539 \text{ \AA.}$ and $\epsilon=8000$. A diagram is given which shows the spectrum of narceine in comparison with those of narcotine, opianic acid, and hydrocotarnine; certain similarities in the curves are pointed out. It is stated that a spectrographic estimation of 0.05 mg. of narceine in 2 c.c. of solvent may be effected.

H. J. E.

Phosphorescence caused by Active Nitrogen. W. JEVONS (*Nature*, 1923, 111, 705—706; cf. Lewis, this vol., ii, 361).—In the course of an observation of the spectrum resulting from the introduction of aluminium chloride vapour into a stream of active nitrogen, it was noticed that after long exposure a solid deposit was produced which exhibited a bright green fluorescence when brought into contact with active nitrogen some days later.

A. A. E.

Photochemical Studies. XVI. The Inapplicability of the Photoelectric Law to Photochemical Reactions. J. PLOTNIKOW (*Z. wiss. Photochem.*, 1923, 22, 110—116).—From a review of recent work on the subject, the author concludes that Einstein's photoelectric law expressed by the equation $mv^2/2=h\nu$, in which the symbols have the customary significance, is inapplicable to photochemical reactions (cf. A., 1922, ii, 248).

J. S. G. T.

The Photochemical Decomposition of Solid Substances. ALBERT NOYES, jun. (*Compt. rend.*, 1923, 176, 1468—1470).—A theoretical paper in which Perrin's radiation theory (A., 1919, ii, 177) is developed in the sense of a slight modification in dealing with solid substances. This modification is necessary as a certain amount of energy is required to separate the molecules and also to remove the products of the decomposition from the surface. The reaction velocity for a given frequency is represented by $dx/dt=kI(h\nu-h\nu_0)$, where I is the intensity of the light and $h\nu_0$ the energy used in separating the molecules from each other. If energy of several frequencies is used, the equation becomes $dx/dt=kI[(h\nu_1-h\nu_0)+(h\nu_2-h\nu_0)+\dots+(h\nu_n-h\nu_0)]$.

H. J. E.

Inhibition of the Photochemical Decomposition of Hydrogen Peroxide Solutions. II. WILLIAM THEODORE ANDERSON, jun., and HUGH STOTT TAYLOR (*J. Amer. Chem. Soc.*, 1923, 45, 1210—1217; cf. this vol., ii, 278).—Using the method previously described, the authors have investigated the decomposition of hydrogen peroxide by ultra-violet light in the presence of a number of inorganic acids, bases, and salts as inhibitors of the decomposition. The inhibition constant is given for perchloric, nitric, sulphuric, phosphoric, boric, and hydrochloric acids, sodium, potassium, ammonium, barium, ethylammonium, and phenylammonium hydroxides, sodium, potassium, ammonium, and magnesium sulphates, sodium and barium nitrates, potassium perchlorate, sodium fluoride and chloride, ammonium chloride and bromide, potassium chloride and bromide, and barium bromide. With the exception

of the nitrates, which show a weak absorption of light throughout the ultra-violet, the substances are practically diactinic to the incident radiation. The bases are found to be excellent inhibitors, the acids good inhibitors, and the bromides and chlorides moderately strong inhibitors, whilst all other inorganic compounds examined were found to be without action. The inhibition was shown by neutral salt action to be a function of the concentration of the hydrogen-, chloride-, bromide-, and hydroxyl-ions. A tentative hypothesis of the mechanism of the action has been put forward which is based on an ionisation of the hydrogen peroxide, and the facts, which must be covered by any hypothesis of the action, have been enumerated.

J. F. S.

Reduction of Carbon Dioxide by Ultra-violet Light. H. A. SPOEHR (*J. Amer. Chem. Soc.*, 1923, 45, 1184—1187).—The author discusses briefly the work of Usher and Priestley (A., 1911, ii, 817), Stoklasa and Zdobnický (A., 1911, i, 178, 769), Berthelot and Gaudechon (A., 1910, i, 543), and Baly, Heilbron, and Barker (T., 1921, 119, 1025) on the action of ultra-violet light on carbon dioxide. The experiments have in many cases been repeated, but in no case has the production of formaldehyde been confirmed. Paracetaldehyde itself is shown to break up readily under the action of ultra-violet light, forming acetaldehyde and probably glycollaldehyde, which at 60° readily passes into a hexose. Thus paracetaldehyde, far from being a protection against sugar formation, itself, quite independently of the presence of carbon dioxide, yields substances which reduce alkaline copper solutions. The author feels that in the publications named some essential condition or factor has been omitted in the description, or, failing this, a misinterpretation of experimental observations has occurred.

J. F. S.

Photochemistry of Potassium Permanganate. II. Energetics of the Photo-decomposition of Potassium Permanganate. E. K. RIDEAL and R. G. W. NORRISH (*Proc. Roy. Soc.*, 1923, [A], 103, 366—382).—In continuation of previous work (this vol., ii, 362), the authors have investigated the absorption spectrum of a 0.01*N*-solution of potassium permanganate, more especially in the ultra-violet, in order to determine the wavelength of the light effecting the decomposition of potassium permanganate, and to test the validity of Einstein's photochemical law in this connexion. In the absorption spectrum, a band occurred between λ 380 and 270 $\mu\mu$, with its head at λ 313 $\mu\mu$, whilst beyond λ 260 $\mu\mu$ a second band commenced. The visible radiations of the mercury-vapour spectrum were not appreciably effective in decomposing potassium permanganate, and it is considered that the line at λ 3128 Å. is principally responsible for the photo-decomposition by mercury-vapour light. Assuming that the only photo-active line is at λ 3128 Å. and that the coefficient of absorption for green and yellow light is the same as for the ultra-violet light, it is shown that two quanta are probably concerned in the photo-

decomposition of the permanganate-ion. It was found that mixtures of potassium permanganate and oxalic acid were much more sensitive to ultra-violet light than to visible light. The mechanics of the photo-decomposition are discussed from the point of view of atomic structure suggested by Kossel, Lewis, and Langmuir.

J. S. G. T.

Action of Light on Double Tartrates. V. VOLMAR (*Compt. rend.*, 1923, **176**, 1465—1467; cf. this vol., ii, 279).—Solutions of potassium antimonyl tartrate and the corresponding compounds of arsenic, bismuth, copper, and iron undergo decomposition on exposure to ultra-violet light with liberation of the metal, the maximum effect being produced in the case of the bismuth compound. The simple salts of the same metals, both organic and inorganic, are quite stable under similar conditions. The conclusion is drawn that the heavy metal in the tartrates occupies a position in the molecule in accordance with the constitution attributed to it by Jungfleisch. Potassium borotartrate furnishes an exception; the author considers this to be due to the fact that it appears to be, not a definite compound, but a mixture.

H. J. E.

The Capture of Electrons by Swiftly Moving α -Particles. BERGEN DAVIS (*Nature*, 1923, **111**, 706).—The failure of an α -particle, when in the act of ionising a molecule, or immediately after, to attach one or more of the free electrons to itself may be due to the high velocity of the α -particle. When its velocity has fallen from 20.6×10^8 cm./sec. to 8.2×10^8 cm./sec. one electron is taken up, and at a velocity of 3.1×10^8 cm./sec. the second electron is taken up. The limiting parabolic velocities for an electron falling into the *K*-ring of (a) a doubly charged α -particle, and (b) one having a single charge are calculated to be 6.2 and 3.2×10^8 cm./sec., respectively. It is therefore suggested that if the α -particle is moving with a velocity greater than that of the fall of an electron into the *K*-ring, the electron will fail to reach the *K*-ring and effect a combination. In that case, all α -rays, of whatever initial velocity, should capture the first and second electrons at the same velocity.

A. A. E.

The Employment of Normal Radium and Uranium Solutions for Emanation Measurements. P. LUDEWIG and E. LORENSER (*Z. Physik*, 1923, **13**, 284—291).—The constancy and usefulness of normal solutions of radium and uranium as standards for the determination of radioactive material has been tested by comparison of the amounts of emanation liberated under comparable conditions from a number of radioactive solutions over wide intervals of time. A number of normal solutions of radium from the Physikalisch Technischen Reichsanstalt, analysed by measurements of the emanation, agreed within 1%, and a series of uranium solutions prepared in the Freiberg Radium Institute agreed within 0.5% with the Reichsanstalt solutions. The temperature at which the emanation is transferred to the ionisation chamber does not play

any part. The radium and uranium solutions showed no deterioration when tested over a period of twelve months. The accuracy of this method is about 1%.
W. E. G.

Electrolytic Dissociation of Hydrogen Selenide and Hydrogen Telluride. DE HLASKO (*J. Chim. Phys.*, 1923, 20, 167—172).—The electrical conductivity of sodium hydroselenide has been determined at 25° in an atmosphere of hydrogen and the following values of the molecular conductivity have been found, μ_{100} 112, μ_{500} 115, and μ_{1000} 118. From these values, the value of μ_{∞} is deduced as 120.5, and since at this temperature the sodium ion has the value $\lambda_{Na^+}=50$, the value of λ_{SeH^+} is about 70. Using the same method and apparatus, the electrical conductivity of solutions of hydrogen selenide has been measured at 25° in an atmosphere of hydrogen. The following data are recorded: 0.1N $\mu=17.9$, $\kappa=1.79 \times 10^{-3}$, $\alpha=0.0424$, $K_{H_2Se}^{25}=\alpha^2/(1-\alpha)\nu=1.88 \times 10^{-4}$; 0.0249N, $\mu=35.3$, $\kappa=8.80 \times 10^{-4}$, $\alpha=0.0836$, $K=1.90 \times 10^{-4}$; 0.0137N, $\mu=46.0$, $\kappa=6.54 \times 10^{-4}$, $\alpha=0.1091$, $K=1.88 \times 10^{-4}$; 0.00817N, $\mu=59.5$, $\kappa=4.86 \times 10^{-4}$, $\alpha=0.1410$, $K=1.86 \times 10^{-4}$, the mean value of the ionisation constant, K , being 1.88×10^{-4} . A similar series of measurements has been made for hydrogen telluride solutions at 18°. The following data are recorded: 0.093N, $\mu=56$, $\kappa=5.24 \times 10^{-3}$, $\alpha=0.148$, $K_{H_2Te}^{18}=\alpha^2/(1-\alpha)\nu=2.40 \times 10^{-3}$; 0.0667N, $\mu=63$, $\kappa=4.215 \times 10^{-3}$, $\alpha=0.166$, $K=2.23 \times 10^{-3}$; 0.06173N, $\mu=66$, $\kappa=4.061 \times 10^{-3}$, $\alpha=0.174$, $K=2.26 \times 10^{-4}$; 0.06024N, $\mu=67$, $\kappa=4.061 \times 10^{-3}$, $\alpha=0.176$, $K=2.26 \times 10^{-3}$; 0.03442N, $\mu=85.5$, $\kappa=2.942 \times 10^{-3}$, $\alpha=0.225$, $K=2.22 \times 10^{-3}$; 0.02326N, $\mu=107.5$, $\kappa=2.497 \times 10^{-3}$, $\alpha=0.283$, $K=2.59 \times 10^{-3}$; 0.01186N, $\mu=136$, $\kappa=1.607 \times 10^{-3}$, $\alpha=0.360$, $K=2.50 \times 10^{-3}$; 0.00278N, $\mu=208.5$, $\kappa=5.79 \times 10^{-4}$, $\alpha=0.549$, $K=1.80 \times 10^{-3}$. The mean value of the dissociation constant is 2.27×10^{-3} . According to the present experiments, hydrogen telluride is a stronger acid than hydrogen fluoride. The increase in the strength of the hydrogen acids of the elements of group VI thus increases rapidly with increasing atomic weight, as is shown by the dissociation constants of these substances thus: H_2O , $K=0.64 \times 10^{-14}$, H_2S , $K=0.91 \times 10^{-7}$, H_2Se , $K=1.88 \times 10^{-4}$, H_2Te , $K=2.27 \times 10^{-3}$.
J. F. S.

The Question of Unipolar Conductivity of Metallic Sulphides. The Investigation of the Electrical Properties of Silver Sulphide and Cuprous Sulphide. GEORGI GRIGOREVITSCH URAZOV (*J. Russ. Phys. Chem. Soc.*, 1919, 51, 311—352).—The conductivities of silver sulphide and cuprous sulphide were investigated at different temperatures, using an alternating current. The samples investigated were prepared synthetically taking great precautions to ensure their uniformity, etc. It is shown that the conductivity of these sulphides changes with temperature in accordance with the formula $\lambda_t=\lambda_0 \times e^{\alpha t}$. The presence of excess of either metal or sulphur greatly increases the conductivity of the sulphides, particularly the presence of sulphur in cuprous sulphide. The transition points of the different modification of the sulphides

are clearly shown on the conductivity curves. Both sulphides are shown to decompose into their components under the influence of a direct current, as evidenced by the isolation of the components at the electrodes and the detection of a considerable back *E.M.F.*

G. A. R. K.

The Critical and Dissociation Potentials of Hydrogen.

A. R. OLSON and GEORGE GLOCKLER (*Proc. Nat. Acad. Sci.*, 1923, 9, 122—126).—An apparatus is described for the measurement of the current voltage curves. The dissociation potential of hydrogen is found to be 3.16 volts. Values are obtained for the dissociation potentials of five members of the Lyman series. Breaks on the current voltage curves, corrected for the dissociation voltage, 3.16 volts are recorded at 11.98, 12.68, 12.98, 13.14, and 13.24 volts, and these are in good agreement for the calculated values of the Lyman series. In addition, three breaks occur at 14.86, 15.35, and 15.62 volts, which are ascribed to the hydrogen molecule.

W. E. G.

Luminous Discharge in Bromine. A Possible Determination of the Ionisation Potential of Bromine.

W. ALBERT NOYES, jun. (*J. Amer. Chem. Soc.*, 1923, 45, 1192—1195).—Using practically the same apparatus and method as was previously employed in the investigation of the luminous discharge in iodine (this vol., ii, 209), the ionisation potential of bromine is found to be 12.5 ± 0.5 volts. The fact that for tubes of a given length approximately the same multiple of the ionisation potential of bromine as of iodine was obtained is accounted for by the higher heat of dissociation of bromine, the molecules having little or no electron affinity. The higher electron affinity of bromine would thus be counterbalanced by a lower concentration of the monatomic gas. The facts agree with the work of Gibson and Noyes on the sparking potentials in gases (A., 1922, ii, 812). J. F. S.

The Ionising Potentials of Nitrogen and Hydrogen.

H. D. SMYTH (*Nature*, 1923, 111, 810; cf. *Proc. Roy. Soc.*, 1922, [A], 102, 283).—In the case of nitrogen, the three critical potentials, 16.9, 24.1 ± 1.0 , and 27.7 ± 1.0 volts, are interpreted as corresponding respectively to the transitions $N_2 \rightarrow N_2^+ + e^-$; $N_2 \rightarrow N^{++} + N + 2e^-$; and $N_2 \rightarrow 2N^+ + 2e^-$. If this is correct, the first ionising potential of atomic nitrogen is about 11 volts, and the second about 18 volts. The ionisation of molecular hydrogen in the neighbourhood of 16.5 volts does not appear usually to be accompanied by dissociation.

A. A. E.

Collodion Membrane for Liquid Junctions.

HAROLD A. FALES and MORTIMER J. STAMMELMAN (*J. Amer. Chem. Soc.*, 1923, 45, 1271—1272).—With the object of preventing the mechanical intermixing of one liquid with another during the measurement of hydrogen-ion concentrations by the *E.M.F.* method, the authors have covered the ends of the electrode vessels with a film of collodion. The membrane is best produced by allowing some collodion to

evaporate in the air until it becomes thick and then dipping the end of the syphon tube of the electrode vessel into it, withdrawing, and allowing the collodion to dry. This process is repeated several times. The membrane may only be used when the collodion is equally permeable to all the ions in the solutions used. If this is not the case, large potential differences will be set up owing to the setting up of the "Donnan equilibria"; measurements given in the paper show that very constant *E.M.F.* measurements can be obtained with this device. J. F. S.

Calculation of Isoelectric Points. P. A. LEVENE and HENRY S. SIMMS (*J. Biol. Chem.*, 1923, **55**, 801—813).—On the assumption that the ionisation of each acidic and basic group in a poly-acidic, poly-basic amphoteric substance takes place independently of the degree of ionisation of other groups in the molecule, the following approximate formula has been deduced for the isoelectric point of the ampholyte: $I = \sqrt{(\Sigma Ka)/(\Sigma Kb)} \cdot \bar{K}_w$. The accurate expression is also given in the original. Since the values of the dissociation constants of the weaker acidic and basic groups are negligible in comparison with those of the strongest, the above formula may be simplified, without much error, to $I = \sqrt{Ka/Kb} \cdot \bar{K}_w$, in which K_a and K_b represent the dissociation constants of the strongest acidic and basic groups, respectively. The latter formula is identical with the one usually employed for the calculation of the isoelectric point of a monoacidic, monobasic ampholyte. Using the above expressions for the calculation of the isoelectric point of aspartic acid, the value $P_1 = 2.76$ was obtained in each case. E. S.

Transport Numbers of Sodium and Potassium in Mixed Chloride Solution. R. F. SCHNEIDER and S. A. BRALEY (*J. Amer. Chem. Soc.*, 1923, **45**, 1121—1134).—The transport numbers of sodium and potassium and the transport ratio have been determined in mixtures of the chlorides of these metals in solutions varying in concentration from 0.1*N* to 1.6*N*. The ratio of the molecular concentration of the two salts was varied from 3KCl:1NaCl to 1KCl:3NaCl. The equivalent conductivity of the mixtures have also been determined. The ionic conductivities have been calculated from the transport numbers and the equivalent conductivities of the different solutions examined. The results show that the solutions are highly complex and in no way in accord with the Ghosh hypothesis of complete dissociation. The mobility of the sodium-ion at a total concentration of 0.2*N* and a ratio of 3KCl:1NaCl has been shown to be practically zero. The deviations between the calculated values and the experimental values of the transport ratios are not due to hydration of the ions alone, but must be due also to the formation of complexes in solution. The present results agree well with those of Smith and Ball (*A.*, 1917, ii, 247) and Smith and Webb (*A.*, 1920, ii, 361), in which they found that the sodium-ion fraction increases with increase in total concentration above 0.2*N*. Below this concentration, the sodium-ion fraction decreases with respect to that of the potassium-ion. See also

A., 1921, ii, 662. Various explanations of the behaviour observed are discussed.

J. F. S.

Production of Sulphuric Acid and Sodium Hydroxide by Electrolysis of Sodium Sulphate. E. R. WATSON (*J. Soc. Chem. Ind.*, 1923, **42**, 251—252T).—By the electrolysis of 40% aqueous sodium sulphate solution, employing a platinum, iron, or copper cathode and a platinum, lead, or carbon anode, a current density of about 4 amperes per sq. dcm., and a potential difference between the electrodes of about 5 volts, starting the electrolysis at about 30° and allowing the temperature to rise to about 40°, conversion into sodium hydroxide and sulphuric acid can be effected with a current efficiency of about 90%, and an energy efficiency of about 50%, provided electrolysis is not carried beyond an average conversion of about 25%. Nearly all the sodium sulphate may be crystallised out of the alkaline liquor, leaving sodium hydroxide in the mother-liquor nearly pure, and sodium hydrogen sulphate may be similarly obtained from the acid liquor. Sulphuric acid is best produced from the sodium hydrogen sulphate by distillation.

J. S. G. T.

Electrochemical Properties of Bismuth and Antimony in Alkaline Solution. G. GRUBE and F. SCHWEIGARDT (*Z. Elektrochem.*, 1923, **29**, 257—264).—The behaviour of bismuth and antimony employed as anode in solutions of sodium hydroxide and potassium hydroxide has been investigated. Both bismuth and antimony dissolve anodically in the form of tervalent ions in strong alkali solution. Thus, as much as 1 g. of bismuth may be dissolved in 1 litre of concentrated alkali hydroxide solution, with the formation of an alkali bismuthite. The anode then becomes passive and covered with coloured higher oxides of bismuth. In the case of antimony, concentrated solutions of potassium antimonite may be obtained in this manner without the anode being rendered passive. Passivity of the antimony anode results, however, if the current density exceeds 7.5 amperes per sq. dcm., and the anode then becomes covered with a white non-conducting layer of oxide. A solution of potassium antimonite is a strong reducing agent and readily absorbs oxygen from the air. The process of its electrolytic oxidation at a polished platinum electrode is not, however, reversible, and it is shown that production of potassium antimonate in this manner is effected, not by a direct process of anodic oxidation, but owing to the oxidising action of oxygen evolved in the form of gas at the electrode. The electrode potential, ϵ , of antimony in a 10N-solution of potassium hydroxide at 20°, the process of solution being represented by $\text{Sb} + 4\text{OH}' + 3\oplus \rightarrow \text{SbO}_2' + 2\text{H}_2\text{O}$, is given by $\epsilon = -0.675 + 0.058/3 \log c_{\text{SbO}_2'}$. For the oxidation process to antimonate, the corresponding equation is $\text{SbO}_2' + 2\text{OH}' + 2\oplus \rightarrow \text{SbO}_3' + \text{H}_2\text{O}$, and the value of ϵ is given by $\epsilon = -0.589 + 0.058 \log (c_{\text{SbO}_3'}/c_{\text{SbO}_2'})/2$. The value of the electrode potential of antimony in a solution containing 1 g. ion of SbO_3' in 10N-potassium hydroxide solution is -0.641 volt. The value of the antimonite-antimonate potential difference is reduced

as the alkalinity of the solution is increased, and is determined by the OH' concentration of the solution. J. S. G. T.

Thermostats. A. TIAN (*J. Chim. Phys.*, 1923, 20, 132—166).—A general discussion on the erection of thermostats. A method is described whereby a thermostat having several ranges may be constructed. J. F. S.

Critical Quantities. W. HERZ and EBERHARD NEUKIRCH (*Z. physikal. Chem.*, 1923, 104, 433—450).—The authors record a number of determinations of critical temperature, density, and pressure. These include the following: chloroform, $t_c=262.5 \pm 0.2^\circ$, d_c 0.496; diethyl amine, t_c $223.8 \pm 0.2^\circ$, d_c 0.243; triethylamide, t_c $262.2 \pm 0.2^\circ$, d_c 0.257; acetone, t_c $235.6 \pm 0.2^\circ$, d_c 0.252; methyl sulphide, t_c $229.0 \pm 0.2^\circ$, d_c 0.301; ethyl bromide, t_c $230.8 \pm 0.2^\circ$, d_c 0.507; *n*-butyl alcohol, p_c 48.4 ± 0.5 atm.; pyridine p_c 60.0 ± 0.5 atm., phenol, p_c 60.5 ± 0.5 atm.; *o*-cresol, p_c 49.4 ± 0.5 atm.; *p*-cresol, p_c 50.8 ± 0.5 atm.; ethyl bromide, p_c 61.5 ± 0.5 atm.; monomethylaniline, p_c 51.3 ± 0.5 atm. The values have been used for testing some of the numerous formulæ connecting these values with other physical properties. J. F. S.

Thermal Data relating to Condensed Hydrogen. FRANZ SIMON and FRITZ LANGE (*Z. Physik*, 1923, 15, 312—321).—A comparatively simple form of thermostat for attaining, by the use of liquid hydrogen, temperatures down to 9° abs. is described, and its application to determine thermal data relating to liquid and solid hydrogen detailed. The authors find that the molecular heat of solid hydrogen can be expressed in terms of the absolute temperature by means of a single Debye function, taking $\beta\nu=91$, the limit of error being $\pm 1.5\%$. The result indicates that solid hydrogen must be considered thermally as monatomic. Within the same limit of error, the molecular heat of liquid hydrogen between 15° and 19° abs. is expressed in terms of the absolute temperature T by $0.33+0.206T$. The molecular heat of fusion is $28.0 \pm 0.1_5$ cal., and the molecular heat of evaporation of liquid hydrogen between 14° and 20° abs. is represented by $219.7-0.27(T-16.6)^2 \pm 1.1$ cal. J. S. G. T.

The Chemical Constant of Hydrogen. FRANZ SIMON (*Z. Physik*, 1923, 15, 307—311).—Thermal data relating to solid hydrogen determined by Simon and Lange (cf. preceding abstract) are applied to calculate the value of the chemical constant of hydrogen. The value so calculated for C is $-1.11_1 \pm 0.030$ which leads to the value $C_0(=C-1.5 \log M)-1.56_7 \pm 0.030$, which is in close agreement with the theoretical value, $C_0=-1.588$. Values of the vapour pressure of solid hydrogen in cm. of mercury between 7° and 13.94° abs. are calculated by means of the formula $\log p = -\frac{40.123}{T} + 2.5 \log T - \frac{1}{4.571} \int_0^T \frac{E(91)}{T^2} dT + 5.30 + 10^{-10}T^6 + 3.67 \times 10^{-11}T^7 + 0.7700$, where T is the absolute temperature and $E(91)$ the Debye function taking $\beta\nu=91$. J. S. G. T.

Influence of Surface Tension on Melting and Freezing. ERNST RIE (*Z. physikal. Chem.*, 1923, 104, 354—362).—A theoretical paper in which, after a general survey of the influence of surface tension on the melting and freezing points, it is shown that the thermodynamic investigations of Pavlov (A., 1909, ii, 19, 295; 1910, ii, 1033) on this subject are untenable. The influence of surface tension on the melting point has been developed thermodynamically, and formulæ have been deduced showing the change in melting point. One of these has the form $T_K - T_0 = 2S_{2,3} \cdot T_0 / s_3 q r$, where T_K is the melting point when the surface tension is taken into account, T_0 when the surface tension is neglected, $S_{2,3}$ is the free energy per unit surface at the interface liquid solid, s_3 is the density of the solid phase, q , the latent heat of fusion, and r the radius of curvature of the solid particle. It is shown that a liquid may be supercooled, but only in exceptional cases may a solid be superheated. The indefiniteness of the melting point of amorphous substances, and particularly of crypto-crystalline substances, is explained by the variation of the size of the particles. A new hypothesis of the structure of glasses is put forward, which differs from that put forward by Tammann ("Metallographie," Leipzig, 1914). The points of difference in the two hypotheses are discussed, and an experimental method of deciding between the two hypotheses is indicated.

J. F. S.

Theory of Electrolytes. Lowering of the Freezing Point and Related Phenomena. P. DEBYE and E. HÜCKEL (*Physikal. Z.*, 1923, 24, 185—206).—A mathematical paper in which the authors discuss the physico-chemical properties of electrolytes in connexion with the theory of electrolytes. Among other results, the following statements are arrived at. 1. For all electrolytes in low concentrations the percentage divergence of the lowering of the freezing point from the classical value is proportional to the square root of the concentration. 2. If the dissolved molecule dissociates into $v_1 \dots v_s$ ions of different kinds with valencies $z_1 \dots z_s$, then for dilute solutions the percentage divergence of the lowering of the freezing point from the classical value is proportional to a valency factor w , where $w = (\sum v_i z_i^2)^{3/2} / (\sum v_i)^{3/2}$. 3. For dilute solutions, the percentage divergence of the lowering of the freezing point from the classical value is inversely proportional to the three halves power of the dielectric constant of the solvent. These three statements represent limiting conditions. The authors are of the opinion that their calculations fully confirm the hypothesis that the strong electrolytes are completely ionised in solution.

J. F. S.

Fused Salts. II. W. HERZ (*Z. Elektrochem.*, 1923, 29, 274—276; cf. A., 1922, ii, 739).—Using Stefan's formula for the internal pressure of a liquid expressed in terms of the latent heat of evaporation and the specific volume of the liquid, values are deduced for the respective internal pressures of the fused halide salts of lithium, sodium, potassium, rubidium, and caesium. The values range from 7,650 atmospheres in the case of rubidium iodide to 59,800

atmospheres for lithium fluoride. Cæsium iodide is the only exception to the rule that the value of the internal pressure decreases with increase of atomic weight of either the alkali or halide constituent of the salt, the value in this case being too high to conform with the rule. Values of the diameters of molecules of the respective fused salts, calculated by means of Ostwald's formula, range from 0.23×10^{-8} cm. in the case of lithium fluoride to 0.56×10^{-8} cm. for cæsium bromide. The values, generally, are of the order of one-half or one-third those calculated by Lorenz. The product of the coefficients of thermal expansion of the fused salts and their respective boiling points on the absolute scale is very approximately a constant. Values of the respective critical pressures of the fused salts calculated by the application of Walden's formula (A., 1909, ii, 547) must be regarded only as lower limits, as molecular association occurs in the fused salts. J. S. G. T.

Vapour Pressure and Density of Sodium Chloride Solutions.

W. R. BOUSFIELD and C. ELSPETH BOUSFIELD (*Proc. Roy. Soc.*, 1923, [A], **103**, 429–443).—Standard values of the respective vapour pressures and densities of aqueous solutions of sodium chloride at 18° are given for the whole range of possible concentrations, viz., 0–26% of sodium chloride by weight. P denoting the percentage of sodium chloride, p the vapour pressure of water at 18° , taken as 15.383 mm. of mercury, and δp the lowering of vapour pressure due to solution of sodium chloride, the authors find: for $P = 26.05$ to 22.45 , $\delta p/p = 0.0363 + 0.00694P + 0.0001434P^2$; for $P = 22.45$ to 14.90 , $\delta p/p = 0.0263 + 0.0016P + 0.0002576P^2$; for $P = 14.90$ to 6.92 , $\delta p/p = 0.0051 + 0.00437P + 0.0001666P^2$; for $P = 5.55$ to 1.40 , $\delta p/p = 0.00613P + 0.000012P^2$. The values of the density, P_{18} , of the solutions at 18° are given by the relation $P_{18} = 0.99862 + 0.007112P + 0.0000168P^2$, correctly to within ± 0.00002 . A simple method, for the determination of approximate values of the molecular weights of substances, based on the result that for values of P between 1 and 5%, the values of $\delta p/p$ and of P are nearly proportional to $\delta \rho$ is described.

J. S. G. T.

Polysaccharides. XIX. The Heats of Combustion of the Carbohydrates. P. KARRER and W. FIORONI (*Helv. Chim. Acta*, 1923, **6**, 396–401; cf. A., 1922, i, 1119).—The heat of combustion of lactose has been redetermined, and the value found, 3948 cal., agrees well with those for maltose (3949), cellobiose (3944), and sucrose (3945). The values found for lactose acetate (4466) and for sucrose octa-acetate (4472) agree well with the calculated value, 4465, for the octa-acetates of the disaccharides. The heat of combustion of anhydrous galactose found, 3720 to 3723.8, is about 20 cal. lower than the values for dextrose and lævulose, possibly on account of the difficulty of obtaining it quite free from water. The value found for galactose penta-acetate (4422.5) is, however, practically identical with that of glucose penta-acetate (4424.5). The heat of combustion of lævoglucoantriacetate, 4530.5, agrees well with the value calculated from that of lævoglucoan, 4533.

Glucose- $\alpha\beta$ -anhydride-3:5:6-triacetate gave the value 4594.8, in accordance with the rule that α -anhydrides have higher heats of combustion. The heat of combustion of glucosan should show whether or no it is an α -anhydride, but attempts to obtain it in a pure crystalline condition suitable for the work by the dehydration of dextrose were not successful. The heats of combustion do not support the opinion of Haworth and Law (T., 1916, 109, 1314) that l  vulose and sucrose contain an ethylene oxide group.

The heat of combustion of rhamnose is 4379 cal.; rhamnose triacetate, 4654.8 cal. (calc. 4643); arabinose, 3731 cal.; xylose, 3735 cal.; xylan, 4242.8 cal.; xylan diacetate, 4548 to 4535 cal. The value for xylan calculated from xylose is 4260 cal. and from xylan diacetate 4266 cal., so the value found is evidently too low, probably on account of impurity in the xylan used for the determination. E. H. R.

Free Energy and Heat of Formation of Zinc Iodide. T. J. WEBB (*J. Physical Chem.*, 1923, 27, 448—454).—With the object of determining the heat of formation of zinc iodide and with the further object of testing the Nernst heat theorem, the author has measured the *E.M.F.* of the cell $\text{ZnHg}(10\%)|\text{ZnI}_2(\text{sat})||\text{AgI}|\text{Ag}$ at 25° and 18°. The decrease of the free energy and the temperature coefficient of the free energy have been calculated from the *E.M.F.* measurements. The *E.M.F.* of the cell is found to be 0.39872 volt at 25° and 0.39938 volt at 18°, and the temperature coefficient -0.000094 volt/degree, which gives the value 19.7 Cal. as the heat of the reaction $\text{Zn} + 2\text{AgI} = \text{ZnI}_2 + 2\text{Ag}$. Since the heat of formation of two molecules of silver iodide is 30.2 Cal., the heat of formation of zinc iodide is 49.9 Cal. A direct calorimetric determination of the heat of formation of zinc iodide has been carried out and the value 49.8 Cal. obtained. The heat of solution of zinc iodide is found to be 11.6 ± 0.3 Cal. J. F. S.

The Heat of Formation of some Isomorphous Mixtures of Organic Compounds. N. N. NAGORNOV (*J. Russ. Phys. Chem. Soc.*, 1919, 51, 301—310).—The heats of formation of the following pairs of organic compounds which are known to form isomorphous mixtures were determined: chlorocinnamaldehyde and bromocinnamaldehyde; *p*-dichloro- and *p*-dibromo-benzenes; and *p*-dichloro- and *p*-chloriodo-benzenes. The method of investigation consisted in observing the difference in the heat of solution in benzene of the isomorphous mixtures (prepared by melting together the components and subsequently powdering the fused mass) and ordinary mixtures of the compounds in question. It is shown that these isomorphous mixtures, like those of inorganic salts, are produced with absorption of heat which is least in the first pair of substances, the mixture of which shows a liquidus curve above the straight line joining their melting point (K  ster, A., 1892, 396); it is greatest in the third pair of substances the mixture of which shows a liquidus curve passing through a minimum below the melting point of the more fusible component (A., 1911, i, 27). The system naphthalene-*m*-dinitrobenzene

which forms a definite compound was also investigated, and it is shown that when the components are melted together in the correct proportions the heat of solution of the product differs from that of a mechanical mixture; the compound is, however, completely dissociated in benzene solution; the heat of formation of the compound is -165 cal. The system naphthalene-*p*-dibromobenzene, which merely forms a eutectic corresponding with 40% naphthalene, was investigated for comparison; the formation of the eutectic is found to be unaccompanied by any absorption of heat.

G. A. R. K.

Some Density Determinations. A. C. EGERTON and W. B. LEE (*Proc. Roy. Soc.*, 1923, [A], 103, 487—499).—The accuracy of the Archimedes method of determining densities is increased by using certain mobile and heavy organic liquids such as ethylene dibromide and carbon tetrachloride, which reduce air-bubble difficulties and damping. The respective boiling points, at 760 mm. pressure, of ethylene dibromide and carbon tetrachloride were found to be $131.65 \pm 0.1^\circ$ and $76.7 \pm 0.1^\circ$. The following values were found for the density of ethylene dibromide at the various temperatures specified: 15.68° , 2.188632; 16.26° , 2.187440; 16.87° , 2.186211; 17.33° , 2.185210; 17.79° , 2.184333; 18.29° , 2.183243; 18.95° , 2.181847; 19.51° , 2.180750. The results are probably correct to within 0.000005. Corresponding results for carbon tetrachloride were obtained as follows: 15.67° , 1.60258; 16.10° , 1.60182; 16.49° , 1.60100; 17.15° , 1.59982; 17.75° , 1.59834; 18.26° , 1.59753; and are probably correct to 0.00005. A method of preparing a sample of lead or cadmium suitable for the determination of density, and involving filtering, casting, and heating the metal in a vacuum is described. From nine determinations on three different samples of metal, the density of lead at 20° was found to be 11.3437, correct to 1 part in 100,000 parts. Values of the density of uranium lead, determined at 16.3° , were 11.2957 and 11.2962, corresponding with an atomic weight of the metal equal to 206.26. The value of the density of cadmium was found to be influenced by the treatment the metal had undergone. Values determined at 16.3° ranged from 8.6435 to 8.6557. Values, consistent to within 1 part in 20,000, were obtained by employing 1.5 g. of the metal.

J. S. G. T.

The Pressure of Gaseous Mixtures. I. MASSON and L. G. F. DOLLEY (*Proc. Roy. Soc.*, 1923, [A], 103, 524—538).—With a view to determine the validity or otherwise of the laws of additive volumes and pressures in the case of binary mixtures of gases, the authors have investigated the isothermal behaviour at 25° of mixtures of ethylene, argon, and oxygen at pressures up to 125 atmospheres. The results indicate that the volume of an argon-ethylene mixture is usually markedly greater than the sum of the separate volumes, all being measured at the same pressure. The maximum relative difference occurs at a mixture-pressure of about 75 atmospheres. With a fixed mixture-pressure there is a

particular molecular ratio for which the difference attains a maximum positive value. This optimum ratio depends on the mixture-pressure and varies between about 75 and 45 molecules of ethylene%. Mixtures rich in ethylene and measured at the higher pressures approach the additive volume more nearly and eventually the volume-differences become negative. In the case of argon-oxygen mixtures, a very small positive difference in total volume is found. When oxygen is mixed with ethylene, the volume differences are slightly larger than those occurring in the case of argon-ethylene mixtures. In the case of argon-ethylene mixtures rich in ethylene and under high pressures, the total pressure is greater than the sum of those of the constituents taken separately. At moderate densities, where the mixtures are less rich in ethylene or under lower pressures, the pressure of the mixture is less than the additive value. In the case of argon-oxygen mixtures, the deviations from the additive value of the pressure are much smaller than those characterising the ethylene-argon mixtures, and their sign is that of a cohesion effect, tending towards an upper limit. With oxygen-ethylene mixtures, the deviations of pressures approximate to those of the corresponding argon-ethylene mixtures. The maximum decrease from the additive value occurs at an optimum molecular composition of 50—60% of ethylene. The results indicate that whilst both the law of additive volumes and the law of additive pressures are invalid, the former is the more inaccurate. The latter fails because it neglects the fact that the space in which each gas is enclosed is already partly filled by molecules of the other, and because no allowance is made for the mutual attraction between molecules of one constituent and those of the other. The attractions of oxygen and argon molecules for ethylene molecules are substantially the same. Assuming that internal pressure or cohesion in a gas of moderate density is due partly to the formation of molecular aggregates of varying complexity, the authors conclude that at the ordinary temperature these complexes are in reversible equilibrium with their original constituents. Regarded from the point of view of the current electronic theory of molecular structure, it would appear that molecular cohesion between any two gases would be that of the gas or gases of the argon group the electronic configurations of which the gases simulate. J. S. G. T.

The Viscosity of Lubricating Oils at Low Temperatures.

MASATOSHI OKOCHI and MASAICHI MAJIMA (*Rikwagaku Kenkyujo Ihd*, 1923, 2, 23—37).—The viscosity was measured by passing the oil through a glass capillary (10 cm. long) by the aid of suction or of compressed air, at temperatures varying from 27° to -18°. From the data, the viscosities were calculated by the formula: $\eta = \pi R^4 / 8 V l \cdot (P_e - P_i)$, where R = radius of the capillary, V = volume of oil flowing through the capillary, l = length of the capillary, and P_e and P_i = pressures of the oil at the exit and entrance of the capillary. The results were given in tables and diagrams. The oils used for the investigation were as follows: (1) rape seed-, (2) gingell-, (3) refined rape seed-, (4) camellia-, (5) mobile-,

(6) soja bean-, (7) spindle-, (8) whale-, (9) olive-, and (10) machine-oils, (11) petroleum, (12) liquid paraffin, and some mixtures. The increase of viscosity owing to the decrease of temperature is almost expressed by hyperbola; the formula $\eta = (a/T - b)^{1/\alpha}$ is proposed, where α , a , and b are constants. The values of η calculated from the formula are almost identical with the experimental figures. But in (2), (6), and (8), they do not coincide at low temperatures, and some critical temperatures were observed, due to the formation of solid particles. The increase of η of petroleum by lowering the temperature is very small, and η with other oils is decreased by addition of petroleum.

K. K.

Sorption Capacity of Carbon. J. B. FIRTH (*J. Soc. Chem. Ind.*, 1923, 42, 242—244T).—The author has investigated the sorptive power and catalytic activity of carbon prepared in various ways. Six different varieties of carbon were prepared and examined. (1) Sucrose was carbonised at as low a temperature as possible and the product purified; (2) material obtained as above was heated in a vacuum for two hours at 600°; (3) material as in (1) was heated at 900° for two hours in a vacuum; (4) a solution of 100 g. of sucrose in 100 c.c. of water was mixed with 50 g. of zinc chloride in 100 c.c. of water, evaporated to dryness, and carbonised. The material was purified with hydrochloric acid and washed until all chloride had been removed, dried, and heated in a vacuum at 600° for two hours; (5) fifty g. of zinc chloride were melted and 100 g. of sucrose slowly added; the resulting carbon was purified; (6) fifty g. of pure kieselguhr were made into a paste with a concentrated solution of sucrose, dried, and carbonised. The six forms were then treated with 25 c.c. of *N*/10-iodine solution and the amount sorbed determined after five minutes, thirty minutes, two hours, and twenty-four hours. The results show that the activity is much improved by heat treatment and by the mixing with kieselguhr and zinc chlorides. The catalytic activity of varieties (1), (2), and (3) was compared by measuring the decomposition of hydrogen peroxide at 18° in the presence of these substances. The results show that the catalytic activity is increased by heat treatment and that the activity gradually decreases as the reaction progresses. On keeping, the activity of the carbon appears to decay, and the decay becomes more permanent the longer the carbon is preserved. The increased activity is attributed by the author to the breaking down of complex carbon molecules into something simpler and so increasing the attractive force.

J. F. S.

Adsorption by Activated Sugar Charcoal. II. F. E. BARTELL and E. J. MILLER (*J. Amer. Chem. Soc.*, 1923, 45, 1106—1115; cf. A., 1922, ii, 741).—The hydrolytic adsorption of sodium picrate, ammonium picrate, sodium eosin, and ammonium eosin by ash-free sugar charcoal, and the relative adsorption of a number of acids and bases by the same adsorbent has been determined, and finally the change in the hydrogen-ion concentration of a number of aqueous solutions of salts due to adsorption has also been

determined. It is shown that the adsorption of acid dyes is accompanied by considerable hydrolysis and liberation of alkali hydroxide, which remains in solution. Ashless sugar charcoal does not adsorb the strong inorganic bases. The adsorption of a salt of a strong base and a readily adsorbed acid results in hydrolysis and the liberation of the free base. The effect on adsorption of the substitution of hydroxyl and amino-groups in organic acids has been investigated, and it is shown that the introduction of the hydroxyl group decreases the adsorption of the acid to a more or less marked extent, depending on the nature of the acid into which it is introduced. The introduction of the amino-group decreases the adsorption of the acid, the extent also depending on the nature of the acid into which it is introduced. The effect of the amino-group is considerably greater than that of the hydroxyl group. A number of the conflicting results of other investigators have been reproduced by means of neutral, activated, ash-free charcoal and an explanation of their causes has been advanced. J. F. S.

Adsorption of Silver Salts on Silver and Gold Surfaces.

E. G. RUDBERG and H. VON EULER (*Z. Physik*, 1923, **13**, 275—283; cf. this vol., ii, 13).—The amount of silver-ion adsorbed per square metre of surface reaches a maximum at a silver-ion concentration about 0.03 *N*. The silver is possibly attached to the silver surface according to the equation $\text{Ag} + \text{Ag}^+ = \text{Ag}_2^+$. The amount of adsorption is independent of temperature, and is the same from aqueous as from alcoholic (96%) solutions. No detectable adsorption was observed when the metals were placed in dilute solutions of sodium sulphate or sulphuric acid. Ammonium thiocyanate is adsorbed by an oxidised silver surface, but not by a clean surface. Probable values for the diameter of the adsorbed silver-ions are discussed (cf. this vol., ii, 13). W. E. G.

The Adsorptive Power of Aluminium Hydroxide. I and II.

H. VON EULER and ELSA ERIKSON (*Z. physiol. Chem.*, 1923, **128**, 1—8, 9—13).—Aluminium hydroxide prepared according to the method of Willstätter and Racke (*A.*, 1922, i, 823) does not absorb sucrose at p_H 6.5. Less than 1% of leucine is adsorbed by 3.3 g. of aluminium hydroxide from a 0.08/*N*-solution of that amino-acid of p_H 5.4—9.0. The adsorption of nucleic acid depends on the p_H and varies from 0.61 g. of sodium nucleate per 1 g. of aluminium hydroxide at p_H 3.5 to 0.33 g. at p_H 7.6. At a p_H 5.7, the adsorption of phosphate is not complete within twenty-six hours. The adsorption reaches a maximum at p_H about 3.2, when 0.426 g. PO_4 is absorbed per 1 g. of aluminium hydroxide. At p_H 4.9, 0.401 g. is adsorbed and at p_H 2, 0.330 g. W. O. K.

Negative Adsorption. III. Action of Gelatin on Sodium Chloride Solution. M. A. RAKUSIN and TATIANA GÖNKE. **IV. Action of Gelatin on Acids.** M. A. RAKUSIN and TATIANA GÖNKE. **V. Action of Agar-agar on Ammonium Chloride Solution.** M. A. RAKUSIN. **VI. Action of Gelatin on Aqueous Ethyl Alcohol.** M. A. RAKUSIN and TATIANA GÖNKE (*Biochem. Z.*, 1923, **137**, 341—355).—Aqueous solutions of a variety of sub-

stances acting on air-dry gelatin increase in concentration as shown by density determinations. Some gelatin passes into solution, but the main effect is attributed to negative adsorption. More exact investigation of the action of sodium chloride on gelatin shows that the actual concentration of chloridion falls off, the increased density being due to gelatin. Similarly, five organic and four inorganic acids exposed to gelatin show a falling off of titre. The falling off of the concentration of ammonium chloride solution when exposed to agar-agar containing 19% of water is due to dilution by the water of the agar-agar. When air-dried gelatin was exposed to aqueous alcohols containing more than 40% of alcohol there was no change of density of the solutions, but weaker solutions increase in density through solution of the gelatin.

H. K.

Osmotic Pressure. I, II, and III. MICHAÏL KIRIANOVITSCH LEVAT-EZERSKI (*J. Russ. Phys. Chem. Soc.*, 1920, **51**, 231—241, 241—244).—II. Two formulæ are deduced for the osmotic pressures of solutions—Schiller's formula, $P=(p_0-p)s/\sigma$, where P is the osmotic pressure, p_0 and p are the vapour pressures of the solvent and the solution, respectively, and s and σ the relative volumes of the vaporised solvent and the solution, respectively, and Kistiakovski's formula (*A.*, 1899, ii, 730), $P=p_0v_0/\sigma_0\ln \cdot p_0/p + p-p_0$, where v_0 and σ_0 are the relative volumes of the vaporised and liquid solvent, respectively, and l and n are constants. These formulæ are shown to approximate very closely to each other at low concentrations. Experimentally-determined values for the osmotic pressures of sucrose solutions are in good agreement with those calculated from Schiller's formula, up to 70 atmos.; but no similar agreement exists for solutes other than sucrose. A simple linear relation exists between the osmotic pressure of a solution and the depression of freezing point produced by the solute, the osmotic pressure being 11·898 atmospheres for each degree of depression of freezing point of water by the addition of sucrose. For electrolytes, this relation is modified, and the osmotic pressure is then given by the formula $P=P_{\text{calc.}}t_{\text{exp.}}/t_{\text{calc.}}$, where $P_{\text{calc.}}$ is the osmotic pressure calculated for non-electrolytes, $t_{\text{calc.}}$ the depression of freezing point calculated from the formula $t=Em/M$, and $t_{\text{exp.}}$ the depression of freezing point found experimentally. Osmotic pressures of aqueous solutions of sodium chloride, nitrite, and hydroxide, and calcium chloride calculated from this formula agree well with experimental values.

III. The importance of the relation between osmotic pressure and depression of freezing point of aqueous solutions, $P=11\cdot9\delta$, where P is the osmotic pressure in atm. and δ the depression in degrees, and the desirability of obtaining similar relations for other solvents, are pointed out. It is surmised that the factor 11·9 is connected with the latent heat of liquefaction of ice, and it is shown that the accepted molecular depression for water (1·86), if divided into the molecular volume (22·4 l.) gives a value differing only by 0·14 from the above factor.

R. T.

Thermodynamics of Activity and Osmotic Coefficients.

NIELS BJERRUM (*Z. physikal. Chem.*, 1923, **104**, 406—432).—A theoretical paper in which several forms of the Gibbs's differential equation between the affinities of the components of a mixture have been put forward. It is shown that these may be deduced in a simple direct manner from the second law of thermodynamics. The main point of Gibbs's equation is stated as follows. The work required to transform a finite quantity of a mixture into one which differs from it to an infinitely small extent is infinitely small. From this statement, the various forms of Gibbs's equation may be directly deduced. The different possibilities in defining the activity coefficient f and the osmotic coefficient ϕ are pointed out and emphasised. The method of deduction and the limits of applicability of the equation $1 + cd \log_e f / dc = \phi + cd\phi / dc$, previously deduced (A., 1919, ii, 9), are discussed and it is shown that this equation is applicable up to the highest concentration when the concentration, C , is expressed in g. mols. per litre of solvent. Similar equations for solutions of several substances are deduced. If f_i and f_k are the activity coefficients of the components S_i and S_k and c_i and c_k their concentrations, then $\delta f_i / \delta c_k = \delta f_k / \delta c_i$. The significance of this equation for the deduction of equations for ionic activity coefficients is pointed out and illustrated by examples. It is further shown that it is possible to resolve the osmotic pressure into a number of osmotic partial pressures, and osmotic coefficients can be deduced for each component of a solution of several substances exactly as is the case with the activity coefficients. It is shown to be impossible to determine the partial osmotic pressures by means of semi-permeable membranes. J. F. S.

Mutual Solubility of Liquids. I. Mutual Solubility of Ethyl Ether and Water. II. Solubility of Water in Benzene.

ARTHUR E. HILL (*J. Amer. Chem. Soc.*, 1923, **45**, 1143—1155).—The author describes two new methods for the determination of the mutual solubility of liquids in one another. The first method depends in the application of the phase rule to the volumes obtained by mixing the two liquids in two different ratios by weight, in two separate experiments at the same temperature. If m and m' are the weights of the first component used in the two experiments, x is its concentration in g. per c.c. at equilibrium in the upper phase in both experiments, and y its concentration in the lower phase. If now a and a' are the measured volumes of the two upper phases at equilibrium and b and b' those of the lower phases, then it follows that $ax + by = m$ and $a'x + b'y = m'$, so that x and y , the concentration of the first component in g. per c.c., is known in each phase by solving the two equations. If now n and n' , the weights of the second component, are used instead of m and m' in the equations, the concentrations of this component in the two phases are also known. By adding together the weight of each component in 1 c.c. of a given phase, the density of that phase at once follows, and consequently the mutual solubility in g. per gram can be calculated. This method is carried out in a double

flask, the lower bulb of which has a capacity of 100 c.c. or 300 c.c. and the upper bulb of 300 c.c. or 100 c.c. The two bulbs are connected by a tube 1 cm. diam. of 5 c.c. capacity graduated in 1/10 c.c., and the upper flask has a graduated neck of the same type. Suitable volumes of the liquids are placed in the flasks and shaken at the required temperature, allowed to settle, and the volumes measured. Using this method, the mutual solubility of ether and water has been determined at -3.83° , 0° , 10° , 15° , 20° , and 25° , with the following results: ether layer contains 1.409% of water at 30° , 1.338% at 25° , 1.264% at 20° , 1.240% at 15° , 1.164% at 10° , 1.078% at 0° , and 0.978% at -3.83° . The water layer contains 5.340% of ether at 30° , 6.027% at 25° , 6.896% at 20° , 7.913% at 15° , 9.040% at 10° , 11.668% at 0° , and 12.752% at -3.83° . The second method, whilst not so generally applicable, can nevertheless be used for many pairs of liquids. The method depends on the solubility of silver perchlorate in many organic solvents; this solubility is much increased by the presence of traces of water in the solvents. The method consists in making a curve of the solubility of silver perchlorate in a given organic solvent which contains known amounts of water and then saturating that solvent with water and determining the solubility of the perchlorate in the saturated solution and deducing the solubility of water in the solvent from the curve. The solubility of water in organic solvents is much increased by the presence of silver perchlorate so that the reference curve can be drawn far beyond the water concentration represented by the solution saturated with water. This method has been applied to the determination of the solubility of water in benzene and the following results have been obtained: 5.4° , 0.034%, 15.0° , 0.054%, 25° , 0.073%, 37.5° , 0.115%, 50° , 0.156%, 57.5° , 0.185%, 65° , 0.230%, and 69.5° , 0.265%. J. F. S.

A Critical Solution Temperature for Solids in the Binary System Ammonium Chloride-Manganous Chloride Dihydrate. FREDERICK WILLIAM JEFFREY CLENDINNEN and ALBERT CHERBURY DAVID RIVETT (T., 1923, 123, 1344—1351).

Binary Critical Solution Temperatures as Criteria of the Purity of Acetic Acid. DAVID CHARLES JONES (T., 1923, 123, 1374—1384).

Ternary Critical Solution Temperatures as Criteria of Liquid Purity. DAVID CHARLES JONES (T., 1923, 123, 1384—1395).

Molecular and Crystal Symmetry. JOHN W. EVANS (*Nature*, 1923, 111, 740); G. SHEARER and W. T. ASTBURY (*ibid.*, 740—741).—Comments on, and a reply to Barker's note (this vol., ii, 388). A. A. E.

The Abnormal Reflection of X-Rays by Crystals. GEORGE L. CLARK and WILLIAM DUANE (*Proc. Nat. Acad. Sci.*, 1923, 9, 131—135).—Further details are given of the X-peak reflections, characteristic of one of the chemical elements in the crystal examined

(cf. A., 1922, ii, 483). The value for the wave-lengths producing these peaks is obtained by determining the critical voltage below which the reflections do not occur. For potassium iodide, this voltage corresponds with the critical voltage for the *K*-series of iodine. Some of these reflections obey the law $n\lambda = 2d \sin \theta$ (cf. following abstract). Others, however, are reflected abnormally and do not obey this law. The peaks for these reflections are smaller than the normal *X*-peaks, and there are always two of these, on the two sides of the peak representing reflection from the 100 planes and at equal angles from it. The same is true for the 010 planes and the 001 planes. No adequate explanation has yet been found for this peculiar reflection in the *X*-peak.

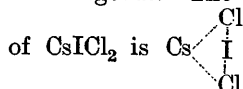
W. E. G.

The Reflection by a Crystal of X-Rays Characteristic of Chemical Elements in it. GEORGE L. CLARK and WILLIAM DUANE (*Proc. Nat. Acad. Sci.*, 1923, 9, 126—130).—By the method previously described (preceding abstract) the *X*-rays characteristic of caesium, iodine, and bromine have been identified. These rays produced by the excitation of atoms in crystals obey the law $n\lambda = 2d \sin \theta$. By the critical voltage method, the 100 and 110 planes of potassium iodide yield values characteristic of iodine which agree very closely with the true values. With the tri-iodide the same kind of iodine spectra have been obtained. Assuming the wave-lengths corresponding with the peaks, the distance between the iodine planes may be calculated from the equation $n\lambda = 2d \sin \theta$, and it is shown that the original unit cube of KI with $d = 0.3532 \text{ \AA}$. has expanded to an edge length of 0.470 \AA . For caesium, four orders of characteristic caesium peaks appear, together with the values for I_α and I_β , and it becomes possible to analyse separately the space distributions of both the caesium and iodine atoms. d_{010} for caesium is 0.643 \AA ., and for iodine 0.1609 \AA .; hence planes containing iodine atoms are one-fourth as far apart as those containing caesium atoms. From the similar results obtained for other planes it is deduced that the crystal unit for CsI_3 is a rectangular parallelepiped with caesium atoms at the corners, and iodine atoms at the centre and equidistant along the body diagonal. CsIBr_2 has also been investigated with similar results.

W. E. G.

The Significance of the Experimentally Determined Crystal Structures of the Alkali Polyhalides. G. L. CLARK (*Proc. Nat. Acad. Sci.*, 1923, 9, 117—122).—A *résumé* of the previous work on the polyhalides (cf. Clark and Duane, A., 1922, ii, 483, also preceding abstracts, and Wyckoff, A., 1923, ii, 311). The crystal structures of polyhalides, KI_3 , CsI_3 , CsIBr_2 , CsICl_2 , have now been determined, and, in spite of the fact that three crystallographic systems are represented, the atoms are arranged in the same manner in unit parallelepipeds in all four cases. The metal atoms occupy the corners of the cell, and the halogen atoms, positions inside the cell on the body diagonal with the heaviest atom in the centre. The structure is closely related to the simple halide unit cube, the dimensions being changed, and the cubic symmetry

destroyed. The halogen atoms constitute a singly acting group just as truly as they do in the formation of complex ions in solution. The stability of the polyhalides is directly proportional to the atomic volumes of the metals. Thus the polyhalides of sodium do not exist, and only the polyiodide of potassium is stable. From the size of the unit cell, it is shown that the atoms in the I_3 group are considerably flattened in the direction parallel to the cell diagonal. The nearest approach to a mechanical formulation



W. E. G.

The Properties of some Silver Organosols. JOHN KENNETH GILES and CYRIL SEBASTIAN SALMON (T., 1923, 123, 1597—1608).

The Protective Action of Potassium Oleate on Gold Sols in Water-Alcohol Mixtures. ERIC KEIGHTLEY RIDEAL and LOUIS LEIGHTON BIRCUMSHAW (T., 1923, 123, 1565—1570).

The Theory of Gels. IV. SAMUEL CLEMENT BRADFORD (*Biochem. J.*, 1923, 17, 230—239).—Granules composing jellies of gelatin and agar are spherites. These gelatin spherites give the shadow-cross in polarised light. The author concludes that the forces which hold gelatin and agar in solution are the same as those that operate between other solutes and solvents, and that the setting of jellies of the natural emulsoids is merely a process of crystallisation.

S. S. Z.

Purification of Liquids by the Simultaneous Action of Centrifugal Force and an Electrical Field. ALFRED MARX and JEAN ROZIÈRES (*Compt. rend.*, 1923, 176, 1396—1398).—No satisfactory method of separating from a liquid a colloid held in suspension has been devised either in the nature of centrifugal or electrical action. By a combination of these two methods, the authors have effected complete separation in a short space of time, employing a potential difference of 40,000 volts and a speed of 2700 revolutions per minute. Details of the apparatus and methods of working are given, together with some observations which indicate the efficiency of the process.

H. J. E.

The Swelling of Agar-agar. FRED FAIRBROTHER and HAROLD MASTIN (T., 1923, 123, 1412—1424).

Relation of Hydrogen-ion Concentration to the Flocculation of a Colloidal Clay. RICHARD BRADFIELD (*J. Amer. Chem. Soc.*, 1923, 45, 1243—1250).—The amount of electrolyte necessary to flocculate colloidal clay has been determined in the case of hydrochloric, sulphuric, phosphoric, acetic and citric acids, potassium chloride, and dipotassium phosphate. The hydrogen-ion concentration of the solutions in which flocculation took place has been determined both electrometrically and by the indicator method. The results show that with the exception of citric acid the acids flocculate the clay at about the same Sørensen value,

but with citric acid a greater acidity was necessary. Changes in the Sørensen value from 6.2 to 8.0 increased the electrolyte requirement ten times in the case of mixtures of potassium chloride and hydroxide. Further increases in alkalinity were without effect. Dipotassium phosphate mixtures showed a similar variation in flocculating power with changes in hydrogen-ion concentration. The phosphate curves differ, however, from the chloride curves in three respects, namely, the break occurs in more acid mixtures, the amount of electrolyte required is greater, and the curve shows a second minimum in alkaline mixtures. The general results indicate that the flocculating power of potassium salts is strongly influenced by the nature of the anion, even when they are compared at the same Sørensen values. Secondary reactions appear to be responsible.

J. F. S.

Equilibrium of Steam in the Presence of Iron and Tungsten and Oxides of these Metals. LOTHAR WÖHLER and R. GÜNTHER (*Z. Elektrochem.*, 1923, 29, 276—285).—The authors have investigated the equilibrium of iron and steam in the presence of the respective phases Fe/FeO, FeO/Fe₃O₄, and Fe₃O₄/Fe₂O₃, employing both the process of oxidation and of reduction to attain equilibrium. Below 570°, the authors find, in agreement with the results of Reinders and van Groningen (*A.*, 1922, ii, 153) and of Chaudron (*A.*, 1921, ii, 584) that the value of the equilibrium constant K_2 for the phases Fe₃O₄/FeO is the same as the value of K_3 for FeO/Fe. The quadruple point of the system Fe/FeO/Fe₃O₄/O₂, below which FeO is unstable and decomposes into Fe and Fe₃O₄, is therefore about 570°. The equation of the reaction isochore for the three systems is deduced in the general form $\log K = C - Q/4.571T$, where Q denotes the respective heats of reaction. Combining these equations with the equation representing equilibrium in the dissociation of steam, expressions are deduced representing equilibrium in the dissociation of the various iron oxides. Similarly, expressions are derived for the respective oxygen pressures in the case of the three phases at various temperatures and approximate values calculated for the respective heats of oxidation of the oxides. Values of the *E.M.F.* of oxidation cells employing the phases FeO/Fe and Fe₃O₄/FeO, calculated by the formula $E = 0.0002T \log (p_1/p_2)/4$, agree closely with the experimental values found by Treadwell (*A.*, 1917, ii, 117). Conditions are detailed under which the reduction of ferric oxide to pure ferrous oxide by means of a mixture of steam and hydrogen in which the H₂O/H₂ ratio lies between the value of K_2 for Fe₃O₄/FeO and of K_3 for FeO/Fe may be effected. Below 560°, the reduction of Fe₃O₄ proceeds directly to metallic iron. A method of preparing pure tungsten dioxide and pentoxide respectively is described, and the equilibrium constants of steam and the respective phases WO₃/W₂O₅, W₂O₅/WO₂ and WO₂/W are determined. The equations of the respective reaction isochores are given by $\log K_1 = -1375/T + 2.235$ for WO₃/W₂O₅; $\log K_2 = -1000/T + 1.218$ for W₂O₅/WO₂; and $\log K_3 = -1904/T + 1.554$ for WO₂/W. Equations are deduced for the equilibrium

dissociation of the various oxides, and values calculated for the respective oxygen pressures at various temperatures in the case of these as for the iron oxides. J. S. G. T.

The Theory of Acid-Alkali Solution Equilibrium as Applied to Salts of Moderately Strong but Sparingly Soluble Acids. EDMUND BRYDGES RUDHALL PRIDEAUX (T., 1923, 123, 1624—1634).

Mixed Crystals and Double Salts: A Comparison of Systems Containing Water, Ammonium Chloride, and a Chloride of Manganese, Iron, Cobalt, Nickel, or Copper. ALBERT CHERBURY DAVID RIVETT and FREDERICK WILLIAM JEFFREY CLENDINNEN (T., 1923, 123, 1634—1640).

Velocity of Chemical Reactions. J. A. CHRISTIANSEN and H. A. KRAMERS (*Z. physikal. Chem.*, 1923, 104, 451—471).—A theoretical paper in which an hypothesis of unimolecular gas reactions is developed on the basis of an activation of the reacting molecules by the absorption of radiation. J. F. S.

The Propagation of Flame from a Spark in a Closed Tube through a Homogeneous Inflammable Mixture. OLIVER COLIGNY DE CHAMPFLEUR ELLIS (T., 1923, 123, 1435—1452).

The Formation of the Explosive Wave. P. LAFFITTE (*Compt. rend.*, 1923, 176, 1392—1395).—The distance traversed by the flame in a mixture of oxygen and carbon disulphide vapour before the starting of an explosion wave depends on the diameter of the tube and the author's experimental results, recorded photographically, are shown in the form of a diagram based on these two factors. The formation of an explosive wave may be advanced or retarded by variations in the composition of the mixture; when these exceeded 1% a change in the experimental values was observed. If the interior of the tube is not perfectly smooth, the transformation from combustion to explosion occurs considerably earlier, usually at the point where the irregularity ceases. H. J. E.

Catalytic Combination of Ethylene and Hydrogen in the Presence of Metallic Copper. Measurements of Reaction Velocity and Adsorption Isotherms at 0° and 20°. ROBERT N. PEASE (*J. Amer. Chem. Soc.*, 1923, 45, 1196—1210).—The kinetics of the catalytic combination of hydrogen and ethylene in the presence of metallic copper has been investigated at 0° and 20°, and measurements of the velocity of reaction and the adsorption isotherms have been made. It is found that within limits, the velocity increases with the hydrogen concentration but decreases as the ethylene concentration is increased, the particular relation being $\Delta P = KV''_{H_2(\text{total})} \cdot (V_{\text{Sat.}} - V_{C_2H_4(\text{ads})})$, in which ΔP is the decrease in pressure from the fifth to the fifteenth minute; $V_{H_2(\text{total})}$ is the initial volume of hydrogen; $V_{\text{Sat.}}$ the saturation capacity of the catalyst surface for ethylene; $V_{C_2H_4(\text{ads})}$ the volume of ethylene adsorbed. For the copper catalyst most completely investigated,

$n=0.8$ and $V_{\text{Sat.}}=9.30$ c.c. The expression $V_{\text{H}_2}^n \cdot (V_{\text{Sat.}} - V_{\text{C}_2\text{H}_4(\text{ads})})$ is taken to be proportional to the adsorption of hydrogen in the presence of ethylene. The temperature coefficient of the reaction velocity has been found to be 1.62 for 10° rise between 0° and 20° . It is pointed out that this effectually disposes of the possibility of diffusion playing a dominant part in the process. The similarity between the conclusions drawn in the present work as to the kinetics of the ethylene-hydrogen combination and those of Armstrong and Hilditch as to the catalytic hydrogenation of unsaturated organic liquids is pointed out (A., 1920, ii, 102, 364, 422, 423, 608; 1921, ii, 582; 1922, ii, 41, 756, 757). J. F. S.

Catalytic Decomposition of Hydrogen Peroxide in a Bromine-Bromide Solution, and a Study of the Steady State.

WILLIAM C. BRAY and ROBERT S. LIVINGSTON (*J. Amer. Chem. Soc.*, 1923, 45, 1251—1271).—It has been shown that in acid solution hydrogen peroxide oxidises bromide to bromine and reduces bromine to bromide, and these two reactions can take place independently in the same solution. When the rates of these two compensating reactions are equal, the effective action is the catalytic decomposition of hydrogen peroxide. This constitutes a "steady state" in which the concentrations of bromine, bromide, and acid remain constant in a given experiment. At the steady state, the rate of decomposition of the peroxide in the dark at 25° in sulphuric acid solutions of concentration above $0.2N$ is represented by the equation $-d[\text{H}_2\text{O}_2]/dt = K[\text{H}_2\text{O}_2] \cdot [\text{H}^+] \cdot [\text{Br}^-]$. At the steady state, the functional equation, $R = [\text{Br}_2]/[\text{H}^+]^2 \cdot [\text{Br}^-]^2$, is shown to hold for sulphuric acid concentrations below N , where R is a constant having the value 0.20. The value of R increases slightly with decreasing temperature, but decreases to a very small value when the reaction mixture is exposed to sunlight. Definite evidence that the catalyst is completely accounted for by the two compensating reactions is obtained by measuring the rate of each at a distance from the position of the steady state. The results of these determinations agree closely with those predicted from the steady state-data and the assumption of a kinetic or rate-determining mechanism involving hypobromous acid. The ratio of the specific reaction rates of the two reactions is equal to R , and at the steady state each reaction accounts for half the peroxide decomposed. $\text{H}_2\text{O}_2 + 2\text{Br}^- + 2\text{H}^+ \rightarrow \text{Br}_2 + 2\text{H}_2\text{O}$; $\text{H}_2\text{O}_2 + \text{Br}_2 \rightarrow \text{O}_2 + 2\text{Br}^- + 2\text{H}^+$. The possibility of choosing catalysts by means of free-energy data is discussed and some examples of the method of calculation are given. A method is described for the volumetric estimation of hydrogen peroxide in the presence of bromide, which is as follows. To the aqueous solution enough water is added and then sulphuric acid to make the volume about 150 c.c. and the acid concentration 0.3–0.5*N*. Then, immediately and rather rapidly, potassium permanganate solution is added until a distinct pink colour remains for two to three seconds. (An excess of 1.0–3.0 c.c. of 0.1*N*-permanganate is recommended.) The solution is stirred vigorously, a moderate excess of potassium iodide solution added, and after waiting a short

time, but in no case longer than a minute, the liberated iodine titrated with thiosulphate. The method is shown to be accurate to within 0.2—0.3%. J. F. S.

Decomposition of Potassium Perchlorate and its Catalysis by Ferric Oxide. CARL E. OTTO and H. SHIPLEY FRY (*J. Amer. Chem. Soc.*, 1923, 45, 1134—1142).—The rate of decomposition of potassium perchlorate both alone and in the presence of ferric oxide as catalyst has been determined for various amounts of catalyst at temperatures ranging from 450° to 600°. The results show that the reaction is unimolecular and takes place according to the equation $\text{KClO}_4 = \text{KCl} + 2\text{O}_2$. During the reaction the particles of ferric oxide catalyst increase in size fivefold. There is no evolution of chlorine either in the presence or absence of the catalyst. The velocity coefficient is in keeping with the law of Arrhenius over the range investigated. With ferric oxide as catalyst, the increase in the velocity coefficient at constant temperature is proportional to the weight concentration of the catalyst. The expression $(K_c - K_0)/C$ varies with the temperature in keeping with Arrhenius's law. The above-mentioned results indicate that the addition of the catalyst does not accelerate the reaction already proceeding, but that a concomitant reaction occurs which involves the catalyst, probably in the formation of an intermediate compound, whilst the original reaction proceeds with unchanged velocity. The total velocity is the sum of the velocity of uncatalysed reaction and that of the reaction due to the catalyst. Only the velocity of the latter reaction is influenced by the concentration of the catalyst. This deduction is possible because the decomposition reaction velocities of the catalysed and the uncatalysed decompositions are of the same order of magnitude. From this point of view, an expression like that of Arrhenius has been developed, by which the velocity coefficient under any condition of temperature and concentration of catalyst can be calculated. The expression has the form $K = C \cdot 10^{A/T+B} + 10^{A_0/T+B_0}$, where $A = -10587$, $B = 11.5679$, $A_0 = -13246$, and $B_0 = 14.0348$. J. F. S.

Oxidation of Copper and the Reduction of Copper Oxide by a New Method. W. G. PALMER (*Proc. Roy. Soc.*, 1923, [A], 103, 444—461).—The rate of oxidation of copper and the rate of reduction of the oxide formed have been studied in the case of a film of copper about 0.001 mm. thick, by continuous determination of the electrical conductivity of the film. It is shown that the oxidation process is not controlled by the rate of diffusion of oxygen into the film. At any definite temperature, the rate of oxidation in the presence of oxygen is proportional to the square root of the pressure of oxygen, up to about 300 mm., and the value of dR/dt is constant, R denoting the resistance of the film at time t . At higher pressures, the rate of oxidation is independent of the pressure. It is assumed that oxygen condenses on the copper as single atoms and that at pressures above 300 mm. the film is completely saturated with atomic oxygen. In the case of the oxidation of copper reduced from oxide at 150°, cuprous oxide first formed begins to be oxidised

to cupric oxide at about 165° . Above 190° , cuprous oxide is again formed, as the rate of oxidation of the latter does not change rapidly with temperature. Metal prepared by reduction at 200° gives rise at all temperatures to cupric oxide only. Results obtained by the oxidation of copper in the presence of hydrogen and of carbon monoxide together with oxygen indicate that the catalytic formation of water or carbon dioxide on the copper increases abnormally the number of copper atoms in a state to be oxidised when brought into contact with an oxygen atom. Initially, the action of the reducing gases is restricted to a slow reduction to metal of oxide already formed, the purely catalytic production of water or carbon dioxide commencing later. It is probable that increased oxidation is most pronounced when the amount of adsorbed reducing gas is comparable with or even exceeds the amount of oxygen on the film. In the case of the reduction of copper oxide by carbon monoxide, the rate of reduction is proportional to the amount of copper in the film and independent of the amount of oxide. When reduction is effected by hydrogen, in general the rate of reduction decreases very rapidly to a low value, although much oxide may be still unreduced. Reduction may be restarted by exhausting and admitting another sample of gas until the pressure is the same as formerly. In this case, the variation of R with t is expressed by the relation $dR/dt = K''R - c'$, where K'' and c' depend on the pressure of hydrogen. c' is the velocity constant of the condensation of water on reduced metal. K'' and c' vary in the same direction when the pressure of hydrogen is altered.

J. S. G. T.

The Theory of Ionisation accompanying Combination as the Basis of the Ionic Theory, as deduced from Investigations of the Nature of Non-ionised Acids. A. HANTZSCH (*Z. Elektrochem.*, 1923, 29, 221—246).—Various experimental data, *e.g.*, the velocity of inversion of sucrose and the rate of decomposition of diazo-acetic esters by undissociated acids, the determination of the strengths of undissociated acids by means of indicators, and the effect of solvents on the degree of acidity, are critically examined in order to elucidate the nature of the process of solution of an electrolyte, more especially in the case of strong undissociated acids. In contradistinction to the ordinary form of the ionic theory which attributes acidity to the presence of ionised hydrogen atoms, and the electrolytic theories proposed by Bjerrum and by Lorenz in which chemical activity is likewise associated with the non-ionised portion of a strong electrolytic solution, the author considers that the ionising effect of water, more especially in the case of the so-called strong acids, is to be explained on purely chemical lines. The author differentiates between true acids containing ionisable hydrogen and having the formula $X\langle\overset{O}{\parallel}\rangle H$, which are chemically active, and in their optical properties resemble salts, and pseudo-acids containing hydroxyl hydrogen, having the formula $O:X\cdot OH$ or $OX\cdot OH$. The latter are passive as regards acidity and optically resemble esters. A similar classification is suggested in

the case of salts. Generally, true acids are defined as heteropolar hydrogen compounds containing ionisable, active, combined hydrogen which may be directly substituted by strongly positive metals or complex kations without alteration of structural constitution and without appreciable change of optical properties. Their respective strengths are to be determined by reference to their tendencies towards salt formation in the undissociated state, or by the relative stabilities of their respective salts. They form with water or in aqueous solution hydroxonium salts which are relatively weaker acids owing to their comparative instability compared with the free acid. Pseudo-acids are homöopolar hydrogen compounds containing hydrogen atoms which do not exercise an acid function, and, in the case of oxy-acids, are linked with oxygen in the form of hydroxyl. By addition of water, this hydrogen is transformed either partly or wholly into hydroxonium-ions, and the transformation is accompanied by a change of structural constitution and consequently by a change of optical properties. In aqueous solutions, therefore, both forms of acid react qualitatively in the same manner.

J. S. G. T.

Chemical Reactivity. I. Mechanism of the Formation of Valerolactone. W. H. GARRETT and W. C. MCC. LEWIS (*J. Amer. Chem. Soc.*, 1923, 45, 1091—1102).—The mechanism of the change hydroxyvaleric acid \rightarrow valerolactone has been studied at 25° and 35° in the presence of various concentrations of hydrochloric acid and also in the presence of lithium chloride, potassium chloride, and sucrose, which acted as water displacing agents. It is shown that the reaction is bimolecular, the process actually measured being the rate of effective collision between the suitably activated hydroxyvaleric acid molecules and the hydrogen-ions. A characteristic bimolecular constant is obtained at a given temperature, which is not altered by change in concentration of the catalyst, or by the presence of sucrose, potassium chloride, or lithium chloride in the reaction mixture. This constant involves the activities of the reactants, and also the viscosity of the solution raised to a power characteristic of the hydrogen-ion. This power is not a constant, but varies with the relative size of the individuals in the solution, as determined independently from electrical conductivity measurements. There is a sharp contrast in behaviour between the water of hydration of sucrose, on the one hand, and that of potassium and lithium chlorides, on the other, in respect of the effect on the hydroxyvaleric acid molecule. The water of hydration of sucrose is not available as solvent, whereas that of the neutral salts is available. In none of these cases, however, is hydrogen-ion soluble in water of hydration. The point is considered, but no definite conclusion is drawn. The true critical increment of the reaction is found to be 127,500 cal./mol. of hydroxyvaleric acid transformed. This value is considerably less than the corresponding value obtained on the assumption that the reaction is unimolecular, the difference being 3000 cal./mol. The unimolecular critical increment has, however, no real significance for the process actually measured, which is definitely shown to be bimolecular.

J. F. S.

Promotion of Catalytic Reactions. I. SAMUEL MEDSFORTH (T., 1923, **123**, 1452—1469).

Catalysis of Oxygen-Hydrogen Mixtures by means of the Platinum Metals. K. A. HOFMANN (*Ber.*, 1923, **56**, [B], 1165—1172; cf. A., 1922, ii, 276, 490).—It is found that the rate of combination of hydrogen and oxygen under the catalytic influence of the metals of the platinum group (except iridium) depends largely on the previous treatment of the catalysts. Previous treatment with hydrogen weakens their catalytic activity, possibly because of the formation of stable hydrides of smaller reducing and electromotive power. Treatment with oxygen increases their activity possibly because of the formation of an unstable oxide which is easily reduced, thus exposing fresh surfaces of active metal to the gas mixture. If, however, this unstable oxide, either by prolonged exposure to the gas, or by anodic polarisation, is converted to the permanent stable form, then a diminution of catalytic activity is observed.

The case of iridium, however, is quite different. The catalytic potential of the iridium surface towards the oxy-hydrogen mixture is almost exactly the mean (+0.42 volt) between that of the hydrogen electrode (zero) and that of iridium saturated with hydrogen towards pure oxygen (+0.82 volt). The iridium catalyst is therefore practically electrically neutral towards this mixture, and previous treatment with either gas has no effect on its catalytic activity. It is also found that the acidity or alkalinity of the medium containing the iridium is without effect on the velocity of reaction between the hydrogen and oxygen. H. H.

Hydrogenation. E. J. LUSH (*J. Soc. Chem. Ind.*, 1923, **42**, 219—223r).—Nickel turnings, oxidised electrolytically by making them the anode in the combination $\text{Ni}|5\%\text{Na}_2\text{CO}_3\text{ solution}|\text{Ni}$, and subsequently reduced in hydrogen, form a very satisfactory catalyst in the hydrogenation of oils. Such freshly reduced catalyst contains sufficient adsorbed hydrogen to effect considerable hardening even in absence of free hydrogen. The surface layer alone is active; but the mass of nickel appears to act as a hydrogen reservoir. The catalyst remains active for long periods, and may be reactivated by extraction with trichloroethylene. The results of some experiments on the hydrogenation of linseed, soja-bean, olive, and cotton-seed oils are given. E. E. T.

The Calculation of Atomic Weights. KARL FEHRLE (*Z. Physik*, 1923, **13**, 264—267).—A theoretical paper continuing previous work on ideal and experimental atomic weights (cf. A., 1920, ii, 303, 540). A formula is deduced for the change in experimental atomic weight with atomic number. W. E. G.

An Explanation of the Theory of the Rotation of the Atomic Nucleus. II. HERBERT HENSTOCK (*Chem. News*, 1923, **126**, 321—325; 337—340; cf. this vol., ii, 400).—The application of the author's theory to elements of the groups of the periodic system, taken in order, is discussed and illustrated with diagrams. Par-vol. CXXIV. ii. 18

ticular interest attaches to the boron hydrides, in which the boron atoms are supposed to form a chain (B_4H_{10}) or a ring (B_6H_{12} and $B_{10}H_{14}$) in which alternative negative and positive atoms are, respectively, ter- and quinque-valent. When ammonia combines with hydrogen chloride, the nucleus of the nitrogen revolves, and it becomes positive in alternative polarity and the hydrogen atoms become negative; the fourth hydrogen unites with the nitrogen by a normal "edge" and with the chlorine by an electrovalence at one of its positive "edges." In hydrazine, the two nitrogen atoms are, respectively, positive and negative, and the molecule is unstable because the positive nitrogen is combined with hydrogen by negative edges. Nitrogen trichloride is unstable because the normally negative nitrogen is united with chlorine along negative edges. The structures of a number of other compounds are discussed on similar lines. E. H. R.

The Phase Relationships in the Bohr Atomic and Molecular Models. M. BORN and W. HEISEN (*Z. Physik*, 1923, **14**, 44—55).—A theoretical paper in which it is shown that between the movements of the electrons in one and the same atom there must exist phase relationships. Bohr has pointed out this possibility in an explanation of the doublet of orthohelium. It is shown for each atom in the normal condition that the whole system of electronic paths is exactly in phase. Only the relationships in a simple case are studied, where it is possible to follow the reduction of the independent periods. The number of independent quantum phase integrals is not diminished during the process. Some of the principal difficulties of the application of the quantum theory are discussed. W. E. G.

The Application of the Quantum Theory to Atomic Structure. I. Postulates of the Quantum Theory. NIELS BOHR (*Z. Physik*, 1923, **13**, 117).—A summary of the postulates of the quantum theory in which it is sought to present a comprehensive theory of atomic structure which will reconcile the formal nature of the quantum theory with the laws of classical electrodynamics. In the application of the quantum theory to a closed atomic system, there are two fundamental postulates. The first postulate requires that any durable change in the motion of an enclosed system shall consist in a complete transference from one stationary condition to another. The second postulate characterises the relation between the energy exchange between an atom and an electromagnetic field, and states that the emission of radiation consists of a series of pure harmonic waves of which the frequency γ is given by the frequency condition $h\nu = E' - E''$, where E' and E'' are the energies of the atom in the initial and final stationary conditions. Both these postulates necessitate a sharp break with the classical laws of electrodynamics. The relationship between the first postulate and these laws is given by the adiabatic principle of Ehrenfest. This requires that the conditions for the stationary state are of such a kind that they fix certain properties of the motion of the system, which do not change during an adiabatic transformation when the

motion is determined with the help of the ordinary electrodynamic laws. It is shown that sharply-defined stationary states must be present in the atom, and this requirement may be designated as the principle of the existence and permanence of the quantum number. The classical laws may be applied to the radiation process with certain limitations determined by the "correspondence" principle. The light quantum hypothesis of Einstein is not suitable for the presentation of a picture of the problems raised by the quantum theory, but the application of the Planck heat radiation law to the emission and absorption processes is more satisfactory. Emphasis is laid on the importance of the adiabatic and correspondence principles for the further extension of the quantum theory of atomic structure.

W. E. G.

The Model of the Helium Atom. H. A. KRAMERS (*Z. Physik*, 1923, **13**, 312—341).—A theoretical investigation of the Bohr helium model. The simplest form of this model, in which the electrons move in single quantum orbits about the nucleus as centre, is obtained when the electrons move in the same orbit. This model of the normal condition of the atom gives too high a value for the ionisation potential, and is not in agreement with the spectroscopic experiments of Paschen, or the electron-collision experiments of Franck. In this paper, the model chosen to represent the normal condition of the atom is that where the two electrons move in single quantum orbits in planes which make an angle with one another. It is shown that the energy content of this atom is about 3.9 volts too large and the model in a mechanical sense is unstable. The bearing of these results on the relationship between the classical laws of electrodynamics and the Bohr theory is discussed, and it is concluded that even in the simple model of helium with two identical electrons the mechanical laws have lost their validity, and it is doubtful if the energy function calculated from these laws can be expected to agree with the physical energy derived from spectral terms and from ionisation potentials.

W. E. G.

The Normal Paths of the Series Electrons of the Alkalis. A. TH. VAN URK (*Z. Physik*, 1923, **13**, 268—274).—The deviation of the *s*-term quantum number from whole numbers has been ascribed by Schrödinger (*Z. Physik*, 1921, **4**, 347) to the penetration of the inner shells of the atom by the series electrons. This work has been extended, and more accurate calculations have been made of the deviations due to this cause for the alkali metals. They range from +0.74 for sodium to +2.74 for caesium. Lithium, sodium, and potassium give total quantum numbers for the sharp subordinate series of 2, 3, and 4, respectively; for rubidium it is probably 5, and for caesium 5 or 6.

W. E. G.

The Stability of Atomic Nuclei, the Separation of Isotopes, and the Whole Number Rule. WILLIAM D. HARKINS (*J. Franklin Inst.*, 1923, **195**, 553—573; cf. this vol., ii, 145).—Elements with odd atomic weight and isotopic number but with an even atomic number are rare atomic species. A condition for the

existence of these species is that isotopes with the same isotopic number should occur in at least one of the adjacent elements with lower or higher atomic number. This rule indicates the existence of an isotope of zinc with the isotopic number 7. The elements with odd isotopic numbers are discussed with the aid of a diagram. Attention is directed to the group p_2e , which may be of fundamental importance in atom building, since the formula for any element may be represented as $(p_2e)_M(pe)_N$. A separation of 0.1 unit has been effected in the isotopes of mercury. Photographs are given of the tracks of α -particles through nitrogen gas. The method of separation of gases applied by Hertz to helium and neon, the diffusion of a gas through a moving stream of another gas, is discussed with reference to isotopes, and it is shown that the rate of production of the light fraction decreases logarithmically as the separation in terms of atomic weight increases arithmetically. The theory of the separation by fractionation and the loss in value in collecting finite fractions instead of infinitesimal diffusate fractions is further considered. The time taken to produce a given change in the atomic weight of zinc is $1/28$ of that necessary with mercury.

W. E. G.

The Light Elements and the Whole Number Rule. F. W. ASTON (*Nature*, 1923, **111**, 739).—By the use of anode rays of high velocity, it has been shown that the masses of Li^6 , Li^7 , Gl^9 , Na^{23} , Mg^{24} , K^{39} , K^{41} , and Ca^{40} do not diverge from whole numbers in any case as much as 0.1% of the mass measured. Of particular interest is the fact that no difference in mass is detectable between the isobaric atoms Ca^{40} and A^{40} .

A. A. E.

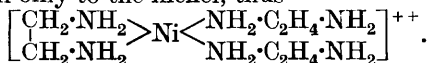
The Electronic Theory of Valency. I. Intramolecular Ionisation. T. MARTIN LOWRY (*Trans. Faraday Soc.*, 1923, **18**, 285—295; *Phil. Mag.*, 1923, [vi], **45**, 1105).—The existence of internal ionisation, as suggested by J. J. Thomson (*A.*, 1914, ii, 450) is postulated in the cases of a number of compounds where the charges on the nuclei are not balanced by the enveloping electrons. A “barb” representing an electrovalency, the following constitutional formulæ are suggested for the respective substances: methylethylaniline oxide, $\text{O} \rightleftharpoons \text{NMeEtPh}$; hydrogen peroxide, $\text{O} \rightleftharpoons \text{O} \begin{smallmatrix} \text{H} \\ \text{H} \end{smallmatrix}$; ozone $\text{O} \rightleftharpoons \text{O}=\text{O}$; hypochlorous acid (non-ionised), $\text{H}-\text{O}-\text{Cl}$. It is shown by reference to the oxy-acids of chlorine, sulphur, phosphorus, silicon, and various dehydrated acids that stability in oxy-acids depends on the presence of a positive charge on the central atom of the ion, which also increases the strength of the acid. The stability of formic acid depends on the existence of the ion $\text{O}=\text{CH}-\text{O}^+$. No significance can now be attached to the conception of “ortho-acids” in which all the oxygen is present as hydroxyl, e.g., $\text{Si}(\text{OH})_4$, $\text{P}(\text{OH})_5$, $\text{S}(\text{OH})_6$, and $\text{Cl}(\text{OH})_7$, as the octet theory imposes a limit of four on the primary covalency of all the lighter elements. Acidity originates in the repulsion between a heavy positive nucleus and the light hydrogen nucleus, and a

maximum of strength and stability is reached in acids containing four atoms of oxygen round the central atom of the iron.

J. S. G. T.

The Electron Theory of Valency Applied to Co-ordination Compounds. C. H. SPIERS (*Chemistry and Industry*, 1923, 42, 534—538).—The author's theory of the structure of co-ordination compounds is similar to that of Lowry (this vol, ii, 313). Lowry's explanation of the reducing action of potassium cobaltocyanide is unsatisfactory; it is due to the complex anion, not to the potassium. His formula for potassium ferrioxalate does not express the different behaviour of the ion and potassium with regard to ionisation. The stability of certain complex ions which exhibit a shortage of electrons may be accounted for on the hypothesis that the innermost pair of electrons, both of the central atom and of the co-ordinated atoms or groups, may be utilised to help the completion of the shell of the central atom (cf. Eastman, A., 1922, ii, 367). This hypothesis reduces the number of complex anions with an incomplete shell to very small dimensions. Thus, out of 32 complex cyanides considered, 26 achieve a complete shell. The utilisation of one inner electron would not appear to be satisfactory; such anions readily gain or lose an electron, for instance, $[\text{Fe}(\text{CN})_6]^{---}$ readily becomes $[\text{Fe}(\text{CN})_6]^{----}$. The assumption that an atom completes its shell to that of the inert gas immediately following is not always correct. Thus titanium in H_2TiO_3 probably completes to 8 instead of 18, uranium in $[\text{UO}_2\text{F}_5]\text{K}_3$ to 18 instead of 32, and copper in $[\text{CuI}_2(\text{S}_2\text{O}_3)_4](\text{NH}_4)_9$ to 32 instead of 18.

The structure of a number of complexes containing ammonia and other nitrogen bases is considered. It is suggested that in ions of the type $[\text{Ni en}_3]^{++}$ two of the diamine molecules are attached by one nitrogen only to the nickel, thus

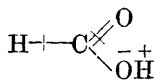
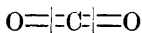
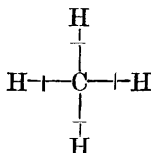


Similar cases arise where the complex contains a dibasic acid residue. The ease with which ammoniacal silver solutions are reduced is accounted for when it is seen that $[\text{Ag}(\text{NH})_2]^+$ has only 16 electrons in its shell even when the two inner electrons are utilised. It readily takes up one electron and decomposes into silver and ammonia. The structure of the oxy-acids of the metals is also discussed. After vanadium these probably complete an 18-electron shell, and this may have something to do with their colour.

E. H. R.

Simplified Method of Writing Electronic Formulæ. ROGER J. WILLIAMS (*J. Amer. Chem. Soc.*, 1923, 45, 1272—1273).—To obviate the confusion which may arise through the use of the same sign to indicate a single link, a negative charge in ionisation and a negative polarity in organic compounds, the author proposes to cross the valency links at the end where there is a positive polarity, the other end of the link obviously representing a negative polarity without any further sign, ionisation being represented as before,

thus avoiding all confusion. Where the polarity is unknown or where there is no desire to represent it, the links are drawn in the usual manner. Examples of the method given are :



J. F. S.

Unification of the Laws of Chemical Combination. E. PUXEDDU (*Gazzetta*, 1923, 53, i, 204—209; cf. A., 1919, ii, 460).—According to the views held by the author, the laws of constant proportions, of multiple proportions, of equivalents, of Gay-Lussac on gaseous compounds, etc., represent nothing but different aspects of a single principle. Balareff's work (A., 1918, ii, 15) is discussed further, and it is pointed out that this author's enunciation of the law of multiple proportions is not an improvement on the older form and is not in accord with the meaning of Dalton's principle. In view of the formulæ of compounds of the protein group, characterisation of the ratios of the weights in which different elements unite with one another as simple is absurd.

T. H. P.

Baeyer Memorial Lecture. WILLIAM HENRY PERKIN (T., 1923, 123, 1520—1546).—A lecture delivered before the Chemical Society on May 10th, 1923.

Inorganic Chemistry.

Active Hydrogen : Its Preparation from Metallic Hydrides.

Y. VENKATARAMAIAH (*Proc. Sci. Assoc. Vizianagram*, 1922, Dec. 6).

—Hydrogen obtained by the decomposition of sodium, potassium, or calcium hydride yields with sulphur traces of hydrogen sulphide.

A. A. E.

Precision Measurement of the Composition of the Constant Boiling Mixture of Hydrogen Chloride and Water. C. W. FOULK and MARION HOLLINGSWORTH (*J. Amer. Chem. Soc.*, 1923, 45, 1220—1228).—The composition of the constant boiling mixture of hydrogen chloride and water has been accurately determined by weighing the silver chloride formed. The following results of the composition of the liquid obtained at various pressures are recorded : 770 mm., 20·197% ; 760 mm., 20·221% ; 750 mm., 20·245% ; 740 mm., 20·269% , and 730 mm., 20·293% . It is shown that the rate of distillation affects the composition to a small extent. The present results are compared with those published by Hulett and Bonner (A., 1909, ii, 342), Morey (A., 1912, ii, 986), and Hendrixson (A., 1915, ii, 797), who give for 750 mm. 20·258% , 20·252% , and

20·253%, respectively, against 20·245% obtained in the present experiments by rapid distillation. J. F. S.

Anhydrous Perchloric Acid. D. VORLÄNDER and ERICH KAASCHT (*Ber.*, 1923, 56, [B], 1162—1164).—The dark reddish-brown colour of the solution obtained by the action of strong sulphuric acid on potassium chlorate is not due entirely to chlorine dioxide, for this substance in solution is at most red or dark yellow in colour. The authors ascribe the dark brown colour to an unstable compound of chlorine dioxide and perchloric acid. Anhydrous perchloric acid saturated with chlorine dioxide at -15° yields a brown, crystalline slurry which melts below 0° , decomposes in ice-water, and is soluble in chloroform to a yellow solution. Neither bromine nor sulphuryl chloride acts on perchloric acid. Dry hydrogen bromide at -15° and hydrogen chloride at -70° are similarly without action. Potassium perchlorate, boric acid, and arsenic can be crystallised from 70% perchloric acid. Attempts to prepare the chloride of perchloric acid by the action of phosphorus pentachloride were unsuccessful, the distilled product always containing large amounts of phosphorus. H. H.

The Ageing of Thiosulphate Solutions. E. ABEL (*Ber.*, 1923, 56, [B], 1076—1079; cf. Hahn and Windisch, A., 1922, ii, 873).—The ageing of volumetric thiosulphate solutions consists in a gradual diminution of activity due to the combined action of atmospheric oxygen and carbon dioxide which is opposed by the increasing alkalinity of the solution followed by a cessation of the change, so that aged solutions are practically constant in their activity under uniform working conditions. It appears to the author that the changes are probably due to the catalytic action of traces of copper. The course of the action is expressed by the schemes: $2\text{Cu}^{++} + 2\text{S}_2\text{O}_3^{--} = 2\text{Cu}^+ + \text{S}_4\text{O}_6^{--}$; $2\text{Cu}^+ + \frac{1}{2}\text{O}_2 \rightarrow 2\text{Cu}^{++} + \text{O}^{\cdot}$; $\text{O}^{\cdot} + 2\text{H}^+ \rightarrow \text{H}_2\text{O}$. The function of the carbon dioxide is to form carbonic acid and thus provide the necessary hydrogen-ions, since otherwise the catalyst would be precipitated and rendered practically inactive by the hydroxyl-ions. Stabilisation of the solutions by addition of alkali (or corresponding compounds which neutralise acids and precipitate copper) is thus satisfactorily explained. The automatic stabilisation of the solutions by ageing is due, not only to consumption of the dissolved carbon dioxide, but also to loss of catalytic activity of the copper.

Attention is directed to the readiness with which traces of copper pass into water which is distilled from copper vessels. It is recommended that the water used for thiosulphate solutions should be distilled in glass vessels, and that due care should be taken to prevent ingress of copper from the laboratory air. Solutions prepared with these precautions maintain their concentration excellently. H. W.

The Viscosity and Molecular Dimensions of Hydrogen Selenide. C. J. SMITH (*Trans. Faraday Soc.*, 1923, 18, 302—307).—The value of the viscosity of hydrogen selenide at $20\cdot0^{\circ}$ is found to be $1\cdot68 \times 10^{-4}$ C.G.S. unit. The value of Sutherland's

constant, C , for the gas, deduced from the empirical relation $C/T_B = a$ constant, for gases of similar constitution and occupying corresponding places in the periodic table, where T_B is the boiling point of the gas on the absolute scale, is 365. The value of the mean collision area of the molecule of hydrogen selenide deduced from these results is 0.86×10^{-16} sq. cm. The series of gases, hydrogen bromide, hydrogen selenide, and arsine have a central atom resembling an atom of krypton, and the increase in the value of the mean collision area of the molecules of these gases on passing from krypton to arsine is to be attributed to the hydrogen nuclei attached to the central atom. As the number of hydrogen atoms in the molecule increases, the distance of each hydrogen nucleus from the centre of the molecule increases at an increasing rate.

J. S. G. T.

Solubilities of certain Metallic Chlorides in Selenium Oxychloride. CLARENCE R. WISE (*J. Amer. Chem. Soc.*, 1923, 45, 1233—1237).—The solubility of a number of anhydrous metallic chlorides in anhydrous selenium oxychloride has been determined. The following solubilities at 25° are recorded: lithium chloride, 3.21%; sodium chloride, 0.57%; potassium chloride, 2.89%; rubidium chloride, 3.56%; caesium chloride, 3.83%; magnesium chloride, 4.96%; calcium chloride, 6.11%; strontium chloride, 5.17%; barium chloride, 3.95%; zinc chloride, 1.10%; cadmium chloride, 0.15%; mercuric chloride, 0.89%; titanium tetrachloride, 0.75%; stannic chloride, 13.73%; arsenic trichloride is miscible in all proportions; antimony pentachloride, 38.64%; manganous chloride, 0.16%; ferric chloride, 23.40%; nickel chloride, 0.15%; and cobalt chloride, 0.17%. Cupric chloride, silver chloride, and lead chloride are less soluble than 0.1%. The solubility is given in terms of 100 g. of saturated solution. The presence of a trace of water makes a great difference in the solubility. This is shown in the case of the solubility of barium chloride, where the following values are obtained for selenium oxychloride containing the number of molecules of water stated per molecule of oxychloride: anhydrous, 3.95%; $\frac{1}{10}$ H₂O, 3.86; $\frac{1}{8}$ H₂O, 3.37; $\frac{1}{4}$ H₂O, 2.32; $\frac{1}{2}$ H₂O, 1.40; 1 H₂O, 0.45. The following double compounds have been isolated during the present work: TiCl₄.2SeOCl₂; SnCl₄.2SeOCl₂; SbCl₅.2SeOCl₂; FeCl₃.2SeOCl₂; KCl.SeOCl₂; RbCl.SeOCl₂; CaCl₂.3SeOCl₂; MgCl₂.3SeOCl₂. Caesium chloride forms a yellow, gelatinous mass which is too indefinite for analysis. None of the other chlorides investigated give double compounds.

J. F. S.

Spatial Distribution of the Valencies of the Tervalent Nitrogen Atom in Connexion with the General Theory of Asymmetry of Molecules and of Optical Activity. A. E. USPENSKI (*J. Russ. Phys. Chem. Soc.*, 1920, 51, 288—295).—The question of the spatial distribution of the valency directions of trivalent nitrogen is discussed, and shown to be definitely settled in the cases of singly and doubly linked nitrogen atoms, but not in the case of nitrogen atoms contained in heterocyclic rings.

R. T.

Peroxidation of Nitric Oxide. II. E. BRINER and G. MALET (*J. Chim. Phys.*, 1923, 20, 173—200; cf. A., 1922, ii, 563).—With the object of clearing up the different views held with regard to the mechanism of the oxidation of nitric oxide, the authors have investigated the range of oxidation below 50% by the method of absorption of the nitrous gases. The retardation of the commencement of the reaction, which is essential if the necessary observations are to be made, has been achieved by operating with very dilute mixtures of nitric oxide and oxygen and the losses which always accompany the absorption of dilute mixtures of nitrous gases have been evaluated by means of correction curves. The absorption curves show that the oxidation takes place continuously and in a single stage, with the formation of nitrogen dioxide. Nitrous anhydride which is found in the products of the reaction is the result of a secondary reaction. When the results are considered kinetically, they show that the reaction is of the third order and must be expressed $2\text{NO} + \text{O}_2 = 2\text{NO}_2$ (N_2O_4). Calculations connected with this process ought therefore to be made with equations suited for reactions of the third order, except in those cases where the excess of oxygen is sufficiently great (at least twenty times the theoretical quantity), and here it is correct to use the simpler equations of second order reactions. This case is realised in the practical problem of the recovery of nitrous gases obtained in the fixation of nitrogen by the electric arc processes. Using these equations, the authors have calculated the absolute velocity constants from the absolute concentrations and the relative velocity constants from the percentage composition. The equation $K = 1/t \cdot x/(b-x)$, where K has the value 0.032 for ordinary temperature and pressure, may be employed for calculating values of technical significance such as the relationship between the amount of oxidation and the temperature, the time necessary to ensure 50% oxidation, and the volume of the chambers necessary to furnish any given amount of oxidation. J. F. S.

Physico-chemical Investigations of the Properties and Electrolysis of Solutions of Alkali Azides. E. BRINER and P. WINKLER (*Helv. Chim. Acta*, 1923, 6, 429—435; *J. Chim. Phys.*, 1923, 20, 201—216).—When an alkaline solution of azoimide is electrolysed pure nitrogen is liberated at the anode, but the quantity obtained is not theoretical, and Peratoner and Oddo (A., 1896, ii, 245) attribute the deficiency to formation of nitric acid. If the formation of nitric oxide could be proved by the interaction of anodic nitrogen and nascent oxygen, this would furnish an argument in favour of the atomic fixation of nitrogen, the atomic nitrogen coming from the decomposition of the N_3 -ion. The formation of nitric acid by the electrolysis of an alkaline solution of an azide has been confirmed. Such a solution evolves much free oxygen with the nitrogen, but the amount of nitric acid formed is very minute. When a neutral azide solution was electrolysed and a stream of oxygen was led into the anodic nitrogen, no nitric oxide was found in the gases, and the amount of nitric acid in

solution was even less than from the alkaline solution. When ozone was used with the oxygen, the nitric acid reaction in the solution became very distinct. When hydrogen was led into the anode chamber very minute quantities of ammonia were formed, but when an aluminium anode was used, causing the formation of nascent hydrogen by solution of the metal in the alkaline liquid, ammonia was formed freely. Only one-third of the nitrogen of the azide is converted into ammonia, the other two-thirds escaping as nitrogen. It may be taken, therefore, that the azoic group decomposes according to the equation $N_3 = N_2 + N$, giving rise to an atom of nascent nitrogen. E. H. R.

Certain Physical Properties of Arsenic Trioxide in Water Solution. ERNEST ANDERSON and LEROY G. STOREY (*J. Amer. Chem. Soc.*, 1923, **45**, 1102—1105).—The density, refractive index, and hydrogen-ion concentration of solutions of arsenious oxide of various concentrations in water have been determined, and preliminary experiments are described on the determination of the amount of the oxide converted into arsenious acid. The following values of d_{25}^{25} are recorded for solutions containing the number of grams stated per litre of solution. 1.796 g., 1.0014; 3.212 g., 1.0025; 5.060 g., 1.0039; 6.425 g., 1.0050; 7.184 g., 1.0057; 8.561 g., 1.0068; 10.13 g., 1.0080; 11.35 g., 1.0089; 12.85 g., 1.0102, and 14.368 g., 1.0013. The density composition curve is a straight line, represented by the equation $\bar{W} = -1288.36 + 1288.39d$, where d is the density and W the number of grams of arsenious oxide per litre of solution. The refractive index, measured by means of an immersion refractometer, also varies in a linear manner with the composition and is represented by $W = -10062.7 + 7550r$, where r is the refractive index at 22°. The solubility of arsenious oxide in water has been determined at 0°, 15°, 25°, 39.8°, 48.2°, 62°, 75°, and 98.5°, and the following values in g. per 100 c.c. of water have been obtained: 0°, 1.21; 15°, 1.66; 25°, 2.05; 39.8°, 2.93; 48.2°, 3.43; 62°, 4.45; 75°, 5.62, and 98.2°, 8.18. The solubility is represented by the equation $W = 1.21 + 0.021t + 0.000505t^2$. Arsenious oxide is least soluble in 3.2*N*-hydrochloric acid (cf. Wood, T., 1908, **93**, 413). Attempts to measure the hydrogen-ion concentration of solutions of arsenious oxide by *E.M.F.* measurements were unsuccessful, owing in all probability to a reduction of the oxide (cf. Gladstone and Tribe, T., 1878, **33**, 306), but using the Sørensen indicator method the value $P_H = 6.6$ was obtained. The molecular weight of arsenious oxide determined in water solution by the ebullioscopic method is 92.5 and by the cryoscopic method 99.17, which appears to indicate that at 0° some form of arsenious oxide is present, possibly $HAsO_2$. J. F. S.

Silicon Hydrides. XV. Trisilane and Chloroform. ALFRED STOCK and PAUL STIEBELER (*Ber.*, 1923, **56**, [B], 1087—1091).—The violently explosive action between the silanes and carbon tetrachloride or chloroform (cf. Moissan and Smiles, A., 1902, ii, 308; Stock and Somieski, A., 1916, ii, 319) is only observed in the presence of oxygen, mere traces of which are sufficient to

induce the change. The rôle of the oxygen has not been elucidated, but its activity does not appear to depend on the initial formation of water.

The reaction between trisilane and chloroform in the molecular ratio 1 : 4·3 has been investigated at 50° in the presence of aluminium chloride (in the absence of the latter, the change proceeds too violently or not at all). Reaction occurs mainly in accordance with the equations: $\text{Si}_3\text{H}_8 + 4\text{CHCl}_3 = \text{Si}_3\text{H}_4\text{Cl}_4 + 4\text{CH}_2\text{Cl}_2$ and $\text{Si}_3\text{H}_8 + 5\text{CHCl}_3 = \text{Si}_3\text{H}_3\text{Cl}_5 + 5\text{CH}_2\text{Cl}_2$. Small quantities of methane and methyl chloride are also produced, whilst a little chloroform remains unattacked. The chlorotrisilanes are mixtures of isomerides. H. W.

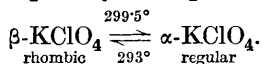
Influence of certain Fluxes on the Transformations of Quartz. N. PARRAVANO and C. ROSSELLI DEL TURCO (*Gazzetta*, 1923, 53, i, 249—257).—The authors have investigated the influence of small proportions of ferric oxide, phosphoric anhydride, boric anhydride, lime, and tungstic oxide on the character of the refractory obtained from quartzite. [Cf. *J.S.C.I.*, 1923, July.]

T. H. P.

A Critical Search for a Heavier Constituent of the Atmosphere by Means of the Mass-spectrograph. F. W. ASTON (*Proc. Roy. Soc.*, 1923, [A], 103, 462—469).—From the results of analysis by the mass-spectrograph of liquid oxygen residues derived from more than 400 tons of air, the author concludes that a gaseous inert element heavier than xenon is certainly not present in air to the extent of 1 part in 10^{15} parts and probably not to the extent of 1 part in 2×10^{16} parts of air by volume. The results do not support Thomson's suggestion of the presence of molecular krypton and xenon in the air (A., 1922, ii, 565). The origin of a faint band corresponding with mass 260 appears to be connected with the presence of xenon, but the connexion is not necessarily a direct one. A faint band corresponding with mass 260 is attributable to a complex molecule of mercury with a multiple charge.

J. S. G. T.

New [Crystalline] Forms of Perchlorates. D. VORLÄNDER and ERICH KAASCHT (*Ber.*, 1923, 56, [B], 1157—1162).—Enantiotropic forms of the alkali perchlorates are described and their transition points determined by microscopic, thermometric, and dilatometric methods. When, for instance, potassium perchlorate is heated to a temperature well below its decomposition point, it changes to a regular, optically isotropic form, thus :



It is found that the transition temperatures of the dimorphous forms of the alkali perchlorates fall, although not in a regular manner, with increasing atomic weight of the metal: NaClO_4 , 308°; KClO_4 , 299—300°; RbClO_4 , 279°; CsClO_4 , 219°; NH_4ClO_4 , 240°. The transition point of the ammonium salt lies between

those of the rubidium and caesium salts, thus coming into line with the other physical properties of ammonium salts.

Thallium perchlorate has a transition point at 266° , and the anhydrous silver salt at $155\text{--}159^{\circ}$, although the latter begins to decompose at the transition point. Silver perchlorate, however, appears to change from a weakly to a strongly doubly refracting form at a temperature between 102° and 110° . The anhydrous perchlorates of lithium, magnesium, calcium, and strontium exist only in one form, this being another example of the similarity between lithium and the metals of the alkaline earths.

Barium perchlorate exists in two forms, which are, however, both optically anisotropic, and are transformed one into the other at 284° . Tetramethylammonium perchlorate exists in rhombic and regular forms, transition point about 350° . Phenyltrimethylammonium perchlorate melts and decomposes before reaching a transition point. Potassium permanganate could not be shown to exist in two forms.

H. H.

The Freezing-point Curve for Mixtures of Potassium Nitrate and Sodium Nitrate. HENRY VINCENT AIRD BRISCOE and WALTER MATTHEW MADGIN (T., 1923, 123, 1608—1618).

The Normal and Acid Sulphates of Sodium. P. PASCAL and ERO (*Mém. Poudres*, 1923, 20, 1—16).—The system $\text{Na}_2\text{SO}_4\text{--H}_2\text{SO}_4\text{--H}_2\text{O}$ was studied. The following salts are in equilibrium with the liquid phase at various concentrations and temperatures: Na_2SO_4 ; $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$; $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$; $\text{Na}_2\text{SO}_4 \cdot \text{NaHSO}_4$; NaHSO_4 ; $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$; $\text{NaHSO}_4 \cdot \text{H}_2\text{SO}_4$; $\text{NaHSO}_4 \cdot \text{H}_2\text{SO}_4 \cdot 1.5\text{H}_2\text{O}$; $2\text{NaHSO}_4 \cdot \text{Na}_2\text{SO}_4$. Below 120° , the solubility of sodium sulphate was determined at different temperatures in sulphuric acid of different concentrations, and the liquid and solid phases were analysed when equilibrium had been attained. Further points on the diagrams were obtained by observing the temperatures at which solid began to be deposited from solutions of known composition. Finally, the form of the isothermals was definitely fixed by thermal analysis. Sodium hydrogen sulphate melts at 185° and its monohydrate at 112° . The salts $\text{NaHSO}_4 \cdot \text{H}_2\text{SO}_4$ and $\text{NaHSO}_4 \cdot \text{H}_2\text{SO}_4 \cdot 1.5\text{H}_2\text{O}$ have no definite melting points. The former is liquid above 107.5° , and the latter at 131° . The salt $\text{NaHSO}_4 \cdot \text{Na}_2\text{SO}_4$ decomposes at 174° , and partly liquefies with deposition of the neutral anhydrous sulphate. Isothermals with 25° intervals are given for this system on a triangular diagram, and a further diagram gives the regions of stability of the various salts enumerated above. Solutions of pure sodium hydrogen sulphate in water can only deposit the normal decahydrate above 4° , whilst at room temperature they can only give the salt $\text{NaHSO}_4 \cdot \text{Na}_2\text{SO}_4$. In order to obtain crystals of the pure hydrogen sulphate it is essential to have a considerable amount of acid in the solution. Certain deposition of the salt NaHSO_4 can only be obtained from 65% sulphuric acid. Compounds of sodium hydrogen sulphate and sulphuric acid are only deposited from sulphuric acid solutions of above 80%. It is impossible to obtain the salt

$\text{NaHSO}_4, \text{Na}_2\text{SO}_4$ from aqueous solution. The processes for obtaining sulphuric acid by the hydrolysis of sodium hydrogen sulphate are reviewed from the point of view of the diagrams obtained. The whole acidity of the sodium hydrogen sulphate can be obtained as sulphuric acid by depositing the decahydrate from comparatively dilute solution with the aid of refrigeration, or the intermediate salt may be deposited from more concentrated solutions without recourse to refrigeration. In the latter case, the whole of the acidity is not recovered as sulphuric acid. The two methods are analysed with the aid of a further triangular diagram. A diagram of the melting points of mixtures of normal sulphate with sulphuric acid is given.

H. C. R.

Preparation of Sodium Metaphosphate at a Low Temperature. PAUL PASCAL (*Compt. rend.*, 1923, 176, 1398—1400).—When prepared by the action of sodium ethoxide on ethyl metaphosphate in presence of ether at $35\text{--}40^\circ$, sodium metaphosphate exhibits properties which differ from those of the polymeride usually described as metaphosphate. The substance obtained in the reaction has a molecular weight which, in dilute solution, tends to the limiting value 51, corresponding with the complete ionic dissociation of NaPO_3 . The constitution of the salt undergoes no change on being heated at temperatures ranging up to 800° . It is pointed out that as ethyl metaphosphate is a hexametaphosphate, $(\text{EtPO}_3)_6$, the reaction involves the breaking-down of a complex.

H. J. E.

The Behaviour of Calcium Oxide towards Water. V. KOHLSCHÜTTER and W. FEITKNECHT (*Helv. Chim. Acta*, 1923, 6, 337—369).—In a previous paper (Kohlschütter and Walther, A., 1919, ii, 342), it was shown that the slaking properties of lime depend to a great extent on the source of the lime, whether it be made from calcium carbonate, oxalate, or hydroxide. These differences are now shown to extend to other properties of lime, so far as these can be measured quantitatively; these include the "looseness" of the powder; the rate of slaking in moist air, when the first mol. of water is absorbed at a linear rate, and a further 0.5 mol. at a gradually decreasing rate; and the volume change when slaking is completed. Further, the rate of slaking in much water, measured calorimetrically by the rate of heat-development, showed similar differences. Samples of lime made from amorphous oxalate and from nitrate, which were exceptionally dense, slaked very slowly. Calcium chloride and sodium chloride in the slaking water accelerate the rate of slaking, whilst sodium acetate, calcium hydroxide, calcium sulphate, and particularly sodium hydroxide have a retarding action which is most marked at the later stages. The influence of the electrolyte increases with its concentration. Milk of lime prepared from quicklime has a greater viscosity and settles more slowly than that prepared from lime first slaked by water vapour.

The above and a large number of other similar observations lead to the conclusion that the characteristic properties of lime are due to the fact that it is a disperse substance formed by topo-

chemical decomposition of a crystalline substance. The primary particles of the product are probably crystalline, but these, owing to the duration of the heating, aggregate to form secondary particles. The formation of hydroxide is also a topochemical change, consequently the character of the hydroxide depends as much as that of the oxide on the source from which it has been obtained. [See also *J.S.C.I.*, 1923, July.] E. H. R.

System Calcium Oxide-Carbon Dioxide. F. HASTINGS SMYTH and LEASON H. ADAMS (*J. Amer. Chem. Soc.*, 1923, **45**, 1167—1184).—An apparatus is described by means of which the pressure-temperature relations in the system calcium oxide-carbon dioxide can be investigated up to 1390° and 1000 megabars pressure. Using this apparatus, equilibrium pressures have been determined which, together with the previously published data obtained by Johnston (A., 1910, ii, 831), define the system experimentally from 587° to 1339° and from 1 mm. to 779,000 mm. pressure. An equation has been deduced which fits the pressure-temperature curve at all points within the limits of experimental error up to the eutectic point for the system calcium carbonate-carbon dioxide. This equation has the form $\log p = -11355/T - 53.88 \log T + 29.119$. The melting point of calcium carbonate containing only 0.38% of calcium oxide is found to be 1339° at 779,000 mm. pressure. This value probably lies very near to the melting point of pure calcium carbonate. The eutectic between calcium carbonate and calcium oxide has been experimentally determined and found to lie at $1240 \pm 1^{\circ}$ at 30,000 mm. ± 300 mm. The composition as judged from microscopic examination is about 50% calcium carbonate and 50% calcium oxide. The heat change, ΔH , for the reaction $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$ is given by $\Delta H = 51990 - 10.71T$, and the values 48800, 45850, 42640, 40500, 38360, and 36210 cal. are calculated for 25° , 300° , 600° , 800° , 1000° , and 1200° , respectively. The free energy change, $-\Delta F$, of the reaction is given by $-\Delta F = 120.136T - 24.670T \log T - 51991$ if the final pressure is one atmosphere, and $-\Delta F = 120.149T - 24.670T \log T - 51991$ if the final pressure is one megabar. It has been shown both from thermodynamic and experimental evidence that only one crystalline form of calcium carbonate exists within the temperature range investigated. J. F. S.

Separation of Isotopes of Zinc. A. C. EGERTON and W. B. LEE (*Proc. Roy. Soc.*, 1923, [A], **103**, 499—515).—Two sets of distillations of pure zinc were carried out in high vacuum under conditions to obtain a slightly different concentration of the isotopes in the final residue of the last distillate. For the determination of densities, the metal was cast in a vacuum and seeded with about 1 mg. of a particular kind of zinc. The first set of distillations gave a residue of slightly increased density, but the distillate was of the same density as the original zinc. The second set of distillations, carried out under improved conditions yielded a residue of increased density (about 1 part in 3,700 parts), and a distillate of decreased density (about 1 part in 3,600 parts). The density

of ordinary zinc at 16.3° , determined from seven samples of the metal prepared as described, was found to be 7.1400 ± 0.0006 . The possibility of attributing the difference of densities to flaws, allotropes, different physical conditions, and impurities is discussed and shown to be improbable. The degree of separation obtained agrees with Dempster's observations of isotopes of weights 64—70, but is less than half what might be found for equal parts of an isotope of mass 64, and of isotopes 66, 68, and 70. J. S. G. T.

Lithopone. I. The Mechanism of the Chemical Reactions occurring in the Blackening of Zinc Sulphide on Exposure to Light. E. MAAS and R. KEMPF (*Z. angew. Chem.*, 1923, **36**, 293—297).—The blackening of lithopone on exposure to light has been shown to be due to the calcined zinc sulphide it contains. The authors examine the various hypotheses put forward to explain the blackening of the latter compound, and discuss them in the light of their own and other experiments. They conclude that the phenomenon is due to the zinc sulphide forming zinc disulphide and finely divided metallic zinc on the surface of the mass. The mechanism of the process, they consider, is the same as that referred by Fajans to the action of light on silver bromide (*Chem. Zeit.*, 1922, **46**, 910). The ultra-violet rays in the light cause the transference of an electron from a negatively charged sulphur-ion on the surface of the crystal lattice of zinc sulphide to a neighbouring positively charged zinc-ion, whereby free uncharged atoms of zinc and sulphur are formed. The zinc appears as finely divided metal, the sulphur atom combines with neighbouring zinc- and sulphur-ions to form zinc disulphide. Amorphous freshly precipitated zinc sulphide not possessing a lattice structure is not sensitive to light; neither is zinc sulphide which has been ground in a mortar, since here the lattice arrangement has been disturbed. Blackened lithopone brightens in the dark owing to oxidation of the metallic zinc, for it remains black if no oxygen is present. T. S. W.

The Vapour Pressure of Lead. I. A. C. EGERTON (*Proc. Roy. Soc.*, 1923, [A], **103**, 469—486).—The vapour pressure of lead has been determined for the range of temperatures 837 — 1045° (abs.) by determining the rate of effusion of the vapour at high vacuum through an orifice of known area. A difference of 2% in the vapour pressure of lead and of uranium lead was observed at 700° , corresponding with no energy term at absolute zero, and in agreement with the $1.5 \log M$ law for the chemical constant (*Phil. Mag.*, 1919, **38**, 178). At temperature T between 600° and 1200° (abs.) the vapour pressure, p , is expressed by the relation $\log p = 7.908 - 9923/T$. The value of the chemical constant of ordinary lead, deduced from what are considered to be the most accurate measurements of vapour pressure, is 1.8 ± 0.2 , agreeing with the theoretical value 1.853 calculated from $1.5 \log M - C_0$, where M = the molecular weight (207.2) and $C_0 = 1.622$ (A., 1920, ii, 84). The calculated value of the heat of vaporisation of lead at absolute zero is $47,000 \pm 1000$ calories. The latent heat of

vaporisation of the molten metal varies very little with temperature up to 1200° (abs.), and is equal approximately to 45,350 cal. A lowering of vapour pressure occurs when lead is heated in a vacuum for long periods under the conditions of the present experiments.

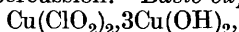
J. S. G. T.

Univalent Thallium in certain Sulphito-salts. G. CANNERI (*Gazzetta*, 1923, 53, i, 182—185).—A number of analogous double sulphites of thallium and bivalent metals of the form $X^{II}(SO_3)_2Tl_2$ have been prepared by passing sulphur dioxide into an aqueous suspension of the hydroxide of the bivalent metal until this is completely dissolved and adding concentrated thallos carbonate solution. In these compounds the bivalent metal functions as co-ordinant and the thallium is situated outside the co-ordinating nucleus. The compounds form microcrystalline powders: *zinc*, pink; *cadmium*, pink; *ferrous*, brick red; *manganous*, white; *nickel*, yellow; *cobalt*, pink.

T. H. P.

The Action of Sodium Hyposulphite on Cupric Chloride in Aqueous Solution. JAMES BRIERLEY FIRTH and JOHN HIGSON (*T.*, 1923, 123, 1515—1519).

Chlorites of Copper and other Metals. GIORGIO RENATO LEVI and C. CIPOLLONE (*Gazzetta*, 1923, 53, i, 200—203; cf. this vol., ii, 421).—*Cupric chlorite*, $Cu(ClO_2)_2$, forms a yellowish-brown precipitate, undergoes rapid change even in a closed vessel, and explodes violently on percussion. *Basic cupric chlorite*,



does not explode when struck. *Potassium cupric chlorite*, $Cu(ClO_2)_2 \cdot 2KClO_2 \cdot 2H_2O$, obtained as a green, crystalline precipitate, explodes on percussion, and forms dark brown concentrated, and green dilute, aqueous solutions. The *double salt*, $CuCl_2 \cdot KClO_2$, is a reddish-brown, stable compound and does not explode on percussion. The *double salt*, $CuCl_2 \cdot NH_4ClO_2$, is similar to the preceding salt. *Rubidium chlorite*, $RbClO_2$; the *double salt*, $CuCl_2 \cdot RbClO_2$; *cæsium chlorite*, $CsClO_2$, which is hygroscopic; the *double salt*, $CuCl_2 \cdot CsClO_2$; *cadmium chlorite*, $Cd(ClO_2)_2 \cdot 2H_2O$, which is very stable and is not exploded by percussion; and *zinc chlorite*, $Zn(ClO_2)_2 \cdot 2H_2O$, which is greenish-yellow and does not explode when struck, have also been prepared.

T. H. P.

Action of Solutions of Alkali Hydroxides on Copper Oxide and on Copper, and the Existence of Salts of Cupric Acid.

H. J. M. CREIGHTON (*J. Amer. Chem. Soc.*, 1923, 45, 1237—1243).—Blue solutions containing copper have been prepared by dissolving cupric hydroxide in concentrated alkali hydroxide, by digesting copper oxide with concentrated solutions of alkali hydroxide at 80—90°, and by electrolysing concentrated solutions of alkali hydroxide between copper electrodes with a high current density at 80—90°. The blue solutions obtained by these methods are identical in their behaviour. The blue substance which is formed when copper oxide is added to molten potassium hydroxide may be the same as the blue component of these solutions. None of

the blue solutions exhibit the characteristic properties of colloidal solutions, particularly those of the solutions of colloidal hydroxide prepared by Ley (A., 1905, ii, 524). Evidence is put forward which indicates that the blue colour of the solutions is due to the presence of an alkali salt of cupric acid. The formation of the salt by the second method can be represented $\text{CuO} + 2\text{OH}' \rightarrow \text{CuO}_2'' + \text{H}_2\text{O}$, and that by the third method by $\text{Cu} + 2\oplus \rightarrow \text{Cu}'' + 4\text{OH}' \rightarrow \text{CuO}_2'' + 2\text{H}_2\text{O}$. The solubility of the alkali cuprates in alkali hydroxides, although quite low, increases rapidly with the concentration of the hydroxide. The potassium salt is apparently more soluble than the sodium salt.

J. F. S.

Revision of the Atomic Weight of Mercury. O. HÖNIG-SCHMID, L. BIRCKENBACH, and M. STEINHEIL (*Ber.*, 1923, 56, [B], 1212—1219).—Mercury was purified by shaking with aqueous mercurous nitrate, then dropping in a fine stream through 1 metre of 5% nitric acid, followed by three distillations in a vacuum, rejecting all but the middle fraction each time. The pure mercury was converted into the chloride or bromide by heating in a quartz vessel in a current of the dry halogen. The mercuric halide thus obtained was twice sublimed and once melted, also in a quartz vessel. Weighed quantities of the halides were reduced in ammoniacal solution by means of halogen-free hydrazine, and the resulting ammonium halide was titrated nephelometrically with silver nitrate. Twelve determinations of the ratio $\text{HgCl}_2 : 2\text{Ag}$ gave $\text{Hg} = 200.61 \pm 0.006$ ($\text{Ag} = 107.88$; $\text{Cl} = 35.457$). Eight determinations of the ratio $\text{HgBr}_2 : 2\text{Ag}$ gave $\text{Hg} = 200.61 \pm 0.00$ ($\text{Br} = 79.916$), mean $\text{Hg} = 200.61$ (see following abstract).

H. H.

The Atomic Weights of Isotopes of Mercury. O. HÖNIG-SCHMID and L. BIRCKENBACH (*Ber.*, 1923, 56, [B], 1219—1221; cf. preceding abstract and A., 1922, ii, 295).—Pure mercury was distilled at a low temperature in a high vacuum, and the atomic weights of the extreme fractions were determined by the method described in the preceding abstract. Light fraction, density 0.999824 (ordinary mercury = 1.000000), atomic weight = 200.564 ± 0.006 ; dense fraction, density 1.000164, atomic weight = 200.632 ± 0.007 .

H. H.

The Arrangement of the Atoms in Crystals of Cinnabar. CH. MAUGUIN (*Compt. rend.*, 1923, 176, 1483—1486).—The reflection of X-rays from the crystal faces was observed and a theoretical consideration of the results obtained shows that no definite conclusion can be drawn until a more exact measure of intensities is available and also some knowledge of the laws of diffraction of X-rays by mercury and sulphur atoms.

H. J. E.

Hydrates and Hydrogels. II. An Aluminium Hydroxide Gel of the Formula $\text{Al}(\text{OH})_3$. RICHARD WILLSTÄTTER and HEINRICH KRAUT (*Ber.*, 1923, 56, [B], 1117—1121; cf. this vol., ii, 167).—The authors have continued the work described in their previous communication on the subject and now describe a method

of preparation of an improved form of hydrogel *C*. The essential condition for the formation of the new variety is the precipitation of an aluminium sulphate solution with a very slight excess of ammonia at 60°. The solution must not be allowed to become more than weakly alkaline, as high concentration of hydroxyl-ion is fatal to success. The gel was obtained free from sulphate as a flocculent, somewhat plastic mass with a faint yellow tinge. It is amphoteric in character, and in contrast with acidic preparations of the gel, adheres strongly to glass surfaces.

It is very easily soluble in acids and in alkalis. In 1% hydrochloric acid, in which the *D*-form is insoluble, it dissolves completely in five minutes on warming, giving a clear solution showing no Tyndall effect. It dissolves immediately in warm 15% hydrochloric acid, and in half an hour in 35% acid. Because of its reactivity, it soon loses its characteristic properties. Storage for three months accompanied by frequent shaking with glass beads renders it insoluble in concentrated hydrochloric acid. After six weeks' contact with 1% ammonia, it becomes insoluble in hot 3% hydrochloric acid, this reagent causing peptisation instead. The composition of the hydrate was determined by drying to constant weight in a vacuum desiccator over phosphoric oxide; the results indicate the constitution $\text{Al}_2\text{O}_3 + 3\text{H}_2\text{O}$. The substance is quite stable in dry air up to 80°, but at higher temperatures it loses water.

The new preparation can be used as a basic absorption medium for enzymes. Towards amylase (pancreatic) and invertase (autolysed yeast) it is nearly as efficient an absorbent as preparation *B* previously described.

H. H.

Chemical Properties of Disperse Substances. Disperse Aluminium Oxide. II. V. KOHLSCHÜTTER and NELLY NEUENSCHWANDER (*Z. Elektrochem.*, 1923, 29, 246—256).—In continuation of previous work (A., 1919, ii, 156), the authors have investigated the chemical properties of disperse aluminium hydroxide prepared from ammonium alum, aluminium sulphate, and basic aluminium acetate, and more especially the dependence of these properties on the mode of preparation of the disperse phase. All varieties of hydroxide were chemically dissolved by strong hydrochloric acid solution, the process of solution being preceded by swelling of the hydroxide. Sols were formed and chemical action occurred when the hydroxide was treated with sufficiently dilute acid. The production of a colloid occurred likewise as an intermediate stage in the process of solution. Whereas aluminium hydroxide was dissolved by strong solutions of sodium hydroxide, a sol was not produced by the action of a dilute solution of the latter. In contradistinction to this result, sols resulted from the action of either acid or alkali on disperse aluminium oxide prepared from fumes of the oxide. Sols resulting from the action of hydrochloric acid were readily differentiated either visually or ultra-microscopically, their respective appearances depending on the mode of preparation of the dried gel. A colloid was not

produced by the action of dilute sulphuric acid on the disperse phase, although a certain amount of chemical action occurred.

J. S. G. T.

Aluminium Antimonides. G. G. URAZOV (*J. Russ. Phys. Chem. Soc.*, 1919, **51**, 461—471).—The system antimony–aluminium has been repeatedly studied and both Gautier (A., 1896, ii, 602) and Campbell and Matthews (A., 1902, ii, 399) conclude that a compound, AlSb, is formed, whilst the former author also suggests the existence of another compound corresponding with 69·27% by weight of aluminium or Al_{10}Sb , owing to a second break in the cooling curves at that point. The existence of the first, but not the second, compound is also confirmed by the microscopic examination of the alloy; this divergence between the results obtained by two different methods is explained by Tammann (A., 1906, ii, 88) by the supposition that the formation of the compound AlSb takes some time and this accounts for the existence of secondary breaks in the cooling curves.

In the present investigation, cooling curves for alloys of aluminium and antimony were constructed, the alloys being kept in the molten state for varying lengths of time. If the observations were made immediately after the contents of the crucible, consisting of equal weights of the components, became homogeneous, three breaks in the curves were observed, corresponding with the separation of AlSb (880°), pure aluminium (653°), and pure antimony (631°), respectively; the latter two phases are not miscible at temperatures near their respective melting points. Keeping the alloy in a molten condition at about 1100° for half an hour is sufficient to ensure the complete interaction of the components and the cooling curve no longer shows a break corresponding with the separation of antimony. The separation of the solid AlSb from an equimolecular mixture takes place at 976°.

A fusibility curve of mixtures of the compound AlSb with aluminium and antimony was constructed and is shown to be of simple character, the compound being unable to form solid solutions with either component; it is also practically insoluble in either component at temperatures near the melting point of the latter.

G. A. R. K.

Atomic Weight of Gallium. THEODORE W. RICHARDS and WILLIAM M. CRAIG (*J. Amer. Chem. Soc.*, 1923, **45**, 1155—1167).—The atomic weight of gallium has been determined by means of the analysis of gallium chloride. The starting material was 60 kg. of non-volatile residues obtained from the distillation of zinc which contained about 60 g. of gallium. The metal was dissolved in 500 g. portions in dilute nitric acid and treated with a slight excess of dilute sulphuric acid to precipitate most of the lead. The filtrate was evaporated until copious fumes of sulphur trioxide were evolved, cooled, and the semi-solid residual mass poured into water to make approximately a 5*N*-solution of sulphuric acid. After removal of the precipitated lead sulphate, the solution was treated with hydrogen sulphide, which removed the rest of the

lead and traces of copper and other heavy metals. The filtrate was diluted ten times, raised to the boiling point, and again treated with hydrogen sulphide, whereby most of the arsenic was removed. The filtrate was boiled and treated with sodium carbonate until a precipitate was barely perceptible. Gallium hydroxide was precipitated from the neutral solution by the addition of ammonium hydroxide, care being taken not to use an excess of ammonia. The gelatinous precipitate was washed by decantation and contained chiefly the hydroxides of gallium, indium, and zinc. The precipitate was treated with excess of potassium hydroxide, which dissolved the gallium and zinc and a little of the indium. The alkaline solution was neutralised with sulphuric acid and then treated with ammonia until a precipitate barely began to form, ammonium sulphate was added, and the solution electrolysed with a current of 10 amperes, the cathode being a stout platinum rod 10 cm. long, and the anode a platinum foil. Metallic zinc and indium were first deposited, but as the deposit contained some gallium it was therefore dissolved and re-electrolysed separately. As the electrolysis proceeded, yielding more gallium, the boiling solution deposited on the bottom of the vessel an insoluble basic gallium ammonium sulphate as a fine, granular powder, whilst at the same time arsine was evolved. The basic salt, which contained practically all the gallium, was dissolved in a slight excess of potassium hydroxide and the gallium deposited electrolytically. The gallium was then treated with warm concentrated nitric acid to remove the more soluble metals, washed, and treated with dilute sulphuric acid. The metal at this stage may possibly contain traces of zinc and other metals. The metal obtained solidified slightly below the true melting point, 29.75° . It was therefore fractionally crystallised eight times and it then melted exactly at 29.75° . The purest crystals were heated at $800\text{--}850^{\circ}$ in a silica boat for twenty-four hours, and the product remaining in the boat then failed to give spectroscopic evidence of the presence of zinc, arsenic, indium, or lead. The pure gallium was converted into chloride by the method previously described (A., 1919, ii, 157, 158; 1921, ii, 264) and fractionated by distillation and sublimation in chlorine, in nitrogen, and in a vacuum. The salt was analysed by essentially the same method as that used in the analysis of aluminium bromide and as the mean of four determinations gave the value gallium=69.716, the extreme values being 69.707 and 69.722. The value was calculated on the assumption that chlorine=35.458 and silver=107.88. J. F. S.

Phenomena of Hydrolysis of Aqueous Solutions of Ferric Chloride. E. PUXEDDU (*Gazzetta*, 1923, 53, i, 210—215).—The results of the author's experiments indicate that the hydrolytic phenomena of aqueous solutions of ferric chloride are far more complex than is indicated by previous investigations. The extent to which the hydrolysis takes place increases with the dilution to a maximum and subsequently diminishes. This is indicated by maxima of turbidity, of the variation with time of the electrical

conductivity, and of the number of mobile particles observable by means of the ultramicroscope. The variation of the conductivity with the time follows at 0° a totally different course from that observed at 25° (cf. Goodwin, A., 1897, ii, 16), the lag period preceding the initiation of the hydrolysis being immensely greater at the lower temperature.

T. H. P.

The Ternary System Ammonium Chloride–Ferric Chloride–Water. FREDERICK WILLIAM JEFFREY CLENDINEN (T., 1923, 123, 1338–1344).

Cobaltous Triple Nitrites, and a Sensitive Reaction for Potassium. V. CUTTICA (*Gazzetta*, 1923, 53, i, 185–189).—By addition to a neutral solution of a cobaltous salt of a more concentrated solution of a lead salt and then of a large excess of alkali nitrite solution (cf. this vol., ii, 76, 77), the following compounds have been obtained as dark green, microcrystalline precipitates: $\text{Co}(\text{NO}_2)_2, \text{Pb}(\text{NO}_2)_2, 2\text{KNO}_2$; $\text{Co}(\text{NO}_2)_2, \text{Pb}(\text{NO}_2)_2, 2\text{RbNO}_2$; $\text{Co}(\text{NO}_2)_2, \text{Pb}(\text{NO}_2)_2, 2\text{NH}_4\text{NO}_2$, and $\text{Co}(\text{NO}_2)_2, \text{Pb}(\text{NO}_2)_2, 2\text{TiNO}_2$. The formation of these compounds probably occurs in two stages, the second stage being represented by the equation $\text{K}_2\text{Co}(\text{NO}_2)_4 + \text{K}_2\text{Pb}(\text{NO}_2)_4 = 2\text{KNO}_2 + [\text{Co}(\text{NO}_2)_6]_{\text{Pb}}^{\text{K}}$. These triple nitrites are highly stable in the air and exhibit marked resistance to the action of cold, dilute mineral acids.

The formation of cobaltous lead potassium nitrite serves as a means of detecting 1 part of potassium in 10,000 parts of solution. [Cf. *J.S.C.I.*, 1923, July.]

T. H. P.

Phosphotungstates with 3WO_3 . F. KEHRMANN and R. MELLET (*Helv. Chim. Acta*, 1923, 6, 443–449).—The sodium, potassium, and ammonium salts corresponding with the formula $3\text{MO}, \text{P}_2\text{O}_5, 6\text{WO}_3, \text{aq.}$ have now been prepared in the pure state and the series is definitely established (cf. this vol., ii, 77). Three mols. of water are firmly held in the series of salts as water of constitution. The sodium salt is prepared by the slow crystallisation of an aqueous solution containing sodium tungstate (3 mols.) and disodium hydrogen phosphate (1 mol.) neutralised with acetic acid. After five recrystallisations from water, it is pure. The sodium phosphotungstate crystallises in aggregates of white, striated prisms having the composition $3\text{Na}_2\text{O}, \text{P}_2\text{O}_5, 6\text{WO}_3, 3\text{H}_2\text{O} + 13\text{H}_2\text{O}$. The *potassium* salt could not be prepared directly from its constituents, but was obtained by precipitating a solution of the sodium salt with potassium chloride. It is far less soluble than the sodium salt and forms brilliant, prismatic needles containing $3\text{H}_2\text{O} + 11\text{H}_2\text{O}$. The *ammonium* salt, prepared from the sodium salt and ammonium chloride, crystallises in brilliant, short, stout prisms containing $3\text{H}_2\text{O} + 6\text{H}_2\text{O}$. The free acid could not be prepared. The analysis of these salts, which offered some difficulty, will be fully described in a future paper.

E. H. R.

The Relation of Actinium to Uranium. A. S. RUSSELL (*Nature*, 1923, 111, 703–704).—From a consideration of the periods of corresponding members of the three disintegration series,

the following scheme giving the element, period, atomic number, radiation, and atomic weight is put forward: Actino-uranium-I; $>5 \times 10^9$ years; 92; α ; 240. Uranium- Y_1 ; 25.5 hours; 90; β ; 236. Uranium- Y_2 ; probably very short; 91; β ; 236. Actino-uranium-II; $>2 \times 10^6$ years; 92; α ; 236. Parent of proto-actinium; >20 years; 90; β ; 232. Proto-actinium; $<1.2 \times 10^4$ years; 91; α ; 232. Actinium; 20 years; 89; β ; 228. Radio-actinium; 19.5 days; 90; α ; 228. Thus, although agreeing with Piccard in assuming that the parent substance of the actinium series is an isotope of uranium of atomic weight 240, the author differs from that investigator in believing that the atomic weight of actinium is not 232 but 228, and that uranium- Y is not the immediate parent of proto-actinium. In view of the fact that there are ten examples of similar types of radioactive transformation in which the period of the first β -particle is greater than that of the second, it is argued that the parent of protoactinium has a longer period than actinium, and consequently cannot be uranium- Y . It is claimed that the data given do not contravene the Geiger-Nuttall relation; they reduce the three exceptions to Fajan's α -ray rule to one only; and the two exceptions to the β -ray rule do not exist.

The ratio of the amounts of actino-uranium and uranium-I in uranium is experimentally found to be 5:95. Hahn's conclusion that uranium- X_1 breaks up dually is confirmed, and the periods of uranium- Y , uranium- Z and uranium- X_2 have been accurately determined to be 25.5 hours, 6.69 hours, and 70.5 seconds, respectively. It is pointed out that the branching ratio, given by Hahn as 996.5:3.5, is approximately equal to the reciprocal of the periods of the two substances formed, namely, uranium- X_2 and uranium- Z .

A. A. E.

Revision of the Atomic Weight of Titanium. Analysis of Titanium Tetrachloride. GREGORY PAUL BAXTER and GEORGE JOSEPH FERTIG (*J. Amer. Chem. Soc.*, 1923, 45, 1228—1233).—An account of preliminary work on the analysis of titanium tetrachloride made for the purpose of atomic weight determination. Titanium tetrachloride was purified by fractional distillation, using the method employed by Baxter, Weatherill, and Scripture in the distillation of silicon tetrachloride and tetrabromide (this vol., ii, 412). The pure titanium tetrachloride was sealed in small bulbs which were broken under 3*N*-nitric acid, treated with nearly the equivalent amount of silver nitrate, the exact equivalent point being determined nephelometrically. Six experiments to determine the ratio $\text{TiCl}_4 : 4\text{Ag}$ gave a mean value of 0.43957, the extremes being 0.43940 and 0.43967, which leads to the mean value 47.85 for the atomic weight of titanium, the extreme values being 47.89 and 47.78.

J. F. S.

Investigations of the Chromates of Thorium and the Rare Earths. I. The System Thorium Oxide-Chromic Anhydride-Water at 25°. HUBERT THOMAS STANLEY BRITTON (*T.*, 1923, 123, 1429—1435).

Thorium Molybdate, $\text{Th}(\text{MoO}_4)_2$. F. ZAMBONINI (*Compt. rend.*, 1923, 176, 1473—1475).—Whilst the thorium molybdate is crystallographically clearly distinct from calcium, strontium, barium, lead, cerium, lanthanum, and neodymium molybdates, the differences between corresponding angles are not greater than those sometimes observed between typical isomorphs. Mixed crystals of thorium and cerous molybdates were obtained containing in one case 1% of the cerium salt, in the other 6% of the thorium compound. The fact that tervalent and quadrivalent elements form such isomorphous crystals is considered to indicate the possibility of element 72 being found in conjunction with rare earths, themselves tervalent, although the new element is quadrivalent.

H. J. E.

The Isotopes of Germanium. F. W. ASTON (*Nature*, 1923, 111, 771).—By the use of an anode containing a fluorine compound of germanium, three isotopes of mass 70, 72, and 74, respectively, with intensity ratio 2 : 4 : 5 have been detected, the values being in reasonably good agreement with the accepted atomic weight.

A. A. E.

Action of Vanadyl Trichloride and of Nitrosyl Chloride on Metallic Oxides. V. CUTTICA, A. TARCHI, and P. ALINARI (*Gazzetta*, 1923, 53, i, 189—194; cf. Bassett and Taylor, T., 1911, 99, 1402).—Vanadyl trichloride acts on magnesium oxide at the ordinary temperature giving a brick red, pulverulent substance which contains 12.4% Mg, 20.4% V, and 25% Cl and yields the hexavanadate, $\text{Mg}_2\text{V}_6\text{O}_{17} \cdot 19\text{H}_2\text{O}$, when treated with water. In a sealed tube at 150—160°, vanadyl trichloride and cupric oxide give *copper chlorovanadate*, $\text{Cu}(\text{VO}_3)_2 \cdot \text{CuCl}$, as a dark green powder. Similarly lead oxide yields the *chlorovanadate*, $\text{Pb}(\text{VO}_3)_2 \cdot \text{PbCl}_2$, as a brick-red powder. At the ordinary temperature, vanadyl trichloride and thalious oxide yields *thalious chlorovanadate*, $\text{Tl}_2\text{O} \cdot \text{VOCl}_3$, as a deep chestnut-brown powder (cf. Ephraim, A., 1903, ii, 487); treatment of this compound with water gives vanadyl chloride and the polyanadate, $\text{Tl}_2\text{O} \cdot 3\text{V}_2\text{O}_5$. From the instability of these compounds towards water, it is probable that the chlorine is combined with the vanadium, the structures being $\text{Cu} \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{VOCl}, \text{CuVO}_3$,

$\text{Pb} \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{VOCl}$, and $\text{VCl}_3(\text{OTl})_2$ (cf. Ephraim, *loc. cit.*).

The action of nitrosyl chloride on cupric oxide yields an unstable compound, which decomposes rapidly in the air, giving cupric chloride. With cuprous chloride or oxide, nitrosyl chloride gives the compound $\text{Cu}_2\text{Cl}_2 \cdot \text{NOCl}$ (cf. Sudborough, T., 1891, 59, 655). Thalious oxide and nitrosyl chloride yield the red compound, $\text{TlCl}_2 \cdot 3\text{NOCl}$, which is moderately stable in the air, but in a vacuum gradually decomposes, with formation of thaloso-thallic chloride.

T. H. P.

Platinum Complexes. L. A. TSCHUGAEV (*J. Russ. Phys. Chem. Soc.*, 1920, 51, 193—231).—[With M. S. GRIGORIEVA.]
cis-Platinodiamminedihydrazine chloride, $\begin{bmatrix} \text{NH}_3 \\ \text{NH}_3 \end{bmatrix} \text{Pt} \begin{bmatrix} \text{N}_2\text{H}_4 \\ \text{N}_2\text{H}_4 \end{bmatrix} \text{Cl}_2$,

white crystals, is prepared by grinding up Peyronier's chloride, $\left[\begin{smallmatrix} \text{NH}_3 \\ \text{NH}_3 \end{smallmatrix} \right] \text{Pt} \left\langle \begin{smallmatrix} \text{Cl} \\ \text{Cl} \end{smallmatrix} \right\rangle$, with hydrazine hydrate. This compound decomposes in cold aqueous solution within fifteen to twenty minutes; when heated, decomposition is almost immediate, with the liberation of platinum black. The dry salt may be kept without decomposition for a few days. The *chloroplatinite*, green crystals, is

prepared, and a *dihydrochloride*, $\left[\begin{smallmatrix} \text{NH}_3 \\ \text{NH}_3 \end{smallmatrix} \right] \text{Pt} \left\langle \begin{smallmatrix} \text{NH}_2 \cdot \text{NH}_3 \\ \text{NH}_2 \cdot \text{NH}_3 \end{smallmatrix} \right\rangle \text{Cl}_4$, white crystals, is obtained by the addition of hydrochloric acid to a solution of the chloride. The dihydrochloride may be kept for some months without noticeable decomposition, and the original chloride is regenerated from it by the addition of the calculated quantity of sodium hydroxide. The addition of potassium chloroplatinite to the dihydrochloride gives a *compound*, $\left[(\text{NH}_3)_2 \text{Pt} \left\langle \begin{smallmatrix} \text{N}_2\text{H}_4 \\ \text{N}_2\text{H}_5 \end{smallmatrix} \right\rangle (\text{PtCl}_4)_3 \right]$, violet

prisms. The chloride on warming with hydrochloric acid yields Peyronier's chloride in the following way: $[(\text{NH}_3)_2 \text{Pt} (\text{N}_2\text{H}_4)_2] \text{Cl}_2 \rightarrow [(\text{NH}_3)_2 \text{Pt} (\text{N}_2\text{H}_5)_2] \text{Cl}_4 \rightarrow [(\text{NH}_3)_2 \text{PtCl}_2] + 2\text{N}_2\text{H}_4 + 2\text{HCl}$. *trans-Platinodiamminedi-hydrazine chloride* is obtained in the same way as the *cis*-compound from Reise's chloride II, $\left[\begin{smallmatrix} \text{NH}_3 \\ \text{Cl} \end{smallmatrix} \right] \text{Pt} \left\langle \begin{smallmatrix} \text{Cl} \\ \text{NH}_3 \end{smallmatrix} \right\rangle$, and

forms an *iodide* and a *chloroplatinite* similar in properties to those of the *cis*-compound. With hydrochloric acid a *dihydrochloride*, white needles, is obtained, and the further action of hydrochloric acid is to regenerate Reise's chloride II, in an analogous way to the *cis*-compound. *Platinotetrahydrazine chloride*, $[(\text{N}_2\text{H}_4)_2 \text{Pt} (\text{N}_2\text{H}_4)_2] \text{Cl}_2$, white needles, decomposing within a few days of preparation, is prepared by the action of hydrazine hydrate on platinoditripropylamine tetrachloride, $[(\text{C}_3\text{H}_7)_3\text{NH}]_2 \text{PtCl}_4$, and can also be obtained from the compounds of platinous chloride with thio- and dithioethers, $[\text{Pt}_2\text{R}_2\text{SCL}_2]$ and $[\text{PtRS}(\text{CH}_2)_2\text{SRCL}_2]$. The *chloroplatinite*, deep red crystals, and the *iodide*, silky needles, of the above compound are prepared, and a *compound*, $\text{Pt}(\text{N}_2\text{H}_4)_2\text{Cl}_2 \cdot 2\text{HCl} \cdot 2\text{H}_2\text{O}$, white crystals, is obtained by the action of hydrochloric acid. *cis-Platinodinitrodihydrazine*, $[(\text{N}_2\text{H}_4)_2 \text{Pt} (\text{NO}_2)_2]$, white crystals, is obtained by warming potassium platinonitrite with hydrazine hydrate. This compound is changed by acids into a *substance*, $\left[\begin{smallmatrix} \text{NH}_2 \\ \text{NH}_2 \end{smallmatrix} \right] \text{Pt} \left\langle \begin{smallmatrix} \text{NO}_2 \\ \text{NO}_2 \end{smallmatrix} \right\rangle$ in which both nitrogen atoms of a hydrazine molecule are united to the platinum.

[With I. I. TSCHERNIAEV.]—*Platino-cis-diamminedi-hydroxylamine chloride*, $\left[\begin{smallmatrix} \text{NH}_3 \\ \text{NH}_3 \end{smallmatrix} \right] \text{Pt} \left\langle \begin{smallmatrix} \text{NH}_2 \cdot \text{OH} \\ \text{NH}_2 \cdot \text{OH} \end{smallmatrix} \right\rangle \text{Cl}_2$, white needles, is prepared by the action of aqueous hydroxylamine on Peyronier's chloride, $[(\text{NH}_3)_2 \text{PtCl}_2]$, and is ionised in solution. Its *chloroplatinite*, purple needles, and *chloropalladite*, red needles, both soluble in hot water, and ionised in solution, are prepared. *trans-Platinodiamminedi-hydroxylamine chloride*, colourless prisms, is obtained in an analogous way to the *cis*-compound, from Reise's chloride, $\left[\begin{smallmatrix} \text{NH}_3 \\ \text{Cl} \end{smallmatrix} \right] \text{Pt} \left\langle \begin{smallmatrix} \text{Cl} \\ \text{NH}_3 \end{smallmatrix} \right\rangle$,

and is less soluble than the *cis*-compound, the salt being fully ionised in solution. On warming with hydrochloric acid, it regenerates Reise's chloride. The *trans*-isomeride may also be obtained by the action of anhydrous liquid ammonia on *trans*-platinodihydroxylamine dichloride, $\text{OH}\cdot\text{NH}_2 > \text{Pt} < \text{NH}_2\cdot\text{OH}$. Lossen

(*Annalen*, 1871, **160**, 242) obtained a substance by this reaction, using aqueous ammonia, which he erroneously described as the *trans*-isomeride, and this is now shown to be $\left[\text{OH}\cdot\text{NH}_2 > \text{Pt} < \text{NH}_2\cdot\text{OH} \right]$,

which on warming with hydrochloric acid regenerates the *trans*-platinodihydroxylamine dichloride, and is probably formed by the hydrolysis of the *trans*-isomeride. The *chloroplatinite*, green needles, and the *chloropalladite*, olive-green crystals both soluble in hot water, are prepared. *trans*-Platinodichloroamminehydroxylamine,

$\text{NH}_3 > \text{Pt} < \text{NH}_2\cdot\text{OH}$, yellow crystals, soluble in hot water, is prepared from *cis*-platinodiamminedihydroxylamine chloride by warming with hydrochloric acid; prolonged heating with the latter results in the production of Kossa's acid, $[\text{Pt}(\text{NH}_3)\text{Cl}_3]\text{H}$. *Platinotriamminehydroxylamine chloride*, $\left[(\text{NH}_3)_2\text{Pt} < \text{NH}_2\cdot\text{OH} \right]\text{Cl}_2$, white

plates, soluble in water, is obtained by heating the mixed chloride, $\text{NH}_3 > \text{Pt} < \text{NH}_2\cdot\text{OH}$, with liquid ammonia in a sealed tube; on

warming with hydrochloric acid it yields Cleve's chloride, $[\text{Pt}3\text{NH}_3\text{Cl}]\text{Cl}$.

Its *chloroplatinite*, pale green needles, yields similarly Cleve's chloroplatinite, $[\text{ClPt}3\text{NH}_3]_2\text{PtCl}_4$. *Platinoamminetrihydroxylamine chloride*, white crystals, is prepared by heating the mixed chloride with hydroxylamine, and its *chloroplatinite*, and *chloropalladite*, purple crystals, are prepared. *trans*-Platinodipyridinedihydroxylamine chloride, $\left[\text{OH}\cdot\text{NH}_2 > \text{Pt} < \text{NH}_2\cdot\text{OH} \right]_{\text{Py}}\text{Cl}_2$, white crystals, is

obtained by warming pyridine with *trans*-platinodihydroxylamine dichloride; on warming with hydrochloric acid, it yields *trans*-platinodipyridine dichloride. Its *chloroplatinite*, pink prisms, is prepared. *trans*-Platinodihydroxylamine dichloride is prepared by warming platinotetrahydroxylamine chloride with hydrochloric acid. This substance is little ionised in solution, and is capable of forming double salts with Reise's chloride I,

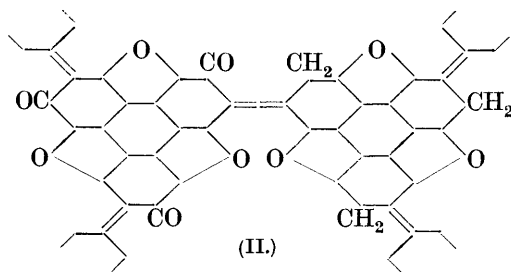
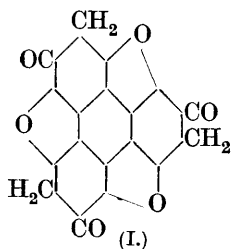
$[\text{Pt}(2\text{NH}_2\cdot\text{OH})\text{Cl}_4]\text{Pt}\cdot 4\text{NH}_3\cdot 2\text{H}_2\text{O}$,
pale yellow crystals, and with caesium chloride, $[\text{Pt}(2\text{NH}_2\cdot\text{OH})\text{Cl}_4]\text{Cs}_2$,
pale yellow crystals. R. T.

Mineralogical Chemistry.

Structure of Native Platinum. S. F. SCHEMTSCHUSCHNY (*J. Russ. Phys. Chem. Soc.*, 1919, **51**, 417—460).—The physical properties, microstructure, and chemical composition of a number of samples of native platinum from the Urals were studied. It is concluded that platinum found in massive rocks is of magmatic origin (cf. Beck, *Ber. Ges. Wiss. Leipzig*, 1907, **59**, 387). Thus, it possesses a microstructure similar to that of alloys, the components of which form solid solutions of various concentrations; the hardness of the samples is greater than that of pure platinum, being a solid solution of metals of the platinum group and also iron, in platinum; the presence of occluded air bubbles and of crystals of the compound OsI_2 is also in accordance with that view.

G. A. R. K.

The Chemical Structure of Coal. WALTHER SCHRAUTH (*Brennstoff-Chem.*, 1923, **4**, 161—164).—The author has previously suggested (A., 1923, i, 443) that the fundamental unit of lignin is a keto-derivative of a hydro-9:10-benzophenanthrene in which the three outside benzene rings are linked up through oxygen (formula I). Such a molecule would possess great reactivity. It could, by enolisation, give rise to esters and ethers, the occurrence of which in lignin is established. Carboxylic acids of high molecular weight, similar in character to the humic acids, might also be derived from it, whilst reduction might lead to the replacement of the oxygen in the furan rings by hydrogen. It would be particularly susceptible to various condensation processes by which it might give rise, in the course of coal formation, to new



molecules of unlimited size (type II), containing possibly also sulphur and nitrogen, which would finally, by elimination of carbon dioxide and water, lead to products not unlike coal itself. Not only does the hydrogenation of coal

indicate the presence in it of unsaturated linkings, but the decomposition products formed under the conditions of temperature and pressure attendant on the formation of the coal itself and, in a more marked degree, by low temperature carbonisation, are directly derivable from a molecule of the above type. The occurrence of purely aromatic hydrocarbons, such as

naphthalene and anthracene, as primary products of low temperature carbonisation is not to be expected, and the fact that low temperature tars do not contain these but are mainly composed of alkylated phenols and hydrogenated hydrocarbons supports the author's argument. Further support is provided by the presence, in these tars, of unsaturated aliphatic hydrocarbons and of acetone. An exact examination of the higher constituents of low temperature tars is at present lacking, but the results so far obtained appear to be in agreement with the above formulation which may thus, at least, be taken as a working hypothesis. W. T. K. B.

Argentojarosite, a New Silver Mineral. WALDEMAR T. SCHALLER (*J. Washington Acad. Sci.*, 1923, **13**, 233). C. A. SCHEMPF (*Amer. J. Sci.*, 1923, [v], **6**, 73—75).—Small, yellow to brown, hexagonal, optically uniaxial and negative scales from Dividend, Utah, resemble jarosite in appearance, but have the composition $\text{Ag}_2\text{O}, 3\text{Fe}_2\text{O}_3, 4\text{SO}_3, 6\text{H}_2\text{O}$, with Ag_2O 18, Fe_2O_3 43, SO_3 28, H_2O 10% and some K_2O and PbO . This is the first record of a silver mineral containing oxygen, and it is sufficiently abundant to be worked as an ore. L. J. S.

Analytical Chemistry.

Polarimetric Estimation of Acidic and Basic Groups in Various Types of Compound. I. Basic Groups. J. GROOT (*Biochem. Z.*, 1923, **137**, 517—530).—By working with sucrose solutions of a constant concentration, the relation between the velocity constant of inversion, K , and the normality N , of the hydrochloric acid is determined over a given range. The function is not quite a straight line, but can be represented by an equation of the type $K=aN+bN^2$, where a and b are constants. Having evaluated these constants, the velocity of inversion by hydrochloric acid is determined in the presence of a small proportion of a basic substance, as, for instance, *o*-aminobenzoic acid. The effective hydrochloric acid concentration is thus calculated and hence the proportion inactivated by the *o*-aminobenzoic acid is known.

H. K.

Use of Potassium Ferrocyanide in Analysis. C. PORLEZZA (*Ann. di Chim. Applic.*, 1923, **13**, 48—53).—The formation of a blue precipitate in an acid solution of potassium ferrocyanide (cf. Tarugi, Report VI. Internat. Congress Applied Chem., Rome, 1906) does not occur in the dark, but takes place fairly rapidly in diffused light in presence of air, hydrocyanic acid being liberated in small proportion. The resultant liquid yields a precipitate of ferric hydroxide when treated with excess of sodium hydroxide. Special precautions must therefore be taken in applying analytical processes involving the use of ferrocyanide in acid solutions (Fresenius and Hintz, A., 1895, ii, 536; Browning, A., 1921, ii, 279; Browning and Porter, A., 1921, ii, 265). The possible causes of the formation of the blue precipitate are discussed. T. H. P.

Use of Bromate in Volumetric Analysis. I. Stability of Bromic Acid in Boiling Solutions. G. FREDERICK SMITH (*J. Amer. Chem. Soc.*, 1923, 45, 1115—1121).—With the object of ascertaining whether or no potassium bromate is a suitable volumetric reagent in reactions where it is necessary to add an excess of the reagent, the stability of solutions of potassium bromate (0.025*N*) which had been acidified on boiling has been investigated. It is shown that solutions of bromate acidified with perchloric acid, nitric acid, or acetic acid, so that the concentration of the acid is 2*N*, are not decomposed on boiling or five minutes; sulphuric acid and phosphoric acid solutions are much less stable. The presence of free bromine has no effect except with acetic acid, but the presence of 10 mg. of potassium chloride causes a slight reduction. The amount of bromide in bromate may be estimated by acidifying the solution and distilling the bromine liberated. Barium bromate may be substituted for potassium bromate with equally good results.
J. F. S.

The Error in Bang's Micro-estimation of Chloride. II. RICHARD PRIGGE (*Biochem. Z.*, 1923, 137, 484—488).—One extraction of blood with alcohol in the Bang micro-method is insufficient to remove the whole of the chloride. A second extraction in which the drop of blood is left in contact with the alcohol for three hours is adequate, but contact for fifteen seconds is insufficient.
H. K.

The Titration of Hypochlorous Acid. A. SCHLEICHER (*Z. anal. Chem.*, 1923, 62, 329—335).—The low results obtained by Clarens (*A.*, 1914, ii, 741) in using Penot's method of estimating hypochlorous acid by titration with sodium arsenite are shown not to be due to loss of chlorine dioxide. Good results can be obtained by mechanically stirring the solution during the addition of arsenite; no preliminary test is then necessary. Addition of potassium bromide as indicator invariably leads to low results. Electrometric titration, using a solution that has been carefully titrated in the usual way with iodide-starch paper as indicator, as a comparison electrode is very satisfactory.
A. R. P.

Free Sulphur in Motor Fuels, etc. W. R. ORMANDY and E. C. CRAVEN (*J. Inst. Petroleum Tech.*, 1923, 9, 133—139).—To estimate free sulphur in light petroleum, etc., 100 c.c. of the sample are shaken thoroughly in a stoppered bottle for fifteen minutes with about 3 c.c. of mercury; 10 c.c. of dilute hydrochloric acid (1:100) are then added, the mixture is again shaken, and the mercury sulphide formed collected on a moistened asbestos filter. The filter and precipitate are washed with dilute hydrochloric acid, then transferred to a beaker, and the sulphide is oxidised and dissolved by heating with hydrochloric acid and a small quantity of potassium chlorate. The solution is filtered and the sulphuric acid in the filtrate is estimated by precipitation as barium sulphate. Various brands of "petrol" examined contained from a trace to 6.3 mg. of sulphur per 100 c.c.
W. P. S.

Estimation of Inorganic Impurities in Organic Compounds Soluble with Difficulty in Water, such as Sulphuric Acid in Picric Acid. T. S. PATTERSON and K. L. MOUDGILL (*J. Soc. Chem. Ind.*, 1923, 42, 211—212T).—Fifty g. of picric acid are placed in a large boiling tube together with 100 c.c. of water, the tube is immersed in a bath of concentrated potassium carbonate solution heated at 130°, and a current of steam is passed into the mixture for thirty minutes. The supernatant liquid is then decanted and the residual picric acid treated twice in a similar way. The decanted liquids are filtered and the sulphuric acid is estimated in the usual manner by precipitation as barium sulphate. An alternative method consists in mixing 100 g. of picric acid with 200 c.c. of nitrobenzene, heating the mixture at 40°, and shaking it with 80 c.c. of water. The aqueous portion is then removed and the extraction repeated four times. The combined aqueous portions are filtered and the sulphuric acid is estimated in the filtrate. W. P. S.

Sensitivity of the Reaction between Silver Nitrate and a Sulphite. O. HACKL (*Chem. Zeit.*, 1923, 47, 466).—Investigation of the reaction which occurs when a few drops of a solution of silver nitrate are added to a solution containing sodium sulphite shows that the appearance of a precipitate is dependent, not merely on the concentration of the solution of sodium sulphite, but also on its volume. For instance, addition of silver nitrate to 100 c.c. of a solution containing 0.00315 g. of $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$ yielded no permanent precipitate, but a distinct precipitate was observed when 1 c.c. of a similar solution was used. By means of silver nitrate, it is possible to detect not less than 0.001 g. of SO_3 (as sulphite) in 10 c.c. of water or 0.0001 g. of SO_3 in 1 c.c. A. J. H.

New Colour Reaction for Detecting Nitrous Acid. AS. ZLATAROFF (*Z. anal. Chem.*, 1923, 62, 384—385).—Nitrites may be detected in waters by treating 10 c.c. with 1 to 2 c.c. of a 0.0025% aqueous solution of Neutral red followed by 2 to 3 c.c. of dilute sulphuric or hydrochloric acid. A deep blue colour shows the presence of nitrites. The method will detect 0.00005 g. of nitrous acid in 1 litre of water, and is not affected by the presence of iron, manganese, or other metallic salts that occur in natural waters.

A. R. P.

Estimation of Phosphoric Acid in Milk and its Application to the Detection of Added Water. A. KLING and A. LASSIEUR (*Ann. Falsif.*, 1923, 16, 141—146).—When a mixture of phosphoric acid solution, a mineral acid, sodium molybdate solution, and ether is shaken and allowed to separate, three layers are formed, an upper ethereal layer, an intermediate aqueous layer free from phosphoric acid, and a lower layer consisting of a yellow liquid (d 1.23); the volume of this yellow liquid is proportional to the amount of phosphoric acid present. To estimate phosphoric acid in milk, the ash of the latter is fused with a small quantity of sodium nitrate, the fused mass is dissolved in 2 c.c. of water and 2 c.c. of hydrochloric acid (1:3), the solution is

filtered and the filter washed first with 10 c.c. of dilute hydrochloric acid and then with 10 c.c. of water. The filtrate is transferred to a pear-shaped bulb provided at its lower end with a narrow graduated stem, 7 c.c. of ether are added (or a quantity more than sufficient to saturate the solution), 15 c.c. of sodium molybdate solution (100 g. of molybdic acid and 32 g. of sodium carbonate per litre) are introduced slowly whilst the mixture is shaken, and the tube and its contents are submitted to centrifugal action for two minutes. The volume of the yellow liquid is then noted. The value of each division of the graduations, in terms of phosphoric acid, is determined by using a standard phosphoric acid solution. It is suggested that the quantity of phosphoric acid in milk may be used as a basis in the detection of added water in a sample.

W. P. S.

Volumetric Method for the Estimation of Phosphorous Acid in the Presence of Phosphoric Acid. A. WINGLER (*Z. anal. Chem.*, 1923, **62**, 335—337).—A measured quantity of the solution containing the mixed acids is treated with a small excess of a saturated solution of bromine in water and the mixture is left for ten minutes in a dark place. Excess of bromine is removed by passing a current of air through the solution until it becomes colourless. The liquid is titrated with *N*/10-sodium hydroxide solution first with methyl-orange then with phenolphthalein. The process may be represented by the equation: $\text{H}_3\text{PO}_3 + \text{H}_2\text{O} + \text{Br}_2 = \text{H}_3\text{PO}_4 + 2\text{HBr}$. The first end-point is obtained when all the hydrobromic and one-third of the total phosphoric acid present are neutralised, and the second end-point when another one-third of the phosphoric acid is neutralised. From these figures the amount of each acid originally present is then readily calculated.

A. R. P.

New Method of Estimating Arsenic in Steels. C. MAZZETTI and P. AGOSTINI (*Gazzetta*, 1923, **53**, i, 257—261).—The steel is dissolved in aqua regia, the solution evaporated to dryness, and the residue dissolved in hydrochloric acid, the insoluble silica and carbon being removed by filtration. The filtrate is treated with a hydrochloric acid solution of stannous chloride, and the precipitated arsenic filtered off under slight suction and washed free from iron. The filter is shaken with water until the paper is pulped, the arsenic being then dissolved in standard iodine solution, and the liquid titrated with standard arsenite solution in presence of sodium phosphate or sodium hydrogen carbonate and starch paste until a yellowish-pink coloration is obtained (cf. Andrews and Farr, *A.*, 1909, ii, 437). [*Cf. J.S.C.I.*, 1923, July.] T. H. P.

Estimation of Carbon in Vegetable Mould. L. J. SIMON (*Compt. rend.*, 1923, **176**, 1409—1411).—The author has now applied the method of sulpho-chromic oxidation (*A.*, 1922, ii, 593) to the estimation of carbon in vegetable mould, and details are given of experiments on three types of soil, (*a*) from an ordinary garden, (*b*) of a putty-like nature, and (*c*) one rich in humus. The

values obtained by the use of chromic acid are low when compared with the standard copper oxide method, but on using silver dichromate as the oxidising agent more accurate results follow. It is suggested that the chromic acid "oxidation deficit" (this vol., i, 81) may afford an indication of the nature of certain substances present in the soil. The method is stated to be simple and rapid.

H. J. E.

A Method for the Estimation of Dissolved Carbon Dioxide.

F. G. HALL (*J. Biol. Chem.*, 1923, 55, 751—755).—The method is specially designed for the estimation of carbon dioxide liberated by aquatic animals in respiration experiments. The gases are extracted from the solution by repeated evacuation; measurement of their volume before and after absorption of carbon dioxide gives the volume of the latter. The evacuation tube is constructed on the principle of Van Slyke's blood gas apparatus, but is of larger dimensions.

E. S.

The Estimation of Silica in Waters. F. DIÉNERT and F. WANDENBULKE (*Compt. rend.*, 1923, 176, 1478—1480).—Small quantities of silica may be estimated colorimetrically by means of ammonium molybdate; heating the solution is obviated in the production of the colour by using this reagent in the presence of a mixture of sulphuric and nitric acids. The method permits of the differentiation of colloidal and non-colloidal silica, and shows that the latter form is that which normally occurs in waters. The method may be used for studying the change from the colloidal to the non-colloidal state. Experimental details are given. [Cf. *J.S.C.I.*, 1923, July.]

H. J. E.

The Estimation of Potassium by means of Sodium Cobaltic Nitrite. EMM. POZZI-ESCOT (*Bull. Soc. chim. Belg.*, 1923, 32, 227).—In reference to Clerfeyt's paper on this subject (this vol., ii, 181) the author directs attention to the fact that all the details of the method were published by de Koninck several years ago, and that this method for the estimation of potassium has been officially adopted in the United States for some time.

G. F. M.

Volumetric Method for the Estimation of Potassium.

M. BULLI and L. FERNANDES (*Ann. di Chim. Applic.*, 1923, 13, 46—48).—Potassium may be estimated accurately by precipitating it as the triple nitrite, $[\text{Co}(\text{NO}_2)_6]\text{PbK}_2$, and titrating the nitrous residue in the precipitate with permanganate solution. [Cf. *J.S.C.I.*, 1923, July.]

T. H. P.

Estimation of Calcium, Magnesium, Potassium, and Sodium in Human Blood. A. MIRKIN and S. J. DRUSKIN (*J. Lab. Clin. Med.*, 1923, 8, 334—339).—Citrated blood is oxidised by heating with a mixture of fuming nitric acid and concentrated sulphuric acid. After evaporation, a little ammonium hydrogen carbonate is added, volatile ammonium sulphate being formed. In the residue, calcium and magnesium are precipitated by ammonium stearate solution and weighed as stearates. These are dissolved

in 0.01*N*-sulphuric acid, the precipitated stearic acid removed by filtration, and the excess of acid titrated with 0.01*N*-sodium hydroxide solution. Hence the respective amounts of calcium and magnesium can be calculated. The filtrate from the precipitated stearate is evaporated to dryness, ignited, and the alkali sulphates are weighed; an estimation of the sulphate present gives the proportions of sodium and potassium. CHEMICAL ABSTRACTS.

Volumetric Method for the Estimation of Magnesium.

M. BULLI and L. FERNANDES (*Ann. di Chim. Applic.*, 1923, 13, 44—45).—Magnesium may be estimated accurately by precipitation as magnesium ammonium ferrocyanide, and determination of the remaining excess of ferrocyanide in solution by titration with zinc sulphate. [Cf. *J.S.C.I.*, 1923, July.]

T. H. P.

Electrolysis of Zinc Oxide and Cadmium Oxide Fused in Sodium Hydroxide. R. SALANI (*Gazzetta*, 1923, 53, i, 229—233; cf. this vol., ii, 54).—The author has investigated the conditions in which it is possible to separate zinc and cadmium electrolytically from a mixture of 5 g. of zinc oxide and 5 g. of cadmium oxide fused in 150 g. of sodium hydroxide. Graphite crucibles cannot be used as they suffer disintegration, and it is found most convenient to employ an iron crucible as anode and a strip of iron as cathode.

T. H. P.

Detection of the Elements of the Hydrogen Sulphide Group with Especial Reference to Spot Tests. F. FEIGL and F. NEUBER (*Z. anal. Chem.*, 1923, 62, 369—384).—One drop of a solution containing 2 mg. of mercury per 100 c.c. yields a distinct blue colour when placed on a filter-paper moistened with alcoholic diphenylcarbazine solution. Cadmium and copper interfere, but their sulphides are soluble in nitric acid. To distinguish mercurous from mercuric salts, the solution is shaken with a benzene solution of diphenylcarbazine. A blue benzene layer indicates mercuric salt, a flocculent precipitate at the interface between the liquids, mercurous salt. Lead, to the extent of 1 part in 33,000 parts, may be detected by the formation of a blue colour when a drop of the solution is placed on a filter-paper moistened with ammoniacal hydrogen peroxide, then, after some time, treated with a drop of an acetic acid solution of benzidine. Bismuth interferes, but lead may be detected in the presence of eleven times its weight of bismuth by carrying out the test with tetramethyldiaminodiphenylmethane instead of with benzidine. A spot test for bismuth consists in placing a drop of the solution on a paper moistened with a solution containing 1 g. of cinchonine (dissolved in very dilute nitric acid) and 2 g. of potassium iodide per 100 c.c. Bismuth gives an orange-yellow colour; if mercury, copper, and lead are present, the mercury forms a white spot inside the orange-yellow bismuth ring, lead gives a yellow ring outside this, and copper a brown ring outside the lead ring. Traces of copper may be detected by the blue colour produced by the addition of a drop of potassium

bromide solution, followed by a drop of benzidine hydrochloride solution to a drop of the test solution on filter-paper. Copper also gives a blue colour with potassium cyanide, and phosphomolybdic and hydrochloric acids which may be extracted from the solution by shaking with amyl alcohol. Cadmium gives a reddish-violet spot on a paper treated with a saturated solution of diphenylcarbazide in 90% alcohol that has been saturated with potassium thiocyanate and contains a little potassium iodide. Copper does not interfere; lead gives a yellow spot inside the cadmium coloration. Addition of stannous chloride to ammonium molybdate solution produces a blue colour which disappears on warming; if only 1 part of arsenic per million is present, the blue colour persists on warming. Antimonious and stannous chlorides both give a blue colour with a solution of phosphomolybdic acid, but only stannous chloride gives a similar reaction on a test-paper impregnated with ammonium phosphomolybdate.

A. R. P.

Estimation of Tin in Wolfram. A Modification of Powell's Method. OCTAVIUS FRANCIS LUBATTI (T., 1923, 123, 1409—1411).

Separation of Tin and Arsenic. LEROY W. MCCAY (*J. Amer. Chem. Soc.*, 1923, 45, 1187—1191).—Quadrivalent tin and trivalent arsenic in dilute sulphuric or hydrochloric acid may be completely separated by treatment with hydrogen sulphide after the addition of a little hydrofluoric acid. The separation is effected by treating the solution in a platinum dish with 2—5 c.c. of 48% hydrofluoric acid, heating for a few minutes, and when cold diluting to 300 c.c. The solution is then treated with a rapid stream of hydrogen sulphide for thirty minutes, when arsenious sulphide alone is precipitated. The separation is both rapid and quantitative.

J. F. S.

The Estimation of Ethylene and its Homologues in Primary Gas. H. TROPSCH and A. V. PHILIPPOVICH (*Brennstoff-Chem.*, 1923, 4, 147—149).—Synthetic mixtures of ethylene and propylene were treated with sulphuric acid of concentrations from 80% to 99% in a 100 c.c. gas-absorption pipette filled with glass spheres of 1 cm. diameter. The quantities absorbed were noted after 0.5 minute, three minutes, five minutes, ten minutes. It was found that 87% sulphuric acid was very suitable for the separation of these gases, since in ten minutes it absorbed all the propylene and scarcely any of the ethylene. It is necessary that the ethylene should not greatly predominate in the mixture. Stronger acid absorbs too much ethylene, weaker acid absorbs propylene too slowly. The lighter homologues of ethylene behave like propylene, synthetic mixtures of air, argon, benzene, and ethylene treated with 87% sulphuric acid for fifteen minutes gave the correct absorption for ethylene when then shaken with bromine water. If the gas contain small amounts of benzene vapour the estimation of ethylene is not affected, as the benzene is absorbed by the 87% sulphuric acid, but if considerable amounts are present the method

fails, as the 87% acid only slowly absorbs benzene and some is left to be absorbed by the bromine water. These considerations, however, do not apply to primary gas, with which satisfactory results are obtained, as it contains but little benzene. T. S. W.

The Determination of *p*-Aminophenol in the Presence of Metol [*p*-Methylaminophenol Sulphate]. W. F. A. ERMEN (*Chemistry and Industry*, 1923, 42, 538).—About 2 g. of the sample are dissolved in 100 c.c. of water with excess of hydrochloric acid, and titrated with *N*/10-sodium nitrite. The *p*-aminophenol is thus diazotised, whilst the metol forms a nitrosoamine which separates as white, crystalline hairs. Sodium acetate is then added, followed by a known excess of *m*-phenylenediamine, which couples with the diazo-compound; coupling is accelerated by warming to 25°. The mixture is cooled and excess of *m*-phenylenediamine titrated with freshly prepared *N*-diazobenzene solution. From the data thus obtained the amounts of *p*-aminophenol and metol present can be calculated. If the sample contains *s*-dimethyl-*p*-phenylenediamine, this must first be removed by washing with alcohol, in which its sulphate is readily soluble. The results obtained are accurate to within 1%. E. H. R.

Folin's Method for the Estimation of Uric Acid in Blood. A. SACHNOVSKA and IVAN ADAMOWITSCH ZALESKI (*J. Russ. Physiol.*, 1919, 2, 36).—Slight modifications have been made in Folin's precipitation method (cf. this vol., ii, 196). The precipitated salts of uric acid are decomposed with hydrochloric acid instead of with hydrogen sulphide, and the final coloured solution is compared with a previously standardised blue glass. E. S.

The Estimation of Uric Acid in Blood. H. BROWN and G. W. RAIZISS (*J. Lab. Clin. Med.*, 1922, 8, 129—134).—Adsorption of uric acid does not take place in the precipitation of blood proteins by the method of Folin and Wu. Equally good recoveries of added uric acid can be obtained either by Folin and Wu's or Benedict's methods. Folin and Wu's method gives correct results for blood uric acid, whilst the high results found with Benedict's method are due to interfering substances. Benedict's reagent is selective and yields results approximately similar to those of Folin and Wu only with high uric acid content. Benedict's method, owing to its speed and requirement of small quantities of blood, can be used for routine clinical analyses, but is not to be recommended for research purposes. CHEMICAL ABSTRACTS.

Exposure to Light as a Source of Error in Estimating Uric Acid by the Folin and Wu Method. HOBART ROGERS (*J. Biol. Chem.*, 1923, 55, 325—331).—In the precipitation method of Folin and Wu (*A.*, 1919, ii, 308; this vol., ii, 196), loss of uric acid results from exposure of the silver precipitate to light. Precautions should therefore be taken to avoid such exposure. E. S.

The Refractometric Estimation of Serum Proteins.

BENJAMIN S. NEUHAUSEN and DAVID M. RIOCH (*J. Biol. Chem.*, 1923, 55, 353—356).—In Reiss's method (A., 1904, ii, 303; *Z. Elektrochem.*, 1908, 14, 613), more accurate results are obtained by deducting from the refractive index of the serum that for water plus 0.0022 for non-protein constituents and then dividing the remainder by 0.00194. Great accuracy cannot, however, be attained, since the last factor depends on the ratio globulin: albumin, which has been found to vary from 12 to 34%, although usually it is about 30%.
E. S.

Modification of Brandberg's Method for the Estimation of Albumin in Urine. V. A. BOLOTOV (*J. Russ. Physiol.*, 1919, 2, 37).—Sulphosalicylic acid is used in place of nitric acid.
E. S.

Test for Albumin and Other Urinary Proteins. WM. G. EXTON (*J. Amer. Med. Assoc.*, 1923, 80, 529—530).—The urine is warmed with an equal volume of a reagent prepared as follows: 200 g. of sodium sulphate decahydrate are dissolved in 700—800 c.c. of water, cooled to 35°, 50 g. of sulphosalicylic acid are added with stirring until dissolution is complete, and the mixture is diluted to 1 litre. The turbidity developed in the presence of albumin is proportional to the concentration of the latter.

CHEMICAL ABSTRACTS.

Ostromisslenski's Reaction for Albumins. M. A. RAKUZIN (*J. Russ. Phys. Chem. Soc.*, 1917, 49, 164—169).—The Ostromisslenski reaction for albumins is found to be given by proteins, and their salts, except the ammonium salt, by amino-acids, by amines and imines, but not by anilides or by "saccharin," by hydroxylamine and oxamide, but not by carbamide, and by alkaloids, with the exception of strychnine. It appears from this that, in general, the reagent (picramic acid) reacts with amino- and imino-groups. Pepsin and trypsin, which do not give the reaction in question, are therefore probably not albumins.
R. T.

The Estimation by Van Slyke's Method of Free Amino-groups in Plant Globulins. A. I. OPARIN (*J. Russ. Phys. Chem. Soc.*, 1917, 49, 266—271).—Van Slyke's method for the estimation of free amino-groups (A., 1911, ii, 779) is applied to the analysis of globulins extracted from various seeds, the time of reaction allowed being, not thirty minutes, as Van Slyke advises, but one hour, in view of the low reaction temperature necessary in this case. The total nitrogen content, determined by Kjeldahl's method, varied from 17.66 to 19.76% in the globulins examined, whilst the free amino-group nitrogen content varied from 0.349 to 0.504%. [Cf. *J.S.C.I.*, 1923, July.]
R. T.

A Modification of Fuld's Method for the Estimation of Pepsin. RICH. EGE (*Z. physiol. Chem.*, 1923, 127, 125—136).—Pepsin may be estimated by determining the amount of edestin

hydrolysed by it in a given time under standard conditions. Sodium chloride and sodium sulphate are added to the hydrolysed edestin until a precipitation occurs. The amount of salt required varies with the activity of the pepsin. W. O. K.

Starch for Use in Diastatic Assays. A. ASTRUC and A. RENAUD (*J. Pharm. Chim.*, 1923, [vii], 27, 333—337).—Potato starch of commercially different kinds often gives widely varying results with the same pancreatin under the same conditions, and it may therefore appear good or bad according to the starch which happened to be used for the assay. The causes of this variation were investigated and neither the age of the potato from which the starch was derived nor the temperature used in drying was found to have any influence on the subsequent action of the enzyme. On the other hand, the method of preparation, particularly the character of the water used in washing and the sifting of the granules were sources of considerable variation. Preferably distilled water should be used in washing, or failing that spring water of constant composition, only granules passing a No. 100 sieve should be used in the assay, and their water content should be 7—8%. The method of preparing the mucilage is of minor importance, but a few minutes' heating are actually quite sufficient, and the formation of clots should, of course, be guarded against. G. F. M.

Estimation of Blood Catalase. Factors Affecting the Ratio between Quantity and Activity of this Enzyme. RUTH OKEY (*Amer. J. Physiol.*, 1922, 62, 417—437).—Catalase activity is determined by titration of the undecomposed hydrogen peroxide with permanganate. Comparatively small variations in temperature may account for certain variations in catalase content previously reported by various investigators.

CHEMICAL ABSTRACTS.

Estimation of Neosalvarsan and its Absorption by Bacteria and Body-cells. E. REMY (*Biochem. Z.*, 1923, 137, 133—143).—The colour produced by the coupling of diazotised neosalvarsan with alkaline resorcinol can be used for the colorimetric estimation of neosalvarsan. In urine, it can be estimated with an error of 3% at a dilution of 1:25,000 and in serum at 1:50,000. The azo-compound has been obtained crystalline, and can be identified in solution with other pigments by the spectroscope, absorption beginning at λ 560 μ . The fixation of neosalvarsan by bacteria or cells is an adsorption, but the adsorption isotherm only holds over small ranges. More adsorption takes place from water than from serum. H. K.

Refractometric Method for the Determination of Watering of Milk. MARIA CASTELLANI (*Ann. di Chim. Applic.*, 1923, 13, 41—44).—A method is described for obtaining rapidly from milk a clear whey, refractometric examination of which serves to indicate if the original milk were watered. [Cf. *J.S.C.I.*, 1923, July.]

T. H. P.

General and Physical Chemistry.

Refraction and Absorption of Light by Zinc Blende at Temperatures up to 700°. MARIA MELL (*Z. Physik*, 1923, 16, 244—265).—Measurements were made of the refractive index and absorption of a specimen of zinc blende coloured slightly greenish-yellow, for temperatures ranging from -80° to 700° , and for wave-lengths between about 400 and 800 $\mu\mu$. The results indicate that in the visible spectrum the dispersion is normal and attributable principally to an oscillator with a frequency in the ultra-violet. The refractive index increases with temperature, and considerably more rapidly for light of short wave-length than for light of long wave-length. Thus for $\lambda=436 \mu\mu$, the results show that the refractive index, n_t at t° , is given by $n_t=2.4885 (1+3.8695 \times 10^{-5}t + 17.9 \times 10^{-9}t^2)$. Similarly, for $\lambda=546 \mu\mu$, $n_t=2.3870 (1+2.7508 \times 10^{-5}t + 11.1 \times 10^{-9}t^2)$, and for $\lambda=578 \mu\mu$, $n_t=2.3717 (1+2.5826 \times 10^{-5}t + 9.5 \times 10^{-9}t^2)$. The transparency of zinc blende increases with increasing wave-length of the light transmitted and decreases rapidly as the temperature increases. A minimum transparency observed in the mean or extreme red region of the spectrum is attributable to an impurity present in the blende. With increasing temperature, the region of selective absorption is displaced from the ultra-violet towards the visible region of the spectrum. J. S. G. T.

II. Spectrochemistry of Olefine-monocarboxylic Acids and their Derivatives. K. VON AUWERS (*Annalen*, 1923, 432, 84—99).—The optical constants of a number of unsaturated monocarboxylic acids, esters, acid chlorides, and nitriles are tabulated and discussed.

For Δ^{α} -unsaturated acids, $C:C(C)(OH):O$, the mean values for specific exaltation of molecular refraction and molecular dispersion are $+0.9$ and $+33\%$, respectively, these figures being very similar to those, $+0.9$ and $+30-40\%$, for the few Δ^{α} -unsaturated ketones, $C:C(R)(R):O$, which have been investigated. Acids which contain the grouping $C:C(R):C(OH):O$ show a considerably smaller exaltation of molecular refraction, $+0.6$, but approximately the same exaltation of molecular dispersion. In general, therefore, not only may Δ^{α} -unsaturated acids be distinguished from isomerides in which there is no conjugation, but the presence of an α -substituent may likewise be detected. There are, however, exceptions; thus nonenoic acid, $CH_3[CH_2]_5 \cdot CH:CH \cdot CO_2H$, and octadecenoic acid, $CH_3[CH_2]_{14} \cdot CH:CH \cdot CO_2H$,

have abnormally low molecular refractions and molecular dispersions, and this is not due to the high molecular weight, since geranic acid, $CMe_2 \cdot CH \cdot CH_2 \cdot CH_2 \cdot CMe:CH \cdot CO_2H$, has large exaltations. It is also indicated that, in unsaturated acids, the grouping $CMe_2:C$, whether conjugated or not, causes a small increase in molecular refraction, and a large increase in molecular dispersion, in contrast

to the behaviour of this grouping in other compounds, *e.g.*, styrenes (but cf. Meyer, A., 1921, i, 855). The esters, acid chlorides, and nitriles have very similar optical properties.

A comparison between stereoisomeric Δ^a -unsaturated acids and esters reveals that the more stable of a pair of isomerides possesses a higher molecular refraction and molecular dispersion, although the difference is sometimes comparatively small. In accordance with this rule, of the β -chloro-derivatives of the two crotonic acids, the *iso*-derivative is the more stable. Stereoisomeric unsaturated acids, in which there is no conjugation, do not differ appreciably in either molecular refraction or molecular dispersion.

The following new data are recorded. Δ^1 -Tetrahydrobenzoic acid has $d_4^{47.2}$ 1.0717, hence $d_4^{47.0}$ 1.0719, n_D 1.48576, n_{He} 1.49023, n_B 1.49882, n_γ 1.50705 at 47.0°, and its ethyl ester has b. p. 84—86°/12 mm., $d_4^{47.15}$ 1.0032, d_4^{20} 0.998, n_D 1.46793, n_{He} 1.47167, n_B 1.47885, n_γ 1.48558 at 14.15°, n_{He}^{20} 1.4690. 1-Methyl- Δ^4 -cyclohexene-4-carboxylic acid has $d_4^{37.7}$ 1.0085, hence $d_4^{39.0}$ 1.0127, n_D 1.47283, n_{He} 1.47630, n_B 1.48496 at 69.0°. Its ethyl ester, prepared from the acid by means of absolute alcohol and concentrated sulphuric acid, had b. p. 115°/19 mm. (cf. Perkin and Tattersall, T., 1905, 87, 1904), $d_4^{37.0}$ 0.9762, hence $d_4^{18.45}$ 0.9758, d_4^{20} 0.975, n_D 1.46413, n_{He} 1.46748, n_B 1.47473, n_γ 1.48126 at 18.45°, n_{He}^{20} 1.4695. A second sample, prepared from ethyl iodide and the silver salt, had $d_4^{17.2}$ 0.9780, d_4^{20} 0.976, n_D 1.46551, n_{He} 1.46886, n_B 1.47622, n_γ 1.48263 at 17.2°, n_{He}^{20} 1.4676. The specific exaltation of molecular refraction for these compounds, +0.45, is decidedly smaller than for their acyclic homologues; the exaltation of molecular dispersion is likewise somewhat lower. W. S. N.

Double Refraction of Flowing Dyestuff Solutions. H. FREUNDLICH, C. SCHUSTER, and H. ZOCHER (*Z. physikal. Chem.*, 1923, 104, 119—144; cf. A., 1916, ii, 65, 442).—Sols of benzopurpurin prepared in the cold show marked double refraction down to a concentration of 0.02% when given a rotatory motion; on warming, the solutions pass into the isotropic condition with the loss of the double refraction, but on cooling, the solutions revert to the anisotropic condition, more rapidly the greater the concentration; thus a 3.7% solution reverts in twelve hours, a 1.9% solution in two days, a 0.95% solution in four days, but solutions more dilute than 0.35% do not revert to the anisotropic condition even after many weeks. The addition of electrolytes to such dilute solutions brings back the double refraction. This process has been studied with various electrolytes, and it is shown that the nature of the anion has but little influence, whilst that of the kation is determinative, and, as in coagulation, the valency of the kation is mainly concerned. Inorganic univalent kations (Li^+ , Na^+ , K^+ , Rb^+ , and NH_4^+), when added to a 0.25% sol, exhibit an optimum action at 40 millimols. per litre; bivalent kations (Mg^{++} , Ca^{++} , Sr^{++} , Ba^{++} , and Cd^{++}) have their optimum action at 0.2 millimol. per litre. These concentrations are considerably lower than those at which turbidity is produced in the sols, the values being 110 and 1.0, respectively. With univalent and tervalent organic kations, the two points lie

so close together that the value for the double refraction cannot be definitely determined and the solutions are bleached by these kations. In the case of univalent inorganic kations, a region is found between 60 and 80 millimols. per litre where the activity of the electrolyte is much reduced, whilst with bivalent inorganic kations a similar region lies between 0.3 and 0.7 millimol. per litre. The Tyndall cone of the sols exhibits no such region, it increases in intensity regularly with increasing concentration of electrolyte. Colloids such as gelatin and albumin in certain concentrations prevent the appearance of the double refraction; they behave as protecting colloids. With respect to the production of turbidity, gelatin at first has a sensitising action and then a protective action. Doubly refracting sols containing electrolytes lose their refraction on warming, and a definite transition temperature exists in each case. Below this temperature, the solution may be heated for hours and still keep its double refraction, but above this temperature the double refraction vanishes. The transition temperature depends on the nature and concentration of the electrolyte, the age of the sol, and its previous treatment. The transition temperature is low for Li^+ and Na^+ , higher for K^+ and NH_4^+ , and considerably higher for Ba^{++} and Mg^{++} , and it increases strongly with increasing concentration of the electrolyte and with increasing age. The transition temperature is reduced by shaking the solution with glass beads. The behaviour of the transition temperature can be regarded as due to a peptisation. The foregoing observations show that in all probability the appearance of the double refraction is due to the formation of long particles which are produced by an ordered coagulation, which is distinct from the usual unordered coagulation. The optimum of the double refraction is to be explained by the unoriented coagulation overcoming the oriented coagulation at higher concentrations of electrolytes. Concentrated benzopurpurin sols exhibit long particles in the ultramicroscope, and also a strong sparkling. No difference could be observed ultramicroscopically between the double refracting and non-refracting dilute solutions. The difference probably lies in the amicroscopic particles in these cases. Similar results have been observed with cotton-yellow GX, but here the process takes place more rapidly, so that the details, as in the case of benzopurpurin, are not readily observed.

J. F. S.

Colloidal Supports for [use in] obtaining Emission Spectra of Solutions. JACQUES ERRERA [with R. MASSAIN] (*Compt. rend.*, 1923, 176, 1874—1876).—The electrolyte to be examined is allowed to penetrate into two cylindrical pieces of gelose, which are fitted into brass tubes and made the electrodes (cf. Gramont, A., 1908, ii, 3).

E. E. T.

Infra-red Spectra. Ultra-red Spectra of Various Substances and Ultra-red Absorption Spectra of Benzene and some of its Compounds. J. E. PURVIS (*Proc. Camb. Phil. Soc.*, 1923, 21, 556—565).—The ultra-red emission spectra of a Nernst filament, a Nernst heater, a Welsbach light, a fish-tail burner, a Bunsen burner,

an acetylene jet and a carbon monoxide jet have been measured. The ultra-red spectra are plotted over the range $1-12\mu$. Curves showing the percentage of the ultra-red radiation of various wavelengths, transmitted by iodobenzene, bromobenzene, and benzene, have been constructed from absorption data obtained with the liquids and vapours, and these results have been compared with those of Coblenz ("Infra-red spectra," Carnegie Inst. of Washington, 1905).
J. F. S.

"Raies Ultimes" and Series Spectra. A. DE GRAMONT (*Compt. rend.*, 1922, **175**, 1025—1029).—The raies ultimes are those lines in the spectrum of an element which are the last to disappear as the content of the element in the substance examined approaches zero. These lines, both in the arc and spark spectra, always belong to the principal series of doublets, types $[H]$ and $[K]$ of calcium, and in the flame they belong to the type $[g']$ of calcium. They are always the first terms of the principal series, as is illustrated by a table of these lines. It should be possible to utilise the "raies ultimes" for the elucidation of the spectra of the elements for which the principal series spectra are not yet known, particularly those of iron, vanadium, titanium, etc. Mercury forms the sole exception to these rules, for the most sensitive line, λ 2536.5, does not belong to a principal series.
W. E. G.

The Fundamental Orbit of Atoms. M. A. CATALÁN (*Anal. Fis. Quím.*, 1923, **21**, 162—165).—In the consideration of the spectrum of an element uncertainty may exist as to which term should be taken as the fundamental orbit of the atom. From a consideration of the values for the terms in a number of spectral series the following rules are deduced. 1. A member of a series must be considered as belonging to a principal or sharp series according to whether $+v=mp_i - ns$ or $+v=ns - mp_i$. 2. For equal values of m and n the terms ms are always less than the terms np_i , i.e., $2s < 2p_i$, $3s < 3p_i$, and so on. 3. The first value of the sharp term corresponds with $m=1$, that of the principal term to $m=2$. A term $1S$ and a term $1s$ never occur together in the same spectrum. The single value for the sharp term for which $m=1$ is the fundamental orbit whether $1S$ or $1s$. The terms $1s$ in the case of the alkali metals and $1S$ in the case of the alkaline-earth metals permit the calculation of ionisation potentials in agreement with observation.
G. W. R.

The Spectrum of Ammonia. W. B. RIMMER (*Proc. Roy. Soc.*, 1923, $[A]$, **103**, 696—705).—Of the three bands associated with the spectrum of ammonia, the ultra-violet band with its centre at about λ 3360 has been investigated by Fowler and Gregory (*A.*, 1918, ii, 282; 1919, ii, 253), and was found to be represented in the solar spectrum. Employing a concave grating giving a normal dispersion of about 5.5 \AA. per mm. in the first order spectrum, the author has investigated the structure of the "Schuster bands" at $\lambda\lambda$ 5635 and 5670 \AA. , and of the α -band of Eder and Valenta in the spectrum of ammonia, the former bands being observed when a discharge is

passed through a vacuum tube through which a stream of ammonia flows, and the latter appearing in the spectrum of the flame of ammonia burning in oxygen. The Schuster bands showed no sign of resolution into lines, and it is probable that these bands do not occur in the solar spectrum. The α -band consists of about 3,000 lines. The wave-lengths and intensities of the strongest and sharpest of these are tabulated. No conclusive evidence that this band occurs in either solar or sunspot spectra was obtained. The observations, whilst confirming the suggestion of Lewis that the Schuster bands probably represent the true spectrum of ammonia and do not depend on dissociation for their emission, indicate further that the α -band is due to an emission centre representing a first stage of dissociation of the normal ammonia molecule into more stable forms, and the ultra-violet band is due to an emission centre which represents a still more advanced stage of dissociation, preceding complete dissociation into the constituent atoms.

J. S. G. T.

Influence of an Electric Field on the Series Spectrum of Helium. W. TSCHULANOWSKY (*Z. Physik*, 1923, 16, 300—313).—The characteristics and behaviour of various series of single lines and doublets in the series spectrum of helium, and more especially the behaviour of the Bergmann series of single lines, $2P-m\Delta$, ($m=4, 5, 6, 7$) and the super-Bergmann series of doublets $2p_n-m\Delta_n$, ($n=1, 2; m=4, 5$), in an electric field, are discussed theoretically and practically. The author concludes that in the case of these lines, as in the cases of the series $2S-mD$, and $2P-mD$, additional lines, necessitating a third quantisation, appear when the helium source of radiation is excited in an electric field (cf. Takamine and Kokubu, A., 1919, ii, 125, 379).

J. S. G. T.

The Ionisation of Helium and the Excitation of the Spectra of this Gas by Slow-moving Electrons. G. DÉJARDIN (*J. Phys. Radium*, 1923, 4, 121—128).—The results obtained are in agreement with the experiments of Davies (this vol., ii, 281). The ionisation of helium under a pressure of a few tenths of a millimetre took place at 25.2 volts, and was accompanied by the simultaneous appearance of the orthohelium and parhelium spectra. When the pressure attained several mm. of mercury, an appreciable ionisation was produced at 20.4 volts, and again the appearance of the two series was noted. It was found impossible to excite these two series separately. When the pressure of mercury in the helium was allowed to rise to 0.1μ , the ionisation commenced below 20.4 volts, but augmented rapidly when the potential passed this value. The band spectrum of helium is observed only when the pressure of the gas passes 3 mm. and the voltage exceeds 20.4 volts. The intensity increases with pressure. The results support the hypothesis of Lenz and Sommerfeld that the band spectra are due to a molecule He_2 resulting from the combination of two abnormal helium atoms. The spark spectrum are best visible at a pressure below 3 mm. and above 80 volts. At higher pressures this spectrum is masked by the band spectra. The rays of the Pickering series were not observed. W. E. G.

The Discontinuity K of Absorption of Krypton and Xenon.

M. DE BROGLIE and A. LEPAPE (*Compt. rend.*, 1923, **176**, 1611—1612).—The position of discontinuity of absorption K in the X-ray spectrum does not appear to have been measured in the case of the rare gases. The authors found for krypton $\lambda = 0.8648 \text{ \AA}$. $N=36$ and for xenon $\lambda = 0.3588 \text{ \AA}$. $N=54$. The measurements were made at atmospheric pressure in glass tubes of 20 cm. in length, the rays traversing the length of the tube. H. J. E.

Fine Structure of the Limits of High Frequency Absorption.

L Limits of Xenon. A. LEPAPE and A. DAUVILLIER (*Compt. rend.*, 1923, **177**, 34—37).—The authors have measured, using a tungsten anti-cathode, the three L -limits of xenon and obtained the values: L_3 2272.4, L_2 2425.3 and L_1 2587.5 X units. E. E. T.

Quantitative Researches on the Ultra-violet Spark Spectra of Copper in Aluminium.

XAVIER WACHÉ (*Compt. rend.*, 1923, **177**, 39—41).—In an alloy containing one metal in small quantities, the quantitative indications afforded by spectrum analysis on its composition depend on the nature (particularly the specific volume) of the metal present in the larger quantity. For equal concentrations, copper is less sensitive in aluminium than in a more dense metal such as zinc. A series of measurements of the spark spectra of various alloys of copper with aluminium was made, and it was found that the total copper spectrum is only obtained when copper is present to the extent of 60% of the total alloy. The spectrum of aluminium is also complete in these circumstances, being so with alloys possessing an aluminium percentage of as low as 20%. The copper spectrum is practically absent with copper present to the extent of only 5 parts in 10,000. E. E. T.

Wave-length Measurements in the Arc Spectra of Gadolinium and Dysprosium.

C. C. KIESS (*U.S. Bur. Standards Sci. Paper*, 466, 1923, 695—706).—A list of 950 lines in the arc spectrum of gadolinium and of 800 in that of dysprosium is given from a wave-length of 550 \AA . in the green and extending well into the ultra-red region. Most of the lines are faint, and a number have the appearance of band heads indicating that each element emits a faintly banded spectrum. The results obtained are in good agreement with those previously obtained by Eder (cf. A., 1918, ii, 189; 1919, ii, 381). A. R. P.

The Zeeman Effect in the Arc and Spark Spectra of Manganese.

E. BACK (*Z. Physik*, 1923, **15**, 206—243).—A detailed account is given of an experimental investigation of the magnitude and other characteristics of the Zeeman effect exhibited by the various triplet and multiplet systems of lines in the arc and spark spectra of manganese determined by Catalán (A., 1922, ii, 726). Interpreted by means of Landé's theory (*Z. Physik*, 1923, **15**, 189), certain series differences determined by Catalán are considered, contrary to the conclusion of the latter, to afford evidence of a fundamental difference in the spectra of Mn and Mn^+ . J. S. G. T.

Regularities in the Arc Spectrum of Iron. F. M. WALTERS (*J. Washington Acad. Sci.*, 1923, **13**, 243—252).—Two hundred and twelve lines of the spectrum of iron have been classified into multiplets. The correlation of these multiplets with temperature classification is fairly satisfactory, but inspection of the Zeeman patterns show that these data are homogeneous for some groups and quite discordant for others. W. E. G.

Structure of the Spectrum of the Neutral Chromium Atom. MIGUEL A. CATALÁN (*Anal. Fis. Quím.*, 1923, **21**, 84—125; cf. this vol., ii, 104).—A full description of the flame, arc, and spark spectra of chromium. Two classes of lines occur which may be attributed to the neutral and ionised atom, respectively. The lines of the first class can be grouped into series of triplets following Rydberg's formula with the universal constant R . They may be classified into (1) a system of series of ordinary triplets (principal, sharp, and diffuse); (2) another system similar and parallel at a distance of 4436·4; (3) a system of narrow triplets (principal and sharp); (4) lines formed by combination of the preceding systems; (5) twelve multitruplets; (6) lines formed by combination of the first three systems and system (5). The ionisation potential of chromium calculated from the term $1s$ is 6·7 volts. The first resonance potential calculated from the triplet λ 4254, 4275, 4290 is 2·89 volts. G. W. R.

Röntgen-ray Spectroscopy Applied to Metallic Compounds. KARL BECKER and FRITZ EBERT (*Z. Physik*, 1923, **16**, 165—169).—Results, as follows, have been obtained by the application of the Debye-Scherrer method of Röntgen-ray analysis, for the respective lengths of side, a , of the elementary cubical cells, and the calculated value, d , of the density of certain metals, metallic compounds, alloys, and mixed crystals: Ta, a 3·32 Å., d 16·3; Cu_2Zn_3 , a 4·01 Å., d 8·17; mixed crystals containing 96·3% Mg_2Al_3 and 3·7% Al, a 4·80 Å., d 2·62; NiAl , a 2·82 Å., d 6·25; Cu_3Al , a 3·47 Å., which is smaller than the values of a (4·07 Å.) for aluminium, and (3·68 Å.) for copper, d 8·52; Ni_6W , a 3·68 Å., d 11·94. The two latter substances are most probably mixed crystals. The crystal lattice of an alloy of tungsten with 6% of nickel corresponds with the typical regular space-centred tungsten lattice. The results indicate that Bain's rule indicating the relation of the crystal symmetry of a compound to the symmetry of the components (*Chem. and Met. Eng.*, 1923, **28**, 21, 63) is not of general application. The crystal lattice of tantalum is space-centred, regular, whilst that of thallium surface-centred is tetragonal, having a 4·75 Å., c 5·40 Å. The calculated value of the density in the latter case is 11·02. J. S. G. T.

A Simple Method for the Measurement of Absorption in the Ultra-violet. CHR. WINTHER (*Z. wiss. Photochem.*, 1923, **22**, 125—130).—The method devised by the author and others (A., 1922, ii, 729) for the measurement of spectral absorption in the ultra-violet by comparison of the absorption with that of p -nitrosodimethyl-

aniline, has been improved by the use of a gauze of copper 0.15 mm. thick, as employed by Ham, Fehr, and Bitner (*J. Franklin Inst.*, 1915, **178**, 299), in place of the liquid as comparison substance. A series of exposures of a photographic plate to the light transmitted by various thicknesses of the substance being investigated is made in the usual manner, and the absorption curve determined by ascertaining a series of points, corresponding with the various thicknesses, where the light transmitted by the substance and the gauze, respectively, produced equal photographic effects on the plate. For visual observations, a plate coated with fluorescent quinine sulphate is employed. Results obtained by the application of the method to the case of a 0.002 molar solution of salicylic acid in alcohol are in close agreement with the results obtained by Henri.

J. S. G. T.

Absorption of the Ultra-violet Rays by Phosphorus and some of its Compounds. J. E. PURVIS (*Proc. Camb. Phil. Soc.*, 1923, **21**, 566—567).—The absorption of ultra-violet light from a condensed cadmium spark by the vapour of phosphorus, phosphine, and phosphorus trichloride has been investigated at various temperatures. The results show that neither phosphorus nor its compounds with hydrogen or chlorine exhibit any absorption bands in the ultra-violet.

J. F. S.

The Absorption Produced by Electrically Luminescent Sodium Vapour. F. H. NEWMAN (*Phil. Mag.*, 1923, **46**, 22—28).—The self-reversal of spectrum lines, and the absorption phenomena exhibited by a mixture of sodium and potassium vapours rendered luminescent by an electrical discharge have been investigated. The potassium lines were throughout faint compared with those of sodium, but became relatively brighter as the voltage applied to the discharge tube was decreased. Raising the temperature of the vapour from 300° to 450° caused strong self-reversal of the *D*-lines as seen through the end of the discharge tube, but no other lines exhibited self-reversal. Contrary to expectation, the intensities of the subordinate series lines were not observed to be increased in a constricted part of the discharge. This effect is attributed to self-reversal of the lines observed in the region of the constriction, where conditions favour absorption of radiation consisting of lines converging to $2p$, rather than of the *D*-lines. Self-reversal of the subordinate lines was less marked when the discharge current was reduced. Absorption of radiation corresponding with the *D*-lines alone was observed when white light passed through the luminous mixture of vapours.

J. S. G. T.

The Ultra-violet Absorption Spectrum of Glyoxal. A. LUTHY (*Compt. rend.*, 1923, **176**, 1547—1548).—The absorption spectrum of a hexane solution of glyoxal, the first case in which narrow bands have been observed for an aliphatic substance, is shown in comparison with that of acetaldehyde. It is divided into three distinct regions, the first of which (between $\lambda=4613$ and $\lambda=3119 \text{ \AA.}$) contains seventeen narrow bands arranged in four groups,

the second one large band in the middle ultra-violet ($\lambda=2800$), and the third a large band in the extreme ultra-violet ($\lambda=1950$).

H. J. E.

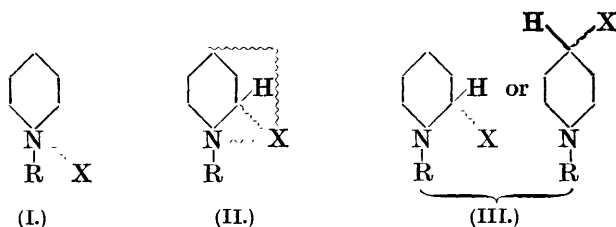
The Ultra-violet Absorption Spectrum of Diacetyl. GUILLAUME C. LARDY (*Compt. rend.*, 1923, 176, 1548—1550).—Diacetyl in hexane solution gives an absorption spectrum which differs from those obtained with other solvents in showing greater resemblance to those obtained for the vapour. Four narrow bands exist between $\lambda=4512$ and 4054 \AA. , and the curve rises steadily in the extreme ultra-violet.

H. J. E.

The Ultra-violet Absorption Spectrum of *p*-Benzoquinone. F. W. KLINGSTEDT (*Compt. rend.*, 1923, 176, 1550—1552; cf. two preceding abstracts).—The spectrum of *p*-benzoquinone in hexane solution is shown in comparison with that obtained by Baly (T., 1906, 89, 502). A large band occurs in the middle region ($\lambda=2790 \text{ \AA.}$), and one of high absorption value ($\epsilon=20,000$) in the extreme ultra-violet ($\lambda=2410 \text{ \AA.}$); the position and intensity of the latter are similar to those which are exhibited by all substances possessing two or three ethylenic linkings. Certain bands in the visible spectrum are also described, these being similar to those obtained in the cases of glyoxal and diacetyl, and it is pointed out that this resemblance is of importance in dealing with the theory of quinone structure.

H. J. E.

Relation between Absorption and Structure. VI. The Structure of 1-Arylpyridinium Salts and Cyclammonium Salts generally. VSEVOLOD ALEXANDROVITSCH IZMAILSKI (*J. Russ. Phys. Chem. Soc.*, 1920, 52, 303—344).—According to the author's views on chromoisomerism (cf. A., 1915, ii, 198; 1916, i, 287), cyclammonium salts exhibit tautomerism, passing from the ammonium (I) to the carbonium (III) formulæ through an intermediate chromonium phase (II), thus



The position of equilibrium depends on a number of factors, such as structure, presence of substituents, and physical influences (solvents, temperature, etc.). The intermediate or chromonium phase is responsible for the development of colour in these compounds; the other two forms are supposed to be colourless or faintly coloured and the compound is coloured only if these "limiting conditions" are not realised. Hydrogen and methyl in place of R in the above formulæ tend to make the nitrogen more basic and thus favour the ammonium phase; the salts are colourless,

show little absorption, and are good conductors. The introduction of the phenyl group, on the other hand, weakens the basicity of the nitrogen, and the carbonium phase is favoured; in extreme cases, the salts (such as the chlorates) are again colourless and show more or less pronounced fluorescence (cf. following abstract). The chromonium phase, or "meso-condition," is favoured by an intermediate state. The nature of the anion (X) is also important; thus, in the phenylpyridinium series, the iodides are the most strongly coloured, bromides less so, and the salts of oxygen-containing acids still less.

Rise of temperature favours the "meso" form and produces a deepening of the colour owing to the well-known tendency of the quinquivalent nitrogen to pass into the tervalent condition in these circumstances (cf. the dissociation of ammonium salts on heating). The solvent in which the heating is carried out has a considerable effect on the change; non-hydroxylic solvents with a low dielectric constant, such as chloroform, favour the production of the coloured form, whilst hydroxylic solvents inhibit the change; these solvents have been shown to affect the dissociation of quaternary ammonium salts in the same way (cf. Wedekind and Paschke, A., 1911, i, 628; von Halban, A., 1911, i, 852). Hantzsch's views of the constitution of these compounds, involving the existence of two isomeric ammonium formulæ, are criticised at length (cf. A., 1911, i, 673); the application of the theory to the chromoisomerism of *o*-quinoneimine and xanthene dyes is discussed and formulæ similar to (II), in which the anion is connected simultaneously to two or more atoms in the molecule, are devised for several of these substances.

Spectrographic measurements on a number of salts of the 1-phenylpyridinium series (cf. this vol., i, 602) were carried out.

To prove the analogy of the 1-phenylpyridinium salts with the chromonium salts of triphenylcarbinol, double compounds with hydriodic acid and tin tetrabromide and tetraiodide were prepared. Phenylpyridinium iodide gives an unstable, yellow compound with hydrogen iodide; a brownish-orange compound with tin tetrabromide, and a nearly black, crystalline compound, $C_{11}H_{10}NI, SnI_4$, with tin tetraiodide, which was analysed. The behaviour of the pyridinium salts towards various solvents is described.

G. A. R. K.

Relation between Absorption and Structure. VII. Fluorescent *N*-Arylpyridinium Salts. V. A. IZMAILSKI (*J. Russ. Phys. Chem. Soc.*, 1920, 52, 344—358).—When exposed to the light of an induction arc, a number of arylpyridinium salts exhibit fluorescence in the solid state; the phenomenon is not observed in solution, and is due almost entirely to the action of ultra-violet rays, because filtration of the light through an uviolet plate or glass prevents it completely; no fluorescence is observed when the compounds are illuminated by means of a Nernst lamp. The occurrence of the phenomenon is closely bound up with the structure of the compounds, and is dependent both on the nature of the

organic radicle R attached to the nitrogen atom and that of the acid radicle X (see preceding abstract). When $R=H$ or CH_3 no fluorescence is observed; nearly all *N*-phenyl derivatives fluoresce to some extent, and the fluorescence is greatly enhanced by the presence of a methoxy- or an ethoxy-group, less so of an hydroxyl group, in the benzene ring; the para-compounds are particularly strongly fluorescent. The methyl group, on the other hand, has an unfavourable effect, whilst halogens and nitro-groups destroy fluorescence altogether (cf. Meyer, A., 1903, ii, 706). The substitution of β -naphthyl for phenyl increases the fluorescence, whilst the introduction of α -naphthyl is unfavourable.

The introduction of hydroxyl into the pyridine nucleus itself (in the 3-position) affects fluorescence adversely; the fusion of the nucleus with an aromatic ring is favourable, but the compounds are greatly affected by the substituents, such as methyl groups, present in the pyridine ring.

The influence of the anion in these salts is considerable in the order $-ClO_4 > -NO_3$ and $-SO_4 > -Cl > -Br > -I$, the chlorates being the most strongly fluorescent.

Acyclic ammonium salts do not exhibit fluorescence, the tetramethyl-, phenyltrimethyl-, phenyldimethylethyl-, and phenylbenzyl dimethyl-ammonium chlorates having been specially investigated. The new salts prepared include *pyridinium chlorate*, white leaflets, m. p. above 250° ; *methylpyridinium chlorate*, crystals, m. p. about 130° ; *phenyldimethylethylammonium chlorate*, colourless needles, m. p. indefinite, about 200° ; *phenyltrimethylammonium chlorate*, yellow powder, m. p. $130-150^\circ$. A list is given of the 103 compounds examined.

From the above facts it is concluded that ammonium salts and pyridinium salts having an ammonium structure do not exhibit fluorescence; the fluorescence of dihydropyridine derivatives (cf. Ley and Engelhardt, A., 1908, ii, 911; 1910, ii, 813), of such compounds as maleinimide and succinimide and of heterocyclic compounds existing in a carbonium phase point to the latter possessing the function of a fluorophore in the cases under discussion. The phenyl group attached to nitrogen may share in this function, but it is not sufficient to produce fluorescence if the nitrogen is quinquivalent, as in the acyclic ammonium salts described above; whilst tervalent nitrogen appears to function as an auxophore. In accordance with this, conditions favouring the basic function of the nitrogen and, consequently, the ammonium form of the salt are unfavourable to fluorescence, whilst conditions diminishing the basicity of the nitrogen have the reverse effect. G. A. R. K.

Investigations on the Dependence of Rotatory Power on Chemical Constitution. XX. The Rational Study of Optical Properties including Refraction. HAROLD HUNTER (T., 1923, 123, 1671—1682).

The Natural Optical Activity of Regular Crystals of Sodium Chlorate and Sodium Bromate. CARL HERMANN (Z. Physik, 1923, 16, 103—134).—Born's theory of the optics of crystals, based

on dynamical considerations applied to the crystal lattice (*ibid.*, 1922, 8, 390), is employed to deduce expressions, in the form of power series, for the respective optical rotatory powers of sodium chlorate and sodium bromate, crystals characterised by being regular and optically isotropic, which are optically inactive when in solution or molten. Observed and calculated values of optical rotatory power for wave-lengths between 4×10^{-5} and 8×10^{-5} cm. are in close agreement in the case of sodium bromate. Complete agreement, at least for the long wave-length region, is obtainable by a slight displacement of the electronic centre of mass. Differences shown in the region of short wave-lengths indicate that the assumptions made in the theory, viz., that the electrons and corresponding anion may be regarded as concentrated in respective points, is unjustified in the region of resonant frequencies. In the case of sodium chlorate, calculated values of the rotatory power are approximately only one-half the experimental values. This result indicates the necessity for considerable alteration in the structure of the lattice model employed in developing the theory, possibly effected by a displacement of the centre of mass of the electrons, a procedure possible only with Vegard's model (this vol., ii, 162) and not with those of Kolkmeier, Bijvoet, and Karssen (A., 1921, ii, 200) or Dickinson and Goodhue (A., 1922, ii, 145). J. S. G. T.

The Behaviour of the More Important Carbohydrates (Dextrose, Galactose, Lævulose, Mannose, Maltose, Lactose, Sucrose) in Strong Acid, Alkali, Sulphite, and Hydrogen Sulphite Solutions. II. The Mutarotation and Rotation of Carbohydrates under the Action of Strong Acids. B. BLEYER and H. SCHMIDT (*Biochem. Z.*, 1923, 138, 119—141).—Arising out of the authors' work on the hydrolysis of lactose by strong acids (this vol., ii, 306), the effects on the specific rotation of various mono- and di-saccharides of concentrations of sulphuric acid up to $28N$ are investigated. The changes of $[\alpha]_D$ shown by such sugars as dextrose and galactose are classified as primary and secondary. The former type of change is a gradual rise of equilibrium $[\alpha]_D$ with increasing concentration of acid up to $22N$. For any given concentration up to this limit, the $[\alpha]_D$ initially reached is constant. The secondary change, shown in acid concentrations of $24N$ and above, is a slow upward change of rotation from the initial equilibrium value, which is ascribed to a gradual condensation of the monosaccharide to form disaccharides (maltose, isomaltose, galactobiose). Lactose shows the same type of primary change as dextrose and galactose; hydrolysis begins at $18N$. Maltose is exceptional in that the variation of $[\alpha]_D$ with acid concentration is much less marked than in the case of the other sugars mentioned, a slight fall up to $12N$ and a rise from $12N$ to $22N$ being observed. In $24N$ acid maltose reaches the same final equilibrium as is attained by dextrose in the same acid concentration. Mannose in $24N$ - H_2SO_4 shows an initial equilibrium lævorotation (cf. the equilibrium dextrorotation in water) which slowly changes to dextrorotation. It is suggested that this is again due to disaccharide formation.

Lævulose shows an increase of $[\alpha]_D$ up to 16*N* acid; above this concentration, a fall in $[\alpha]_D$ associated with decomposition is observed. Sucrose in 28*N*-H₂SO₄ at 15° is immediately hydrolysed. The observations are extended to other acids (hydrochloric, nitric, perchloric, formic, and acetic) with results similar to those already recorded. In its behaviour towards concentrated nitric acid ($d=1.38$) lævulose differs from the other sugars, which show rises in $[\alpha]_D$ followed by falls and the formation of coloured decomposition products. Lævulose shows a continuous slow fall in $[\alpha]_D$ to an equilibrium value which corresponds with the formation of a colourless oxidation product. This has not been identified, but it is suggested that it may be of the type of β -ketogluconic acid.

It is concluded that these results do not accord with the existing theories of mutarotation (Lippmann, Hudson, Fischer, and Tollens), and a new theory is deduced which involves the fusion of the Lippmann and Hudson theories with the "hydration" theories.

J. P.

Rotation Dispersion. I. LIFSCHITZ (*Z. physikal. Chem.*, 1923, 105, 27—54).—Rotation of the plane of polarised light and rotation dispersion is discussed, and it is shown that the existence of optical activity depends on the presence of at least four coupled electrons, which possess only axial symmetry. This system may be carried by a single atom or by several atoms of the molecule, and in the first case the atom carrying the asymmetric electron system is known as the asymmetric atom. A close relationship exists between absorption of light and the Cotton effect. The Cotton effect is to be expected in those bands which may be attributed to the asymmetric or, better expressed, axial symmetric electron systems. An optically active molecule may contain several such electron systems, and consequently the rotation dispersion can, because of internal superposition, exhibit an abnormal character. The relationship between rotation dispersion and absorption and circular dichroism, respectively, in the absorption bands of active substances can furnish valuable information in connexion with analysis of spectra and in the consideration of stereochemical problems. The rotation dispersion of a large number of heavy metal complex derivatives and organic substances has been investigated, and the results have been discussed in connexion with spectroscopic, photochemical, and stereochemical data. The specific rotation of the bivalent cobalt, nickel, and uranyl derivatives of *d*-hydroxymethylenecamphor and nitrocamphor, the trivalent cobalt, chromium, and aluminium salts of *d*-hydroxymethylenecamphor, *d*-hydroxymethylenecamphor, *d*-camphorquinone, oximinocamphor, and camphorquinone-phenylhydrazone has been measured in various solvents and with light of various wave-lengths. The results are presented in tabulated form and also as curves. In the formation of resolvable complexes from active materials, in many cases partial asymmetric syntheses are achieved, the significance and nature of which are discussed.

J. F. S.

The Theory of Photochemical Reactions. W. NERNST and W. NODDACK (*Sitzungsber. Akad. Wiss. Berlin*, 1923, **15**, 110—115).—Various typical photochemical reactions are briefly reviewed, and the authors conclude that whilst in purely photochemical processes light is absorbed in quanta, experimental verification of this fact is possible only for radiation confined within a restricted spectral region, and when the reaction occurs under relatively simple conditions, as the photochemical process is, in general, accompanied by a dark reaction which very materially affects the amount of substance transformed. General thermodynamic considerations indicate, as pointed out by Warburg (A., 1920, ii, 210) that the quantum relation $Q=Nh\nu$ cannot apply in the case of a photochemical process effected by radiation of such long wavelength that the quanta are too small to render the reaction possible. In the case of photochemical processes effected by radiation characterised by very large quanta, *e.g.*, the effect of Röntgen rays on a photographic plate, the amount of substance transformed is very much larger than that calculated from the quantum relation $Q=Nh\nu$, and in all such cases the relation must be replaced by the equation $Q=Nq$, where q denotes the energy of atomic dissociation of the molecule concerned. The photochemical law of equivalence may be shown to hold when the absorbed quantum of energy is not greatly different from the energy necessary to initiate the chemical process concerned and when the photochemical process proper is not accompanied by secondary reactions.

J. S. G. T.

Investigation of the Application of the Photochemical Equivalence Law to Dry [Photographic] Plates. J. EGGERT and W. NODDACK (*Sitzungsber. Akad. Wiss. Berlin*, 1923, **15**, 116—122).—In continuation of previous work (*ibid.*, 1921, **13**, 631), the authors have shown that the photochemical equivalence law is applicable to the process occurring when a silver bromide gelatin emulsion is illuminated with radiations of respective wavelengths 436, 405, and 365 $\mu\mu$, provided the incident radiation is not too intense.

J. S. G. T.

Action of Traces of Impurities on the Photochemical Synthesis of Carbonyl Chloride. J. CATHALA (*Bull. Soc. chim.*, 1923, [iv], **33**, 576—581).—An apparatus for the study of the photochemical synthesis of carbonyl chloride is described consisting essentially of an ampoule containing the liquefied gas, which is allowed to evaporate into a graduated reservoir charged with mercury. A measured volume is displaced by the mercury into a quartz vessel heated to about 850° in an electric furnace, where the carbonyl chloride is completely dissociated and passes after cooling into a jacketed transparent quartz vessel illuminated by the light of a mercury vapour lamp. The product is analysed by estimations of the free and the combined chlorine. The preliminary experiments revealed considerable variations in the yield under similar outward conditions, increasing yields of carbonyl chloride being obtained from the carbon monoxide and chlorine

derived from the dissociation of the vapours evolved from the later fractions of liquefied carbonyl chloride in the ampoule. The introduction of a small quantity of air into the gases at the later stage once again caused a lowering of the yield, but this could not be attributed to the effect of oxygen in this case, as this gas would be eliminated as carbon dioxide in the furnace, and it is therefore the carbon dioxide formed from carbon monoxide and the oxygen dissolved in the liquefied carbonyl chloride which apparently causes the observed retarding action on the photochemical synthesis.

G. F. M.

Photochemical Studies. I. Photochemical Decomposition of solid Oxalic Acid.

W. ALBERT NOYES, jun., and A. B. KOUPERMAN (*J. Amer. Chem. Soc.*, 1923, **45**, 1398—1400).—The photochemical decomposition of anhydrous oxalic acid, hydrated oxalic acid, a saturated solution of oxalic acid in contact with the solid, and formic acid has been investigated. As sources of illumination were used a carbon arc which gave light down to $250\ \mu\mu$, a carbon arc in which the electrodes had been previously soaked in salt solutions, which extended the range to $220\ \mu\mu$, a mercury lamp with a quartz window giving light to $185\ \mu\mu$, and a mercury lamp with a fluorite window giving light to $100\ \mu\mu$. The results show that anhydrous oxalic acid is decomposed by ultra-violet light of wave-lengths shorter than $250\ \mu\mu$. The rate of decomposition is greater for shorter wave-lengths. The rate of decomposition is much increased by the presence of water, but there is a long induction period which is less when water is present than when it is absent. In the case of formic acid, the induction period is small. Since water vapour is one of the products of decomposition, the action may be autocatalytic, and this may be the explanation of the induction period. Other possible explanations of the induction period are that it may be due to the slow production of formic acid, this being then rapidly decomposed. In this case, the rate of reaction would not reach a maximum until the rate of production of formic acid became constant, or the induction period may be due to the slow rate of diffusion of the products of decomposition out of the solid and from the surface. These various possibilities are discussed. After the induction period, the rate of reaction is constant. The wave-length necessary to decompose the solid acid does not agree with that calculated from Perrin's formula, based on a rough determination of the temperature coefficient of the rate of thermal decomposition.

J. F. S.

An Application of the Anti-oxygenising Power of Phenols : Increase in Fastness to Light of Dyes on Fibre. ALFRED GILLET and FERNAND GIOT (*Compt. rend.*, 1923, **176**, 1558—1560; cf. this vol., i, 675).—Treatment of fabrics with dyes which are not fast to light and subsequently with diphenols and other anti-oxygenisers shows that these exert a protective action against light whether they enter into the molecular structure or not. Azo-dyes on cotton and wool and some acid colours such as eosin are protected, but this protection does not extend to nitro-dyes; the

suggestion of auto-oxidation is made with regard to the latter. Fading of triphenylmethane dyes of all types seems to be, not oxidation, but another type of reaction. Basic colours are not protected, quinol in alkaline solution even accelerates the change. In some cases, a considerable excess of the diphenol (10 mols. to 1 mol. of dye) is required to give definite protection. [Cf. *J.S.C.I.*, 1923, Aug.] H. J. E.

Photochemical Transformation of Fluorescent Dye Solutions. PETER PRINGSHEIM (*Z. Physik*, 1923, **16**, 71—76).—In reply to Weigert's criticism (*A.*, 1922, ii, 681) of the author's previous work indicating that the photochemical law of equivalence does not apply when part of the absorbed radiation is re-emitted as fluorescence, the author shows that, in the case of an alkaline aqueous solution of eosin, which ordinarily is only slightly sensitive to photochemical change, and becomes extremely sensitive when a little ethyl alcohol is added to the solution, identical light-absorbing and fluorescent properties are possessed by both forms of solution. In the extremely sensitive solution, fluorescence and chemical reaction are both excited by light confined to the same spectral region, and can both be produced by monochromatic radiation.

J. S. G. T.

Photoelectric Conduction and Chemical Combination. B. GUDDEN and R. POHL (*Z. Physik*, 1923, **16**, 42—45).—The photoelectric properties of certain compounds, viz., carbonates, halides, oxides, sulphides, etc., of metals such as mercury, silver, cadmium, etc., are correlated with various physico-chemical properties of these substances, viz., colour, lattice energy, volatility, solubility, etc., which are attributed by Fajans (*Naturwiss.*, 1923, **11**, 165) to a distortion of the shell of the anionic electrons by the kations.

J. S. G. T.

Radioactive Constants up to 1923. STEFAN MEYER (*Jahrb. Radioaktiv. Elektronik*, 1923, **19**, 334—344).—The constants given in 1920 (*A.*, 1921, ii, 235) are brought up to date. W. E. G.

Characteristic Röntgen Radiation of the First [Lighter] Elements. J. HOLTSMARK (*Physikal. Z.*, 1923, **24**, 225—230).—In continuation of previous work (*A.*, 1922, ii, 543), the author has investigated photoelectrically the limiting values of potential necessary for the excitation of *K*-radiation in lithium and glucinum, respectively. The value found for lithium is 52.6 volts, and for glucinum a provisional value, 95 ± 5 volts, is given. In the case of lithium, a linear relation, differing according as the value of the exciting potential was respectively above or below the critical value, was established between the ratio of the photoelectric effect to the intensity of the exciting cathode rays and the exciting potential. A similar discontinuity was not observed in the case of glucinum. Available data relating to limiting potentials necessary for exciting *K*-radiation in the case of the lighter elements of atomic number 1—11 are tabulated. A linear relationship exists between the square root of the critical exciting potential

and the atomic number (z) of the corresponding elements for values of z equal to 2, 3, 4, and 5. The relationship in the case of the remaining elements is different, and the cause of this difference is briefly discussed in the light of Bohr's theory of atomic structure.

J. S. G. T.

The Quantitative Measurement of Radium Emanation by the α -Radiation. Corrections for Pressure and for the Nature of the Gaseous Mixture. ADOLPHE LEPAPE (*Compt. rend.*, 1923, 176, 1613—1616).—In measuring the radium emanation used for experiments on the ionisation of gases, certain corrections should be made. When the pressure is less than 720 mm., or if any considerable percentage of carbon dioxide is present, the ionising effect of the emanation is sensibly changed. The dimensions of the condenser should also be taken into account. Results of experiments in which these factors vary over a wide range are given.

H. J. E.

The Constant of Polonium. (MLLE) ST. MARACINEANU (*Compt. rend.*, 1923, 176, 1879—1881).—As the result of a large number of experiments, the author obtains the value 139.5 days for the half-change period, the radioactive constant, λ , being $4.96 \times 10^{-3} \text{ (day)}^{-1}$. The best results were obtained with polonium on glass, with or without a screen. The examination of radioactive material deposited on metallic surfaces is not recommended.

E. E. T.

The Collision Area of Molecules of the Rare Gases towards Slow Electrons. CARL RAMSAUER (*Jahrb. Radioaktiv. Elektronik*, 1923, 19, 345—354).—Measurements of the collision areas of molecules of the rare gases have shown that these gases behave in a very different manner from hydrogen and nitrogen. As the velocity of the electron falls, the area of nitrogen and hydrogen molecules increases to a constant value which does not differ widely from that deduced from the kinetic theory. On the other hand, the collision area of the molecules of the rare gases at first increases to a maximum and then decreases rapidly as the velocity of the electron decreases. For argon, krypton, and xenon, the collision area at the maximum is four or five times, and at 0.75 V is one-seventh of that derived from the kinetic theory. These gases are practically transparent to slow-moving electrons. These results are at variance with the electricity laws, which require that the collision area should approach infinity as the electron velocity approaches zero.

W. E. G.

Dielectric Constants of Colloidal Solutions. IV. J. ERRERA (*Kolloid Z.*, 1923, 32, 373—376; cf. A., 1922, ii, 694; this vol., ii, 225).—A continuation of previous work. The dependence of the dielectric constant of vanadium pentoxide sols on the potential difference with different wave-lengths has been investigated and it is shown that the dielectric constant increases with increasing

potential. The dependence of the dielectric constant of vanadium pentoxide sols on the frequency of the alternating current is expressed generally by a curve which is made up of four sections, a concave slowly rising section, a rapidly rising straight line, a saturation section, and a slowly rising section. The experimental results have been briefly discussed in connexion with the dipole theory.

J. F. S.

Calibration of Cells for Conductivity Measurements. II. Intercomparison of Cell Constants. HENRY C. PARKER (*J. Amer. Chem. Soc.*, 1923, **45**, 1366—1379; cf. this vol., ii, 6).—A new method is described for the intercomparison of cell constants over a large range of concentration and the results of several series of such comparisons are given. The range of concentrations through which the intercomparisons were made is twenty-five times as great as that used previously. The effect of platinising and the disposition of the electrodes on a cell constant is shown by the intercomparison curves. It is indicated that there is a gradual transition in the shape of the curve as the electrodes are placed farther apart, the farthest apart giving a curve showing the most nearly constant value. None of the electrodes compared give what may be considered as a fixed value for the derived cell constant. A new effect, similar in some respects to polarisation, is found to occur at high dilutions with all types of cells used in the present work. This effect is shown to amount to at least 0.33% at moderate concentrations, in the case of one type of electrode which has been used in many accurate conductivity measurements. Correction of the existing conductivity data for this effect would tend to increase the values of the equivalent conductivity at the higher dilutions. The limiting values would probably be affected to a considerable extent, the values of the calculated degree of ionisation being reduced in like proportion. A theory to account for this effect, at high dilutions, is put forward, which assumes the presence of an adsorbed layer in contact with the electrodes. The correction for the resistance of this layer is assumed to be positive or negative, according to whether the adsorbed layer contains an excess or a deficiency of the conducting material.

J. F. S.

Membrane Potentials in the Donnan Equilibrium. DAVID I. HITCHCOCK (*J. Gen. Physiol.*, 1923, **5**, 661—663).—It is pointed out that although Loeb's views on the rôle of Donnan's theory in regulating the properties of proteins necessarily leads to results in agreement with the second law of thermodynamics, his work constitutes a distinct advance. Hill, in his criticism (this vol., ii, 221), has offered no other explanation of the facts. W. O. K.

Phenomenon of Electrical Supertension. III. A. SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1923, **26**, 259—265; cf. A., 1919, ii, 91, 387).—A theoretical paper in which the electrical supertension of a palladium or platinum electrode is considered

when the metal is functioning as a cathode. The equilibria are considered on the basis of the theory of allotropy. J. F. S.

Metallised Electrodes from Porous Clay and the Simplest Form of the Acid-Alkali Cell. K. A. HOFMANN (*Ber.*, 1923, 56, [B], 1456—1463).—The behaviour of electrodes made of tubes of porous clay impregnated with platinum, palladium, or iridium has been examined. The electrodes are moistened with 2*N*-sodium hydroxide solution or 2*N*-sulphuric acid and partly immersed in sulphuric acid or sodium hydroxide solution, their upper portions being surrounded by hydrogen or hydrogen and oxygen, respectively. It is found that such electrodes when placed in the oppositely active electrolyte or in a neutral salt solution render the surrounding gas as active as if they were not immersed in the electrolyte but in the moistening acid or alkali. It follows, therefore, that the electrically active layer must lie at the zone of contact of the gas and the moistening acid or alkali, that is, at the surface of the tube above the liquid. Peculiar properties of the impregnated electrodes are (i) the unexpected stability of the sulphuric acid used in moistening the tubes towards the neutralising action of the sodium hydroxide with which the lower end is surrounded, (ii) the much smaller but still considerable stability of sodium hydroxide towards sulphuric acid under similar conditions, (iii) the increase in potential after the current has been allowed to flow, and (iv) the slower attainment of the highest potential by electrodes moistened with sulphuric acid than by those wetted with sodium hydroxide. A probable explanation of these peculiarities is found in the protective action of the layer of neutral salt produced within the tube. H. W.

Intermittent Current Electrolysis. I. The Influence of Intermittent Current on Overvoltage. SAMUEL GLASSTONE (*T.*, 1923, 123, 1745—1750).

Electrolytic Conduction: Sequel to an Attempt (1886) to Apply a Theory of Residual Affinity. HENRY E. ARMSTRONG (*Proc. Roy. Soc.*, 1923, [A], 103, 619—621).—The theory of residual affinity advanced by the author in explanation of the phenomena of electrolytic conduction (*ibid.*, 1886, 40, 268) is illustrated more especially by reference to the work of Tubandt (*A.*, 1921, ii, 426) on the electrical conducting properties of the heated solid halides of silver and lead. In the case of silver iodide, the primarily active unit is AgI, whilst in lead chloride the active unit is PbCl₂. By assuming one or more of these primary units to be distributed at each electrode and that a circuit is formed by these molecules being coupled with complex molecules which differ in structure in the two cases, the author shows how, in the case of silver iodide, silver is deposited at one electrode and withdrawn from the other, while in the lead halides, the halogen is abandoned to the one electrode and taken from the other, results which agree with those obtained by Tubandt. A similar interpretation may equally be applied to the process of electrolysis of aqueous solutions (this vol., ii, 542). J. S. G. T.

A New Method to Determine the Hydration of Ions. The Hydration of the Lithium-ion. G. BABAROVSKÝ (*Rec. trav. chim.*, 1923, **42**, 533—534; cf. this vol., ii, 288).—Corrects some arithmetical errors in the preceding paper. F. A. M.

Ionisation of Alcohols. ROGER J. WILLIAMS and R. W. TRUESDAIL (*J. Amer. Chem. Soc.*, 1923, **45**, 1348—1353).—An attempt to determine the nature and the extent of the ionisation of ethyl alcohol has been made by investigation of the point of equilibrium of the reaction $\text{EtOH} + \text{NaOH} \rightleftharpoons \text{H}_2\text{O} + \text{EtONa}$. The method of determining the amount of water formed consisted in shaking a known amount of the mixture with a known weight of granules of calcium carbide for a definite length of time so that only about 4% of the water was used up. The calcium in suspension as hydroxide was determined nephelometrically and by comparison of this with the values obtained by the action of calcium carbide on samples of alcohol containing known amounts of water the amount of water actually present in the reaction mixture was ascertained. The results for the degree of ionisation into hydrogen- and ethoxide-ions are, from the nature of the method, too high, but, despite this, they appear to confirm the much more accurate value found by Danner and Hildebrand (this vol., ii, 166, 117). Assuming that esterification is a neutralisation reaction, the degree of ionisation of alcohol into ethyl- and hydroxyl-ions is shown by calculation to be zero. The reaction of methyl alcohol with magnesium nitride, calcium hydride, and calcium carbide, respectively, has been investigated, and it is shown that in each case the alcohol reacts as a weak acid, and that there is no evidence to indicate that it ionises in any other way than as a weak acid, namely, $\text{CH}_3\cdot\text{OH} \rightleftharpoons \text{CH}_3\cdot\text{O}' + \text{H}'$. With magnesium nitride, the reaction is $6\text{CH}_3\cdot\text{OH} + \text{Mg}_3\text{N}_2 \rightarrow 3\text{Mg}(\text{O}\cdot\text{CH}_3)_2 + 2\text{NH}_3$, with calcium hydride, $\text{CH}_3\cdot\text{OH} + \text{CaH}_2 = (\text{CH}_3\cdot\text{O})_2\text{Ca} + \text{H}_2$, and with calcium carbide $2\text{CH}_3\cdot\text{OH} + \text{CaC}_2 = \text{Ca}(\text{O}\cdot\text{CH}_3)_2 + \text{C}_2\text{H}_2$. J. F. S.

Atomic Heats of Cadmium and Tin at Low Temperatures. WORTH H. RODEBUSH (*J. Amer. Chem. Soc.*, 1923, **45**, 1413—1416).—The atomic heats of cadmium and tin have been measured by the same method as was employed by Eastman and Rodebush for similar determinations of the alkali metals (*A.*, 1918, ii, 149). The apparatus was of the same kind, but constructed of metal. The present measurements extend over the range 70—100° K. and are sufficiently accurate for use in fixing the curves for the metals over the temperature range 0—298° K. The following values for C_p are recorded: cadmium, 69·66°, 4·67; 72·40°, 4·74; 77·56°, 4·88; 80·09°, 4·96; 85·06°, 5·04; 87·70°, 5·11; 89·91°, 5·15; 94·70°, 5·23; 97·08°, 5·26; 99·37°, 5·31; 298°, 6·25; tin, 69·93°, 4·57; 72·39°, 4·64; 77·71°, 4·83; 84·00°, 4·98; 88·90°, 5·07; 93·56°, 5·17; 96·21°, 5·26; 101·00°, 5·34; 298°, 6·50. J. F. S.

Chemical Constants of Diatomic Molecules. R. R. S. COX (*Proc. Camb. Phil. Soc.*, 1923, **21**, 541—551).—A theoretical discussion in which it appears that no certain conclusion as to the

chemical constants of diatomic molecules can at present be drawn. It seems quite possible that the discordance between the value found and the theoretical value may have a theoretical basis; but this cannot be asserted until further experimental data are available. Accurate and numerous measurements of p and K_p , further information as to the specific heat of the vapour and solid at low temperatures, and measurements of the band spectra are necessary before much further progress can be made. J. F. S.

Heat Capacities and Entropies of Diatomic and Polyatomic Gases. H. C. UREY (*J. Amer. Chem. Soc.*, 1923, 45, 1445—1455).—A theoretical paper in which the entropy constant for diatomic gases having no vibrational energy is evaluated. The entropy of hydrogen (29·25), nitrogen (45·59), hydrogen fluoride (39·84), hydrogen chloride (42·95), hydrogen bromide (45·79), carbon monoxide (45·6), and nitric oxide (45·3) have been calculated from equations deduced in the paper and the values given in brackets found for 25°. These values have been compared, wherever possible, with experimental entropy determinations, and in most cases an exceptionally good agreement has been found. The moments of inertia of oxygen (41×10^{-40}), hydrogen iodide (4×10^{-40}), and chlorine (109×10^{-40}) have been calculated from their observed entropies, and attention is directed to the probability that oxygen and possibly nitric oxide do not follow the equation deduced. The values for the moment of inertia at 25° are given in brackets. The entropy equation for diatomic gases which possess vibrational heat capacity is discussed. The constant for the entropy equation of gases the molecules of which have tetrahedral symmetry has been obtained and the dimensions of the methane molecule are calculated. Using this equation, $S = R \log_e T^{3/2} M^{3/2} V - 11 \cdot 39 + 3/2 R \log_e T + R \log_e I + 99 \cdot 14$, and inserting the value $I = 2 \cdot 232 \times 10^{-41}$ gives the entropy of methane as 34·25. J. F. S.

The Properties of Saturated Fluids in the Region of the Critical Point. J. E. VERSCHAFFELT (*J. Phys. Radium*, 1923, 4, 158—169).—Assuming that the conditions of continuity are satisfied at the critical point, the characteristic equation of a saturated fluid in this region is deduced by expanding p , the pressure, in a series of ascending powers of $v - v_c$ and of $T - T_c$, v_c and T_c being, respectively, the critical volume and critical temperature of the fluid. The values of the constants in the expansion are determined by applying thermodynamic principles. The v, T saturation curve is, on these assumptions, shown to approximate to a parabola of the second degree in the region of the critical point. The author considers that experimental evidence is in accord with the existence of an analytical discontinuity at the critical point in the case of the critical isothermal, and shows that, under these conditions, the saturation vT curve consists of two branches, similarly directed, of a parabola of the third degree. Moreover, it is considered that the existence of the analytical discontinuity referred to is not in discord with the physical continuity of the liquid and gaseous states. J. S. G. T.

The Thermodynamics of the Formation of Mixed Crystals.

K. F. HERZFELD (*Z. Physik*, 1923, **16**, 84—99).—The formula deduced by Grimm and Herzfeld for the heat of formation of mixed crystals (*ibid.*, 77) from consideration of the energy associated with the respective crystal lattices, is applied to obtain thermodynamic formulæ relating more especially to the entropy, miscibility, and the critical temperature of separation into components, in the case of mixed crystals. Reference is also made to the absorption of salts by crystals at low temperatures, and the precipitation of mixed crystals from solutions. The theoretical results are compared with experimental results in the cases of the pairs of salts, KCl, NaCl; KF, RbF; and KBr, KI. J. S. G. T.

Cryoscopic Investigations of some Solutions in Bromine.

WLADIMIR FINKELSTEIN (*Z. physikal. Chem*, 1923, **105**, 10—26).—The cryoscopic constant for highly purified bromine has been determined by measuring the depression of the freezing point of bromine brought about by dissolving carbon tetrachloride in it. Assuming that carbon tetrachloride is unimolecular and has the molecular weight 153·84, the cryoscopic constant is found to be 83·12. The value obtained from van't Hoff's formula, using 16·185 as the latent heat of fusion of bromine and $-7\cdot32^{\circ}$ as the freezing point, is 86·35. The depression of the freezing point of bromine brought about by arsenic tribromide, sulphur monobromide, aluminium tribromide, and tribromoacetic acid has been determined for several concentrations in each case. The results show that the substances arsenic tribromide, sulphur monobromide, and carbon tetrachloride, which do not conduct an electric current in bromine solution, have molecular weights strictly the same as the theoretical values, whilst aluminium tribromide and tribromoacetic acid which do conduct an electric current in bromine solution have molecular weights twice as large as the theoretical value, and the polymerisation constant in these cases is the same for all concentrations. Further determinations were carried out with phosphorus pentabromide, acetamide, and antimony tribromide; all these substances are conductors of electricity when dissolved in bromine, and in consequence of solvation and polymerisation they form complexes which increase in complexity with increasing concentration. In the case of acetamide, the curve between molecular weight and concentration shows a definite maximum which lies at about 2%, and it is at this point it is suggested that the maximum complexity lies, or at least the influence of dissociation is equal to that of complex formation, and at higher concentration than 2% the dissociation is increasingly greater than the complex formation. The electrical conductivity of the solutions examined is closely connected with the formation of complicated complex molecules. J. F. S.

The Investigation of Double Salts in Solution by Ebullioscopic Methods. F. BOURION and E. ROUYER (*Compt. rend.*, 1923, **176**, 1708—1710).—A mathematical investigation of the law of mixtures as applied to the investigation of double salts in solution

by the method of continuous variations when applied to ebullioscopic measurements (this vol., ii, 57).
G. F. M.

A Method for the Determination of Molecular Weights in Aqueous Solution. KASIMIR JABŁOZYŃSKI (*Istny Zjazd Chemików Polskich*, 1923, 19).—A method for the determination of molecular weights in aqueous solution is described, depending on the difference in the rates of evaporation of a given solution and of water under parallel conditions.
R. T.

Sublimation of Plant and Animal Products. ARNO VIEHAENER (*J. Assoc. Off. Afric. Chem.*, 1923, 6, 473—481).—Apparatus is described for the ready sublimation of large or small quantities of material. Observations of crystalline form, melting and subliming points, etc., may be made directly with the microscope.
A. G. P.

The Principle of a General Method of Determining the Calorific Capacity of Solids and Liquids. Application to the Determination of the Water Value of Calorimetric Bombs. CHARLES MOUREU, CHARLES DUFRAISSE, and PH. LANDRIEU (*Compt. rend.*, 1923, 176, 1513—1515).—The essential feature of the method is the use of two separate resistances, identical in design, material, and electrical value, which are placed in two similar calorimeters. The resistances are set up in series and connected with a source of current. In one calorimeter the solid is placed in a known mass of distilled water; in the other there is a weighed amount of water. A thermometer is placed in each calorimeter, these two thermometers being standardised against each other. The method eliminates errors due to inaccuracy of the thermometer and obviates the use of the mechanical equivalent of heat as a factor in calculation. Moreover, no electrical measurements are necessary while the current is passing. Experiments with this form of apparatus are in progress.
H. J. E.

The Heat of Formation of Solid Solutions. G. BRUNI (*Bull. Soc. chim.*, 1923, [iv], 33, 696—697).—The author criticises Landrieu's results (*A.*, 1922, i, 808), and especially his conclusion that solid solutions are differentiated from mixed crystals by the exceedingly small heats of formation of the latter. Previously published evidence is adduced in support of the present author's contention (cf. following abstract).
H. H.

[**The Heat of Formation of Solid Solutions.**] PH. LANDRIEU (*Bull. Soc. chim.*, 1923, [iv], 33, 697—699).—A reply to Bruni (cf. preceding abstract). The author maintains his previous contention and asserts that his critic has fallen into error by quoting thermal data obtained at temperatures at which the crystals studied are unstable.
H. H.

The Heats of Formation of Quinonoid Structures. ZOFJA BŁASZKOWSKA (*Istny Zjazd Chemików Polskich*, 1923, 27—28).—The reactions of the formation of quinonechloroimine from *p*-amino-

phenol, and of quinonedichlorodi-imine from *p*-phenylenediamine are investigated thermochemically. From these and other results, it is concluded that the heat of formation of the quinonoid structure is greater for naphthalene than for benzene compounds, and less for diphenyl derivatives. The introduction into the nucleus of positive groups increases the heat effect. R. T.

Thermochemical Researches on the Diazotisation of Aminophenols. ZOFJA BŁASZKOWSKA (*Izsy Zjazd Chemików Polskich*, 1923, 28—29).—The heat effects of the action on picramic acid and *p*-aminophenol of excess of hydrochloric acid, excess of sodium hydroxide, of diazotisation, and of sodium hydroxide on the product of the latter, and of the formation of the compound with β -naphthol are measured. These results show that the reactions of picramic acid, and in particular that of diazotisation, take a course different from that with the majority of amines, probably a quinonediazide being produced. *p*-Aminophenol, on the other hand, behaves normally. R. T.

Heat of Solution of Thallium in Dilute Thallium Amalgams. THEODORE W. RICHARDS and CHARLES P. SMYTH (*J. Amer. Chem. Soc.*, 1923, 45, 1455—1460).—The heat of solution of thallium in thallium amalgams of 0.0—11.17% thallium has been determined by the adiabatic method. The following values of the heat of solution in joules at 20° of 1 g.-atom of thallium in amalgams of the composition stated are recorded: 0.92%, 2706; 2.49%, 2265; 3.81%, 1917; 5.21%, 1590; 6.89%, 1075; 8.76%, 486; 10.43%, 45; 11.81%, —234. These values are compared with those obtained by Richards and Daniels for concentrated amalgams, and found to be consistent with them (A., 1920, ii, 34). A short extrapolation of the composition-heat of solution curve above 0.92% gives a value for the heat of solution of thallium in an infinite quantity of mercury of 2970 joules, a value which is in fair agreement with 3220 joules, the value obtained by Lewis and Randall (A., 1921, ii, 241) by calculation from the *E.M.F.* measurements of Richards and Daniels (*loc. cit.*) of thallium amalgam concentration cells. J. F. S.

Calorimetry of High Explosives. (SIR) R. ROBERTSON and W. E. GARNER (*Proc. Roy. Soc.*, 1923, [A], 103, 539—555).—A form of calorimetric bomb designed for measuring the heat developed and the volume of the gases produced by the detonation of high explosives under standardised conditions is described. The charge of explosive was compressed to a uniform density throughout and the explosion was initiated by a standard impulse from a fulminating explosive. The following values were found for the heats of detonation of the respective high explosives: trinitrophenol, 916; trinitrotoluene, 926; and amatol, 80/20 (*i.e.*, 80 parts of ammonium nitrate to 20 parts of T.N.T.), 992 cal. per g., the water in each case being considered as gaseous. The corresponding mean values of the total volumes of gases evolved per g. of explosive were: 727, 711,

and 907 c.c., the values differing slightly according as the explosion was initiated by fulminate or azide. In the case of an explosive, e.g., amatol, the composition of which permits of complete combustion, the heat of detonation and volume of gases evolved agree with those deduced theoretically. The products of detonation of high explosives in a vacuum include carbon dioxide and monoxide, water, methane, acetylene, ammonia, hydrogen cyanide, carbon, and a trace of nitric peroxide. When the explosion is incomplete, larger volumes of nitric oxide are produced and the composition of the products is very different from that of a normal detonation. The following factors, amongst others, influence the nature of the products: density of loading in the container and bomb, completeness of detonation, and purity of explosive, nature of the initiator, and degree of tamping of the explosive. Consideration of the gaseous reactions occurring during cooling of the gases produced indicate that the formation of carbon is accompanied by an increase in the heat of detonation, and a decrease in the volume of gases liberated. Conditions determining the pressure and rate of cooling of the gases evolved also affect the heat and gases of explosion. The greater the density of loading and tamping of the explosive, the higher the pressure and the greater the deposition of carbon during the cooling process, the heat of detonation being increased and the volume of gases liberated being decreased thereby.

J. S. G. T.

Piezo-chemical Studies. XIX. Experimental Determination of the Fictitious Volume Change in Solution Equilibria. ERNST COHEN and A. L. TH. MOESVELD (*Z. physikal. Chem.*, 1923, **105**, 145—154; cf. A., 1920, ii, 621).—Four methods are described for the experimental determination of the fictitious volume change in solution equilibria. Two methods are volumetric and two electrical; one method of each kind has been previously described (*loc. cit.*), but the two remaining methods are new. All four methods have been tested experimentally, and the results are recorded and the methods shown to be generally applicable.

J. F. S.

Piezo-chemical Studies. XX. Experimental Proof of Braun's Law by an Electrical Method. II. ERNST COHEN, FUSAO ISHIKAWA, and A. L. TH. MOESVELD (*Z. physikal. Chem.*, 1923, **105**, 155—172).—Braun's law can be expressed in the form $(dc/d\pi)_T : (dc/dT)_\pi = -T\Delta v/Q$, where T is the absolute experimental temperature, $(dc/d\pi)_T$ is the pressure coefficient of the solubility at constant temperature, $(dc/dT)_\pi$ is the temperature coefficient of the solubility at constant pressure, Δv is the fictitious volume change which accompanies the solution of 1 g.-mol. of a substance in an infinitely large volume of solvent at 1 atm. pressure and T° , and Q is the fictitious heat of solution. The four quantities have been determined experimentally for thallous sulphate, dc/dT by direct solubility determinations, $dc/d\pi$ also directly, and Δv and Q from *E.M.F.* measurements. The following values are recorded: $dc/dT=0.1387$ g./degree, $dc/d\pi=0.003377$

g./atm., $\Delta v = -0.0492$ c.c./g., $Q = 14.75$ cal./g., whilst the value of Q calculated from the above equation is 14.82 cal./g. This indicates that Braun's law is true within the limits of experimental error.

J. F. S.

Atomic Volumes and Solubility. ROBERT FLATT (*Helv. Chim. Acta*, 1923, 6, 698—707).—A formula was given by Bodländer (A., 1898, ii, 554) for calculating the solubility of a salt in water from its free energy of formation and the normal potentials of the ions. As for most salts the free energy is unknown, the heat of formation Q can be used and Bodländer's equation can be written $Q = E_k + nRT/mF \cdot \log 1/C + Q_1 + E_a$, where E_k and E_a are the normal potentials of kation and anion, n is the number of ions, m the number of valencies broken during electrolysis, F is Faraday's constant, and Q_1 is the heat of formation of the free anion when this is a complex such as SO_4 . In the case of sulphates, for instance, Q_1 and E_a are unknown, but their sum is a constant for a series of sulphates and can be calculated from the solubility C of a single sulphate. The quantity so determined has been used for calculating the solubilities of a number of sparingly soluble sulphates from a knowledge of Q and E_k .

According to the theory of Born (A., 1919, ii, 214) and of Fajans (*Naturwiss.*, 1921, 9, 729), the solubility of a salt depends on the difference between the sum of the heats of hydration of the ions, $Q_k + Q_a$, and the lattice energy of the crystal, Q_{ka} . The low solubility of the alkaline-earth sulphates and of the perchlorates is to be attributed to the high value of the lattice energy in this isomorphous series rather than to low heats of hydration of the ions. This theory also accounts for the low solubility of lead sulphate, which has a similar crystalline form. The heats of hydration of the ions and the lattice energy are functions of the atomic volume. The values of Q_k and Q_a decrease with increasing atomic volume, and Q_{ka} attains a maximum depending on the atomic volumes of the two ions. It follows that the solubility in an isomorphous series may attain a minimum value. Thus, whilst barium sulphate is less soluble than strontium sulphate, it is also less soluble than barium selenate. In the alkali perchlorate series, rubidium perchlorate has the minimum solubility. The low solubility of lead sulphide and lead chloride compared with the sulphides and chlorides of the alkaline-earth metals is attributed to the two additional electrons in the outer shell of the lead atom which increase the lattice energy and are the cause of the high electrical conductivity of these compounds.

E. H. R.

Viscosity of Saturated Solutions, and Solvation. KONSTANTY HRYNAKOWSKI (*Istov Zjazd Chemików Polskich*, 1923, 16—17).—The viscosity of saturated solutions of various sodium and potassium salts is measured, and the degree of hydration of the solutes hence estimated. All sodium salts examined exhibit solvation, the maximum being obtained for disodium hydrogen phosphate, and the minimum for sodium chloride. Potassium

chloride, bromide, sulphate, and chlorate do not exhibit solvation, which occurs to a small extent in solutions of the iodide and nitrate, and to a marked extent in solutions of potassium hydrogen sulphate, hydrogen carbonate, and dihydrogen phosphate. R. T.

The Structure of Thin Films. IV. Benzene Derivatives. A Condition of Stability in Unimolecular Films. N. K. ADAM (*Proc. Roy. Soc.*, 1923, [A], 103, 676—686).—Unimolecular films of substances, *e.g.*, *p*-hexadecylphenol, *p*-octadecylphenol, and hexadecylaniline, containing one long chain and one polar group in the *para*-position, orient on the surface of water like fatty acids, the phenol group forming the head of the molecule in contact with the water. Measurements of the cross section of the head (*cf.* A., 1922, ii, 687) agreed with the corresponding values of the cross section of the nuclei of aromatic compounds deduced from Bragg's crystal measurements (A., 1922, ii, 128). The films show the usual phenomena of expansion to a two-dimensional vapour. Compounds such as cetyl palmitate, palmitanilide, etc., containing one polar group between two chains, or one chain and a ring, do not adhere to a water surface well enough to give measurable films, although in the expanded state such films are often more stable. The *para*-sulphonic acids of hexadecyl and octadecyl benzene give soap-like solutions in water. J. S. G. T.

The Structure of Thin Films. V. N. K. ADAM (*Proc. Roy. Soc.*, 1923, [A], 103, 687—695).—In continuation of previous work (A., 1922, ii, 687), the author has investigated the structure of thin films of certain α -bromo-acids and esters, ethyl *isoo*leate, the esters, amides, and nitriles of saturated acids, carbamide derivatives, and aldoximes. The results confirm the theory developed in the previous papers. Bromine in the α -position in the bromo-acids and esters increases the cross-section of the molecules in the films. The bromine atom increases the solubility of films of the higher fatty acids, and lowers the temperature of change from condensed to expanded films, but does not appreciably affect the properties of the expanded films. The double linking in the $\alpha\beta$ -position relative to the CO_2Et group increases the cross-section of the molecule in the films, as in *isoo*leic acid. The transition between two forms of condensed film, as in the case of the substituted carbamides, is analogous to that between two polymorphs or allotropic modifications of solid substances. J. S. G. T.

Calculation of [Recent] Adsorption [Data]. L. BERÉNYI (*Z. physikal. Chem.*, 1923, 105, 55—72).—In a recent paper (A., 1920, ii, 591) the author submitted Polányi's theory of adsorption (A., 1916, ii, 474) to a critical test, using the experimental data then available. The present paper is a continuation of this work on the recently published results of Patrick and McGavack on the adsorption of sulphur dioxide by silicic acid gels (A., 1920, ii, 417), Davidheiser and Patrick on the adsorption of ammonia by silicic acid gels (A., 1922, ii, 262), and Berl and Andress on the

adsorption of a number of vapours (methyl alcohol, ether, acetone, benzene, ethyl alcohol, and carbon tetrachloride) by activated charcoal (*Z. angew. Chem.*, 1921, **34**, 369, 377). The calculations show that Polányi's theory is fully confirmed. J. F. S.

Two Types of Adsorption. HILARY LACHS (*Izry Zjazd Chemików Polskich*, 1923, 30—31; cf. A., 1916, ii, 225).—Only substances of a similar electrical charge are able mutually to displace each other on the surface of an adsorptive substance.

R. T.

The Reciprocal Displacement of Substances Adsorbed by Precipitates. ANDRÉ CHARRIOU (*Compt. rend.*, 1923, **176**, 1890—1891; cf. this vol., ii, 261).—If precipitated aluminium hydroxide containing adsorbed chromic acid is washed with a 5% solution of a salt of a monobasic acid (chloride, bromide, iodide, nitrate, or acetate), no chromic acid is removed, and no other substance adsorbed. With salts of a polybasic acid (carbonate, sulphate, sulphide, oxalate, tartrate, citrate, phosphate, or arsenate), interchange occurs between adsorbed chromic and polybasic acids.

Sulphuric acid, adsorbed by aluminium hydroxide, is completely displaced by polybasic, but not by monobasic acids. Phosphoric acid, similarly adsorbed, is not displaced by carbonic or chromic acid. These two acids are mutually displaceable from adsorption on aluminium hydroxide, that acid being displaced which is at the smaller concentration. This (equilibrium) effect is probably obtainable with any two acids of similar basicity.

When arsenious sulphide is precipitated by means of hydrogen sulphide in presence of a barium salt, it contains adsorbed barium. When the precipitate is washed with a solution of sodium or potassium chloride, no displacement of barium occurs, whilst with solutions of aluminium, ferric, or chromic chloride, interchange of barium and tervalent metal takes place. E. E. T.

Isotherms of Adsorption of Salts by Manganese Dioxide. MAX GELOSO (*Compt. rend.*, 1923, **176**, 1884—1887; cf. A., 1922, ii, 589).—When ammonium persulphate is added to a solution of manganese sulphate containing copper or nickel salts, the resulting precipitate of manganese dioxide adsorbs these metals. Freshly precipitated manganese dioxide also adsorbs iron from solution. If γ = the millimolecular concentration of adsorbed material per milligram-molecule of total solid phase, and C = the concentration in milligram-molecules of salt remaining in solution, then $\gamma = KC^m$, where m is less than unity; m is independent of the nature of the adsorbed substance and of the adsorbent. K varies with these, being a specific coefficient of the adsorbed substance.

E. E. T.

A New Explanation of Diffusion. III. Influence of Gravity on Diffusion. ALEXANDR SOMMER-BATĚK (*Chem. Listy*, 1923, **17**, 79—81).—Solutions of $N/10$ -sulphuric acid are placed in one limb of a Y-tube the other limb of which contains water, the liquids

being separated by mercury contained in the lower limb. The mercury is then gradually withdrawn, so that the liquids are free to diffuse into each other. After the lapse of different periods of time, the liquids are again separated, and layers of the solutions withdrawn at regular intervals in the limbs, by means of exits provided for the purpose, and the concentration of the acid is measured. Similar measurements are made for solutions of barium chloride. R. T.

A New Explanation of Diffusion. IV. ALEXANDR SOMMER-BATĚK (*Chem. Listy*, 1923, 17, 115—118).—The influence of the surface on contact on the diffusion of liquids is measured by allowing water and *N*/10-sulphuric acid contained in the limbs of U-tubes of different diameters to interdiffuse at constant temperature for given periods of time. Layers of solution at different heights from the bottom of the U-tube are then siphoned off, and their concentration and density measured. The results obtained show that the rate of diffusion is proportional to the diameter of the tube. Certain irregularities observed in the fall of concentration of layers of solution in the sulphuric acid limb are explained as being due to the diffusion of water proceeding in waves, which are reflected from the meniscus and may in time produce points of interference or amplification in the column, where the concentration is considerably different from that of the layers immediately above and below. R. T.

Dialysis of Small Volumes of Liquid. The Lily-pad Dialyser. R. W. WOOD (*J. Physical Chem.*, 1923, 27, 565—566).—A method is described whereby quantities of solutions as small as a single drop of liquid may be dialysed. The dialyser is prepared as follows. A small circular plate of glass is fastened horizontally to a turn-table which is capable of rapid rotation, a few drops of collodion, considerably thinned by ether, are placed in the middle of the plate, and the plate is set in slow rotation. A small camel-hair brush is brought into contact with the edge of the collodion pool, and the brush moved slowly away from the centre, the velocity of rotation being immediately increased, and as soon as the collodion is drawn into a perfect disk the brush is lifted. If properly carried out, the whole operation should be complete in a few seconds, and a very thin disk of collodion with a thick rim produced. After drying the film for a few moments, a few drops of water are placed on the plate and brought in contact with the edge of the disk which separates the membrane from the plate. The plate is then lowered at an angle of 45° into a bowl of water, when the membrane floats off with a perfectly dry upper surface. The solution to be dialysed is added drop by drop to form a globule in the centre of the membrane. A disk 4 cm. in diam. will support 2 c.c. of liquid. If the liquid passing through the dialyser is required, the membrane can be floated off in a deep watch glass and most of the water afterwards pipetted away. If the collodion is diluted with ether as above, the dialysis is slow,

but if it is diluted with a mixture of ether and alcohol it is much more rapid. J. F. S.

The Origin of Osmotic Effects. IV. Hydronodynamic Change in Aqueous Solutions. HENRY E. ARMSTRONG (*Proc. Roy. Soc.*, 1923, [A], **103**, 610—618; and *Compt. rend.*, 1923, **176**, 1892—1894).—The author summarises evidence and arguments previously advanced regarding the nature of the processes involved in the dissolution of “salts” in water, and advocating an electrolytic explanation of chemical change, and a chemical explanation of electrolysis. “Water” is regarded as a complex saturated with the “gas” hydrone, OH_2 , which is the sole potentially “active” constituent, and becomes active only under conditions which suffice to determine electrolytic change. Ideally pure water would be inert. Electrolysis and chemical change are inseparable reciprocal effects, and change takes place only in a system of three components, such as is known to constitute a voltaic couple. The vapour pressure of water or of a solution is the measure of *free* hydrone molecules present in the liquid. The diminution of pressure when a substance is dissolved in water is a proof that the molecules of hydrone are concerned in the change and are thereby diminished in proportion. The solution acquires attractive properties, due to the presence of solute. The internal activity is increased whilst external activity is diminished. Non-electrolytes all have unit effect per molecular proportion; potential electrolytes have at least twice this effect in sufficiently dilute solutions. The effect produced may be ascribed to the interaction of molecules of the solute and of hydrone. From non-electrolytes, under the influence of conducting impurity, a simple hydrol, $\text{H}\cdot\text{M}\cdot\text{OH}$, is formed, only a single molecule of hydrone being “distributed” on the molecule of the solute, whatever its magnitude. In the case of potential electrolytes, a reciprocal interchange of the radicles of the salt and of hydrone is postulated. The solute is hydrolated and itself distributed on hydrone, the salt $\text{R}\overset{+}{\text{X}}\overset{-}{\text{X}}$ thus giving rise initially to the reciprocal systems $\text{RX} < \overset{\text{H}}{\text{OH}}$ and $\text{H}_2\text{O} < \overset{\text{R}}{\text{X}}$. As the concentration is reduced, the complex $\text{RX} < \overset{\text{H}}{\text{OH}}$ is, under the influence of hydrone, increasingly converted into hydronol, $\text{H}_2\text{O} < \overset{\text{H}}{\text{OH}}$. Ultimately the solution contains the solute only as $\text{H}_2\text{O} < \overset{\text{R}}{\text{X}}$, together with an equal number of molecules of hydronol. The solute then has maximum (bimolecular) effect. The “distributed” reciprocal complexes, including hydronol, are the electro-chemical agents in a solution. The negative radicle in such complexes has greater residual affinity than it has in the original simple molecules; it is specially attractive of hydrone. Each complex attracts a single hydrone molecule, the molecules thus brought into the solution serving to restore the hydrone equilibrium.

The osmotic pressure of an aqueous solution is the hydraulic pressure exercised by the extra molecules of hydrone attracted into it by the distributed complexes, one by each complex, acting as though they were present in the gaseous state. Osmotic pressure is therefore regarded as *hydronodynamic* in origin, the term expressing the general electrochemical and osmotic activity of water.

J. S. G. T.

Investigation of Ferric Hydroxide Sol. I. A Case of Negative Osmosis. JOHS. LINDEMANN (*Kolloid Z.*, 1923, 32, 376—383).—The osmosis of ferric hydroxide hydrosol has been investigated. It is shown that with increasing dilution there is a decreasing relationship between the osmotic pressure and the concentration. This is explained by the assumption that the rate of rise of the liquid column is the resultant of the rate at which the liquid passes in and out of the osmotic cell. The velocity outward is increased by the addition of ferric chloride to the sol and under special conditions this can exceed the velocity of the solvent inward. This would naturally bring about a decrease in the level of the liquid column and so explain the decreasing relationship stated above. It is shown that the electrolyte content of a sol can be determinative of the osmotic pressure.

J. F. S.

Supersaturation. ROGER G. BOUSSU (*Compt. rend.*, 1923, 177, 119—121; cf. this vol., ii, 144).—The effect, on the speed of crystallisation, of agitation of, and the presence of nuclei in, supersaturated solutions of potassium hydrogen tartrate and calcium sulphate has been studied. Powdered glass, and, to a less extent, powdered gas carbon, initiate and accelerate such crystallisations.

E. E. T.

Aqueous Solutions. ANDRÉ KLING and ARNOLD LASSIEUR (*Compt. rend.*, 1923, 177, 109—111; cf. Armstrong, this vol., ii, 542).—The authors consider that simple water molecules may possess one of two structures: H_2O or $\text{H}\cdot\text{OH}$. For further details, the original paper should be consulted.

E. E. T.

The Solubility Laws. ALBERT COLSON (*Compt. rend.*, 1923, 176, 1552—1555).—A critical discussion of views which have been put forward by Le Chatelier with respect to the application of the Clapeyron equation to solutions and to the substitution in that equation of dC/dT for dp/dT , where C is the concentration and p the osmotic pressure. The author points out that, assuming the van't Hoff relation $\rho = L - 2T$, the solubility of sodium chloride should decrease with rise of temperature as ρ , which is zero at 263° Abs. , should become negative with increase of T , L being constant. Moreover, the substitution of concentration for osmotic pressure ignores the existence of hydrates in solution. Mathematical reasons are also given. The case in which hydrated crystals dissolve in their own water of crystallisation on rise of temperature is discussed.

H. J. E.

The Distribution of the Solvent amongst the Dissolved Substances. ANTOINE DOROSZEWSKI (*Bull. Soc. chim.*, 1923, [iv], **33**, 550—559).—A theoretical paper in which it is shown that the author's theory of the distribution of the solvent amongst the dissolved substances in the ratio of the number of molecules of each substance present, gives a satisfactory quantitative and qualitative explanation of the variations of the specific rotatory power of an optically active substance such as sucrose in presence of a dissolved mineral salt such as sodium chloride, and very close agreement is shown between the observed and calculated values for the specific gravity and specific rotatory power of such mixed solutions. Other properties of mixed solutions, such as the electrical conductivity and refractive index, also find an explanation in terms of the theory. G. F. M.

The Graphic Interpretation of the Law of Doroszewski. W. SWIENTOSLAWSKI (*Bull. Soc. chim.*, 1923, [iv], **33**, 560—561).—A graphic method of expressing Doroszewski's law (preceding abstract) is indicated, which facilitates the comparison of the observed and calculated values for any physical property of a mixed solution. The expression is obtained by marking off along the axis of abscissæ the concentrations n_1/n_1+n_2 , and on two vertical lines traced from the points $n_1/n_1+n_2=0$ and $n_1/n_1+n_2=1$ (that is to say, the points where the mixture contains 0% and 100% of the substance *A*) the values Z_A and Z_B representing the values of the physical property corresponding with the two solutions, that is, of a molecule of *A* and *N* mols. of solvent, and a mol. of *B* and *N* mols. of solvent. The straight line joining the two points expresses the change of the physical property in any mixture of the two solutions, the total number of dissolved molecules *N* being supposed invariable. G. F. M.

The Specific Heat of Mixtures of Aqueous Solutions of Sodium Chloride and Sucrose. (MLLE) H. BLASZKOWSKA (*Bull. Soc. chim.*, 1923, [iv], **33**, 562—571).—The densities and specific heats of aqueous solutions of sodium chloride and sucrose, and mixtures of such solutions, of concentrations corresponding with 200, 100, 50, and 25 mols. of water per mol. of dissolved substance, were determined to an accuracy of $\pm 0.06\%$, and the full results are given in tabular form. A perfect agreement was established between the experimental values and those calculated according to Doroszewski's law, according to which the solvent distributes itself among the dissolved substances proportionally to the number of g.-mols. present. Variations from the law did not exceed $\pm 0.12\%$. G. F. M.

The Influence of a Third Substance on the Miscibility of Phenol and Water. A. BOUTARIC and (MLLE) Y. NABOT (*Compt. rend.*, 1923, **176**, 1618—1620).—An application to phenol-water mixtures of Timmermans's generalisation (A., 1907, ii, 229) that the

miscibility curve of two liquids *A* and *B* in the presence of a third substance *C* lies wholly outside the curve for the pure liquids, the reciprocal solubility of the two liquids being diminished. It was found that the variation produced by a known concentration of a third substance varies with temperature, increasing with rise of temperature for mixtures rich in phenol, and conversely. For a given temperature, the variation depends solely on the concentration of the third substance with respect to the phenol; in those cases in which the third substance is soluble in water, the variation is not so great. The experimental results obtained are qualitatively but not quantitatively in accordance with those obtained by Nernst (A., 1891, 1148). The substances used in the experiments were phenyl salicylate, azobenzene, anthraquinone, and naphthylamine.

H. J. E.

Form of a Crystal as a Function of Superficial Energy and of its Density. CONSTANTIN HRYNAKOWSKI (*Bull. Soc. chim.*, 1923, [iv], 33, 548—550).—A theoretical paper in which the relationship between crystal form and the density and superficial energy is mathematically developed from the theory of Gibbs and Curie on the conditions of equilibrium in solutions.

G. F. M.

Researches on the Relation between the Surface, Mass, and Volume of certain Crystals. K. HRYNAKOWSKI (*Istny Zjazd Chemikow Polskich*, 1923, 14—15; cf. *ibid.*, 14).—It is shown that before the expression $dk/d\sigma \cdot \sigma + K = F[\sigma \cdot M_K - f(M_K/d)]$ can be applied to any crystal, it is necessary to obtain the value, P_r , of the function $f(M_K/d) \cdot P_r$, which is the surface of the given crystal, must have as a minimum value that of a sphere of the same volume, P_K , and the ratio P_r/P_K approaches more closely to unity as the symmetry of the crystal increases. For a number of crystalline substances this ratio ranges from 1.579 for copper sulphate to 1.307 for sucrose.

R. T.

Coagulative Power of Series of Electrolytes. AGNES IVANITZKAJA and LIDIE ORLOVA (*Koll. Chem. Beihefte*, 1923, 18, 1—39).—The coagulative power of series of electrolytes has been investigated in connexion with a large number of hydrosols, including the negative sols of mastic, arsenious sulphide, antimony trisulphide, sulphur, gold, platinum, Berlin-blue, manganese dioxide, ferric oxide, and silver bromide, and the positive hydrosols of ferric oxide, alumina, chromic oxide, and silver bromide. The results show that most series of anions with a constant kation are antivalent toward negative sols, but convalent toward positive sols. On the other hand, series of kations with a constant anion are convalent toward negative sols, but antivalent for positive sols. Some few sols, however, give quite irregular results with the series, so that no relationship can be found with the valency; these are to be regarded as exceptions, since they are few in number and occur chiefly in the metal sols or in non-typical sols such as suspensions. Similar experiments were carried out with a few suspensions, including negatively charged suspensions of carbon in solutions

of various alkali hydroxides and tannin, and positive suspensions of ignited alumina and ferric oxide in hydrochloric acid. In these cases, no fundamental difference was found between suspensions and true sols with respect to their coagulation by series of electrolytes. The influence of the addition of methyl alcohol, acetone, glycerol, sodium protalbinat, dextrin, and gelatin in various concentrations to negative suspensions of carbon in potassium hydroxide, positive suspensions of ferric oxide in hydrochloric acid, and hydrosols of gold, platinum, mastic, and silver bromide, on the coagulation phenomena has been investigated. It is shown that the addition of a non-electrolyte to the dispersion medium of a colloidal system changes both the stability of the sol and the orientation of the electrolyte series. The two changes, particularly in the case of anion series, appear to be closely connected. Temperature has apparently no noticeable influence on the coagulation process. It appears generally that the phenomena of coagulation are not the result of any single factor, such as surface tension or dielectric constant, but of very complicated relationships between all the components of the colloidal system, such as the dispersed phase, the dispersion medium, and the coagulating electrolyte. Hence the coagulation series of the electrolytes for different colloidal systems are very different and characteristic. Only in the case of analogous sols are analogous electrolyte series obtained. This is made very clear in the present work, particularly in the series of ferrous-ions, iodate-ions, organic ions, and hydrogen-ions.

J. F. S.

Influence of the Concentration of Reacting Solutions on the Size of the Crystalline Particles of the Precipitates. P. P. VON WEIMARN (*Koll. Chem. Beihefte*, 1923, **18**, 44—75).—A theoretical paper in which the author considers the criticisms made, in connexion with the crystallisation theory of colloids (A., 1909, ii, 132), by Freundlich (*Kapillarchemie*, 1922, 631), by Buchner and Kalff (A., 1920, ii, 232), and by Bancroft (1920, ii, 295). The author maintains his position, and shows that the criticism offered, so far as it attacks the fundamental principles of the theory, is based on a misunderstanding of the theory.

J. F. S.

Non-, Uni-, and Bi-variant Equilibria. XXIII. F. A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1923, **26**, 283—296; cf. this vol., ii, 137).—A continuation of the mathematical treatment of equilibria of n components in $n+1$ phases when the quantity of one of the components is infinitesimally small. More particularly the influence of a new substance on a non-variant equilibrium is considered.

J. F. S.

The Distribution of Substances between the Gaseous and Liquid Phases, or between Two Liquid Phases. WOJCIECH SWIENTOSLAWSKI (*1^{sty} Zjazd Chemików Polskich*, 1923, 17—19).—A formula is deduced from Raoult's law for the distribution of a substance between two liquid phases, or between a liquid and a gaseous phase, namely, $c_1/c_2 \cdot 1/v \sum n = K$, where c_1 and c_2 are the

concentrations of the substance in the liquid and gaseous phase, respectively, v is its molar volume, Σn the total number of molecules present in 1 c.c. of the liquid phase, and k is a constant, the ratio of the densities of the liquid and gaseous substance. Where two substances are present, $1/v\Sigma n = 1/v_1(n_1 + n_2) = z$, where n_1 and n_2 are the number of molecules of each substance contained in 1 c.c. of the liquid phase. The distribution formula then becomes $c_1z/c_2 = k$. For substances obeying Raoult's law, z can vary from 1 to v_2/v_1 , the ratio of the molar volumes of the two substances. In those cases where z is very close to 1, which may occur when the solutions are very dilute, or when v_1 is approximately equal to v_2 , van't Hoff's law is also obeyed, but as a general rule the latter law and Henry's law can only be regarded as approximations.

R. T.

Equilibrium Conditions of Systems of Three Components.

G. G. URAZOV (*J. Russ. Phys. Chem. Soc.*, 1923, **54**, 61—161).—An exhaustive survey is made of graphical methods for the representation of three component systems of all possible types, and under various conditions. The conclusions that can be drawn from such diagrams are pointed out, and the possibility of the prediction on thermodynamical and other grounds of the stability or instability of any system is discussed.

R. T.

Influence of Intensive Drying on Internal Conversion. I.

A. SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1923, **26**, 266—269; cf. A., 1922, ii, 358).—The author assumes that every phase contains two different kinds of molecules, an active and an inactive variety, and that these are in equilibrium. Thus in the case of ammonia $\text{NH}_3\alpha \rightleftharpoons \text{NH}_3\beta$. In intensive drying the equilibrium is shifted to the inactive side, so that the ammonia which remains after the drying contains only inactive molecules.

J. F. S.

Kinetic Reactions. I. H. VON EULER and ERIK G. RUDBERG

(*Z. Physik*, 1923, **16**, 54—62).—The theory developed by the authors in a previous paper (*Z. anorg. Chem.*, 1923, **127**, 244) is applied to the case of the hydrolysis of ethyl acetate. In the case of a solution of concentration 0.05*N*, the equilibrium concentration of acetic acid and ethyl alcohol being 0.87*N* and that of the hydrochloric acid used as catalyst 0.10*N*, the respective concentrations of the ions $\left(\text{CH}_3\text{COEt}\right)^+$ and $\left(\text{CH}_3\text{C}\cdot\text{OH}\right)^+$ inducing the reaction are calculated, and found to be equal to 5×10^{-9} . It is shown that the temperature coefficient of the reaction is dependent on the respective variations with temperature of the coefficient of ionisation of the ester and water, whence it follows that the temperature coefficient of the hydrolysis of ethyl acetate is only slightly greater than that of the ionic dissociation of water. The heat of formation of the salt is therefore small, and it is shown that, as in the case of most salts of inorganic weak bases, the hydrolysis of ethyl acetate increases with increasing temperature.

J. S. G. T.

The Mechanism of Reduction. I. H. J. PRINS (*Rec. trav. chim.*, 1923, **42**, 473—481).—Essentially an amplification of the previous paper (A., 1922, ii, 488). The following views are put forward: (1) Reduction and oxidation of organic substances are often due to a co-action between the components which can only react through their combined action. (2) Owing to this co-action it is possible to dissolve metals in a medium in which they are normally unattacked, the co-action taking place between the undissociated molecules. (3) Nitrobenzene is strongly adsorbed on to zinc and reacts rapidly with the zinc and acetic acid. Phenylhydroxylamine is less strongly adsorbed; it reacts less rapidly and activates the surface of the zinc. Aniline has no influence on the hydrogen evolution and is not appreciably adsorbed by the zinc. (4) The adsorption may be due to the oxygen atom, which may be oriented towards the zinc. F. A. M.

The Mechanism of Reduction. II. H. J. PRINS (*Rec. trav. chim.*, 1923, **42**, 482—495; cf. preceding abstract).—In continuation of the work on co-action and the increased solubility of metals in certain acids in the presence of reducible substances, a detailed examination has been made of the action of acetic acid on zinc in presence of nitrobenzene, phenylhydroxylamine, and aniline.

Nitrobenzene.—In concentrations of about 0.01 to 0.03 mol. solution in 82.4% acetic acid at 78° nitrobenzene does not influence the reaction between pure zinc and acetic acid, but after some time the phenylhydroxylamine formed exerts an accelerating influence on the hydrogen evolution. At 55°, a solution of 0.04 mol. of nitrobenzene in acetic acid has no influence on the hydrogen evolution with commercial zinc. Besides the evolution of hydrogen, a reduction of the nitrobenzene takes place with a velocity ten to twenty times greater than that of the hydrogen evolution, expressed in weight of zinc dissolved, at 55° in 0.0376 mol. solution.

Phenylhydroxylamine.—In a solution of phenylhydroxylamine in acetic acid the velocity of hydrogen evolution is much greater than the normal one, and at the same time the phenylhydroxylamine is rapidly reduced to inactive aniline. The reduction reaction has a velocity about two to three times that of the evolution of hydrogen at 55° in a 0.0376 mol. solution, expressed in weight of zinc dissolved.

Aniline.—When purified by fractional distillation in a vacuum, aniline increases the velocity of the evolution of hydrogen but if the aniline is purified by means of acetone it is found to be without influence. F. A. M.

Measurement of Reaction Velocity and the Temperature Coefficient of Reaction Velocity. F. O. RICE and MARTIN KILPATRICK, jun. (*J. Amer. Chem. Soc.*, 1923, **45**, 1401—1412).—The authors have made a study of the errors occurring in the measurement of velocity of reaction, and have shown how they may be diminished so that the degree of precision of a single experiment is 0.20%. The reaction selected for this investigation was that between acetone and iodine in dilute aqueous solution catalysed

by hydrochloric acid. The results of this action are summarised thus :

Temp.	0°.	24°.	25°.	27°.	35°.
Velocity constant (k)	0.69944	15.187	17.148	21.609	52.840
Degree of precision %	0.10	0.20	0.070	0.14	0.10

The velocity constant k is the average rate of disappearance of iodine in g.-mols. from a litre of solution containing 1 g.-mol. of acetone, 1 g.-mol. of hydrochloric acid, 0.01 g.-equivalent of iodine, and 0.025 g.-mol. of potassium iodide. The degree of precision is calculated by the formula $\sqrt{(e)^2 + (t)^2}$, where e is the mean divergence of k from the mean value, and t is the error in the time readings. Using nitric acid as catalyst, the value $k^{25}=17.137$, with degree of precision 0.14%, which is the same as that given by hydrochloric acid within the experimental error. With sulphuric acid $k^{25}=15.543$, degree of precision 0.21%. A method has been developed for determining the temperature coefficient of a reaction with a high degree of precision by a single experiment. For the above reaction, $k^{25}/k^0=24.517$ with precision 0.12%, $k^{35}/k^{25}=3.0814$, precision 0.12%. Substituting these values in Arrhenius's equation $2.3026 \log_1 k_1/k_2 = Q/R(1/T_1 - 1/T_2)$, the value of Q is found to be 20695.1, precision 0.038%, and 20431.0, precision 0.11%, respectively. The value of Q therefore diminishes slightly with rise in temperature. It is shown that non-electrolytes have no effect on the temperature coefficient up to concentrations of 30%.

J. F. S.

Hydrogenation of Benzene. GREGG DOUGHERTY and HUGH S. TAYLOR (*J. Physical Chem.*, 1923, 27, 533—557).—A number of experiments on the hydrogenation of benzene under different conditions in the presence of catalysts have been made with the object of gaining an insight by kinetic experiments into the mechanism of the catalytic reduction of benzene to *cyclohexane*. The results indicate that the reaction does not occur at all according to the stoicheiometric equation, as calculated from gas concentrations, but at rates governed by the distribution of the reacting materials between the catalyst and the gas phase. The trend of the reaction with change of temperature has been studied, and equilibrium values at higher temperatures have been calculated. The results of the latter show that apparent equilibria in the gas phase, as measured in this way, do not necessarily coincide with those which would be expected on the basis of the ordinary equation representing the reaction. The poisoning effect of water vapour, carbon monoxide, and *cyclohexane* on the reaction has been investigated. It is shown that water vapour in small amounts, up to 2% of the hydrogen volume used in the reaction mixture, has only a slightly depressing effect on the reaction velocity. Carbon monoxide in small amounts, about 2% of the hydrogen volume, has a very marked poisoning effect, particularly at low temperatures of 100° or below. As the reaction temperature is raised, the poisoning is less noticeable. In large quantities, however, round 50% of carbon monoxide the reaction is stopped completely

at 180°. *cyclo*Hexane at low temperatures, 100° or below, has a depressing effect on the reaction velocity. This effect disappears at higher temperatures, in the region of 180°. The experiments show that it is necessary to use great care in making comparative measurements on account of the variability of the nickel catalyst. Different catalysts, although prepared in exactly the same way, may have different activities, and the activity of a given catalyst changes markedly with time and use. The experiments also show that quantitative measurements on a reaction of this kind are difficult, due to the fact that the actual reactant concentrations, on which the velocity of the reaction depends, are those on the catalyst surface, and these concentrations may be independent of, or bear a varying relation to, the reactant concentrations in the gas phase. From experiments at 80° and 90°, it is shown that the temperature coefficient of the reaction is approximately 1.65 for 10° rise. This is evidently the temperature coefficient of a chemical reaction as opposed to that of a diffusion process.

J. F. S.

Kinetics of Febrile Reactions: Study of Autocatalysis.

A. QUARTAROLI (*Gazzetta*, 1923, **53**, i, 345—368).—The author discusses the mechanism of reactions which show an initial period of incubation, an intermediate period of induction, and a final period of extinction, and are hence known as febrile reactions. The particular reactions examined are that between nitrates and formic acid (cf. A., 1911, ii, 1079), and those between dilute nitric acid and copper, silver, mercury, antimony, bismuth, tin, iron, cobalt, nickel, zinc, cadmium, and aluminium.

The results show that, when free from nitrous acid, nitric acid does not act in solution as a true oxidising agent, its oxidising properties being no greater than those of a nitrate or a sulphate in solution. Thus, in presence of a considerable proportion of carbamide, the action of nitric acid on tin yields exclusively stannous nitrate, and, similarly, nitric acid does not convert ferrous into ferric salts or mercurous into mercuric salts, even at the boiling point, if the solution contains carbamide, an amino-acid, an amide, etc.

Oxidation represents a necessary condition for the dissolution in acid solutions of metals of solution tension less than that of hydrogen, so that nitric acid, freed from nitrous acid by means of carbamide, will not dissolve even minimum traces of copper, silver, mercury, bismuth, etc., provided that in certain of these cases action of atmospheric oxygen is excluded. With metals having solution tensions which are not very high but exceed that of hydrogen, such as cobalt, nickel, lead, and iron, it is found, as a general rule, that oxidation facilitates the dissolution, although not to a marked extent. On the other hand, with metals of high solution tension, such as cadmium, zinc, and aluminium, oxidation retards dissolution; aluminium is so sensitive to this retarding effect that even the feeble oxidising action of either nitric acid free from nitrous acid or sulphuric acid is detectable.

In these reactions, there is no doubt that the reaction is pro-

ceeding, although with extreme slowness, during the period of incubation, and that it is only when the catalyst generated reaches a certain concentration that the reaction assumes the comparatively enormous velocity of the induction period. The author considers it to be quite arbitrary and liable to lead to error to assume in all cases that a reaction proceeding at a high temperature proceeds also, but with greatly diminished velocity, at a lower temperature. Thus, calculation of the velocity of a reaction by extrapolation from experimental results is not always justified, since weakening of the impulse of a reaction by altering the condition of dilution or by lowering the temperature may render this impulse incapable of overcoming the passive resistance of the reaction. This view is illustrated by the mechanical analogy of the rolling of a ball down a plane inclined at various angles.

When a metal with a low solution tension, that is, one for which oxidation is a condition indispensable to attack, is treated with nitric acid, there is one concentration of the latter below which action never occurs and another higher concentration above which action always proceeds regularly. With intermediate concentrations, action either does or does not take place, in dependence on infinitesimal factors which cannot be defined; in just the same way, it is impossible to calculate the time of fall of a sheet of paper through a certain height in still air.

Reference is made to the marked analogy existing between the course and mechanism of these reactions—the action of negative catalysts, the influence of the resistance of the medium, and the great disproportionality between the rapidity of the reaction and the original concentrations of the reacting substances—and various physiological and pathological phenomena.

T. H. P.

The Conditions of Reaction of Hydrogen with Sulphur. II. The Catalytic Effect of Oxygen. III. The Mechanism of the Reaction of Hydrogen with Sulphur and its Catalysis by Oxygen. RONALD GEORGE WREYFORD NORRISH and ERIC KEIGHTLEY RIDEAL (T., 1923, 123, 1689—1705).

The Behaviour of Activated Sugar Carbon in Contact with Hydrogen Peroxide Solution. JAMES BRIERLEY FIRTH and FRED SHEASBY WATSON (T., 1923, 123, 1750—1755).

Catalytic Actions at Solid Surfaces. XI. The Action of Alumina and certain other Oxides in Promoting the Activity of Nickel Catalyst. E. F. ARMSTRONG and T. P. HILDITCH (*Proc. Roy. Soc.*, 1923, [4], 103, 586—597).—The authors have investigated the effect of alumina and certain other oxides on the catalytic activity of a simple nickel catalyst and of a nickel catalyst deposited on a support of kieselguhr or kieselguhr extracted with hot aqua regia. In general, the catalytic activity was determined by ascertaining the degree of hydrogenation effected at 180° by 1 g. of catalyst contained in 150 g. of cotton-seed oil through which a current of hydrogen passed. A mode of preparation of a simple

reduced nickel catalyst which afforded concordant results when the preparation was repeated is detailed. Co-precipitation of the respective oxides of aluminium, iron (ferric), magnesium, or silicon (up to about 2%) with the simple nickel catalyst increased the catalytic activity of the latter, but larger amounts reduced the catalytic activity. Co-precipitation of alumina with nickel oxide on the kieselguhr support likewise increased the catalytic activity of the catalyst, but the action was not the same as in the case of the unsupported nickel. The authors consider that the main, and possibly the only, source of stimulation in activity, in both cases, is the production of an increased surface of catalytic nickel owing to the relatively voluminous admixed oxides separating particles of nickel oxide or nickel which would otherwise coalesce. In the case of acid-extracted kieselguhr, removal of the original metallic constituents causes the nickel oxide to penetrate far into the siliceous structure, with the result that it is less accessible both to reduction and to contact with oil and hydrogen. Deposition of alumina on the guhr fills up these inaccessible parts, so that the superimposed nickel oxide is more favourably placed for contact action. It is considered that any oxide of sufficient bulk or apparent volume, resistant to reduction to the metallic state and not specifically toxic to nickel, will act as a "promoter."

J. S. G. T.

Oxidation Catalyses caused by Salts of Copper and Uranium. J. ALOY and A. VALDIGUIÉ (*Bull. Soc. chim.*, 1923, [iv], 33, 572—576).—Salts of copper, particularly those with weak acids, can act both as oxydases and peroxydases. As examples of oxydase action the production of the blue coloration with solutions of quinol in presence of oxygen, the oxidation of pyrogallol, and of tincture of guaiacum, are cited, whilst the peroxydase action is illustrated by the production of the intense red coloration when salts of copper which do not act directly on guaiacol are added to this substance in presence of hydrogen peroxide, by the action of copper salts under similar conditions on indigo-carmin, or benzidine in alcoholic solution, and by the catalysis of the decomposition of potassium iodide by hydrogen peroxide. Uranium salts act as oxido-reducing catalysts, as instanced by the simultaneous oxidation and reduction of dextrose and methylene-blue respectively which is brought about by uranium salts in sunlight in the absence of oxygen. The latter type of catalysis is largely inhibited by the presence of phenols.

G. F. M.

The Periodic Classification of the Elements. BOHDAN SZYSZKOWSKI (*Istny Zjazd Chemików Polskich*, 1923, 54—55).—A connexion is shown to exist between the classification used in analytical chemistry and the periodic classification of the elements. A relation further exists between the mobility of ions and their place in the periodic table. Finally, a relation is established between the periodic classification of elements and the morphological nature of the latter and of their derivatives.

R. T.

Isotopes. A New Relation concerning the Periodic System of the Atomic Species. WILLIAM D. HARKINS (*J. Amer. Chem. Soc.*, 1923, 45, 1426—1433).—It is shown that the periodic system of the atomic species, developed previously by the author (*A.*, 1917, ii, 303), can be most simply represented as a double network of lines, atomic species existing only at the intersections of the lines. The simplest double network is given if the atomic number is plotted on one axis (X axis) whilst the isotopic number is plotted on the other. In this case, a double network of squares is obtained, with alternate heavy and light lines in both directions. It is found that most of the atomic species, and also the most abundant atomic species, occur where both variables are even numbers, that is, where heavy lines intersect each other. The next most favourable type of intersection is that between light lines, where both variables are odd. A moderate number of species of even atomic number but odd isotopic number (and atomic weight) occur, but in general they are not very abundant. In the diagram these lie on heavy vertical but light horizontal lines. The occurrence of these species is related in a very direct way to that of odd atomic and isotopic number (and atomic weight), since in general when the atomic number is not too high, each species of odd atomic weight but even atomic number lies on the same line of constant isotopic number as, and directly between, two atomic species of odd atomic and isotopic numbers (and odd atomic weight). In the neighbourhood of atomic number fifty, this condition is less exacting, since atomic species of even atomic number but odd isotopic number and atomic weight occur when an atomic species of the same isotopic number is present in either the element of next higher or that of next lower atomic number. In general, species of even atomic weight exist at the intersection of heavy lines, where both atomic and isotopic numbers are even. For atomic numbers higher than twenty-eight, that is, in the region of abundant isotopes, this gives a network of squares, continuous in general within the region of stability, and with from four to seven levels in the vertical or n direction. The general form of the region of stability is that of a hyperbolic band, tangential to the M axis at the origin. The species of odd atomic weight form a pattern of their own, which is on the whole like a single set of steps, or of stairs, ascending towards the right. In certain limited regions, one step lies directly over another, but the number of overlying steps is very many less than for those which represent the species of even atomic weight. Attention is directed to a periodicity of two in the number of nuclear negative electrons, and a somewhat less prominent periodicity of two in the number of protons. In both of these, even numbers give predominance over odd numbers in both number of species and in their abundance. Attention is also directed to a periodicity of two in the relative negativeness (number of negative electrons in the nucleus divided by the number of protons in the nucleus) of the nucleus. It is found that for constant even isotopic number the general difference between adjacent atomic species is one α -particle or

p_4e_2 . For odd isotopic number and atomic weight the most common difference is half an α -particle or p_2e , although the difference of a whole α -particle often occurs also. Hypotheses concerning these relations are discussed. The periodic diagram predicts the existence of a considerable number of hitherto undiscovered atomic species (isotopes). Of the nineteen elements of even atomic number for which in each case the most abundant isotope is known, the atomic weight and the isotopic number are both divisible by four in all but three cases. This periodicity is made apparent in the diagram by using specially heavy horizontal lines for isotopic numbers divisible by four. J. F. S.

Separation of Isotopic Ions. JOHN G. PILLEY (*Nature*, 1923, 111, 848).—A claim for priority on behalf of Lindemann against Kendall and Crittenden (this vol., ii, 282). A. A. E.

The Dimensions of Molecules, Atoms, and Ions and the Methods of Measurement. KARL F. HERZFELD (*Jahrb. Radioaktiv. Elektronik*, 1923, 19, 259—334).—A critical résumé of the literature on this subject, in which the relative accuracy of the different methods of determining molecular dimensions is discussed. The collision area of molecules may be determined with fair accuracy from the movement of slow electrons and from viscosity measurements. The critical data give somewhat more accurate relative values for the space occupied by the molecules if the comparison is made for substances with not too widely different critical values. The absolute values are, however, uncertain, and substances with and without dipoles should be treated separately. Good agreement is obtained between the values from viscosity and critical data. In crystals, the distances between the ions can be derived on the assumption made by Bragg as long as extreme cases are avoided (AgI). The methods based on measurements in liquids have little absolute value except for large colloidal particles. With organic molecules, however, the parallelism between the magnitudes deduced from atomic refraction and other properties is very good. The methods based on Röntgen-rays require an essential increase in the accuracy of the experimental method, and dimensions derived from diamagnetic properties are subject to all the uncertainties of the theories of magnetism. Of those methods giving the distance of the nucleus, it is considered that those from optical measurements and fine structure are the most accurate.

Much smaller values are obtained for molecular dimensions in the gaseous than in the crystalline condition, and this is ascribed to the occurrence of phase relationships between the electronic orbits in the latter case which increase the repulsive forces to such an extent that the ions become practically hard, elastic bodies. The forces exerted by molecules in the gaseous state are much weaker. W. E. G.

The Heterocyclic Theory of Valency and Water of Crystallisation. H. T. F. RHODES (*Anal. F'is. Quím.*, 1923, 24, 149—161; cf. A., 1921, ii, 255, 681).—An exposition of the author's heterocyclic theory of valency and the constitution of crystal hydrates. G. W. R.

Stability of Co-ordination Compounds. T. MARTIN LOWRY (*Chemistry and Industry*, 1923, 42, 711—715).—The author distinguishes between two fundamentally distinct types of co-ordination, viz., (1) centric co-ordination, such as occurs, *e.g.*, in ferro- and ferri-cyanides, cobalticyanides, cobaltinitrites, and cobaltammines, in which the principal characteristic consists of a shell of electrons clustered round a metallic atom, and (2) cyclic co-ordination such as occurs, *e.g.*, in compounds containing a chelate group (T., 1920, 117, 1457), and are characterised by the development or completion of a conjugated ring-system by the insertion of a metallic ion. The stability of centric co-ordination complexes depends mainly on the nature of the central atom of metal and appears to attain a maximum in the case of the trivalent cobaltic ion. The stability of a cyclic co-ordination complex depends on the nature both of the conjugated ring system and of the metallic ion. A maximum of stability is attained in conjugated six-atom rings, the polarities of which are identical with those of aromatic compounds. Conjugated four-atom rings are less stable, and the co-ordinated metal is usually ionisable in solution. In the more stable cyclic systems, a proton can take the place of the metallic ion and yield co-ordinated complexes.

J. S. G. T.

Lecture Experiment. Demonstration of Solubilities, or of Indicator Action. R. W. THATCHER (*J. Amer. Chem. Soc.*, 1923, 45, 1471).—Azolitmin, litmus, or any of the common anthocyan pigments of fruits or vegetables, which when in their acid form are soluble in amyl alcohol, may be used. Fifty c.c. of a neutral aqueous solution of the pigment are placed in a tall, narrow, stoppered cylinder and 4 or 5 drops of a *N*/10-alkali other than ammonia are added. An equal volume of neutral amyl alcohol is added, and the mixture gently shaken and allowed to separate. The pigment in its alkaline form will appear exclusively in the water layer. Eight or 10 drops of *N*/10-acid are now added and the mixture is again shaken and allowed to separate, when the pigment in its acid form will have passed into the amyl alcohol layer.

J. F. S.

Inorganic Chemistry.

Determination of the Boiling and Condensation Curves of Mixtures of Hydrobromic Acid and Water under a Pressure of 760 mm. E. CARRIÈRE and CERVEAU (*Compt. rend.*, 1923, 177, 46—48; cf. Pascal, A., 1917, ii, 569).—Two tables of results are given. The first correlates temperature of boiling with the percentage of hydrogen bromide present in the boiling liquid (temperature range, 22—126—101.25°). The second correlates temperature of distillation with the percentage of hydrogen bromide in the distillate (temperature range, 25—126—100.5°). The results conform to the Gibbs-Konovalov law.

E. E. T.

The Electrolytic Dissociation of Hydrogen Tribromide and Tri-iodide. MARJAN HŁASKO (*Istv Zjazd Chemików Polskich*, 1923, 49).—The conductivity of saturated solutions of bromine and iodine in potassium bromide and iodide solutions is measured, and from these data the electrical conductivity of solutions of hydrogen tribromide and tri-iodide is calculated. From this, it is concluded that the acids in question are highly dissociated in solution, being only a few per cent. weaker than hydrogen bromide and iodide.

R. T.

A Hydrate of Iodine. P. VILLARD (*Compt. rend.*, 1923, 176, 1516—1518).—A hydrate of iodine may be obtained by placing the element in contact with water in an atmosphere of oxygen or nitrogen and submitting it to a pressure of 150 atmospheres. On local cooling with methyl chloride, the formation and disappearance of crystals may be observed at $+3^{\circ}$ and temperatures below. For the phenomenon to occur at higher temperatures, the pressure must be increased. Compressed oxygen is a better solvent for iodine than nitrogen (cf. A., 1899, ii, 143), and by using it the crystals may be obtained at $+4^{\circ}$ and 150 atmospheres, also at $+8^{\circ}$ under a pressure of 330 atmospheres. By using 350 atmospheres, the formation at 8° becomes quite rapid. The crystals are of a fine reddish-violet colour, and may be easily seen in contrast with the brown, aqueous solution of iodine. The author states that iodine is the least volatile substance which forms such a hydrate, and suggests that other substances, such as paraffin, which are soluble in compressed gases (*loc. cit.*) will behave similarly under still higher pressures.

H. J. E.

A Potassium Chlorate Mixture for Generating Oxygen. HARUKAZE UDAKA (*J. Chem. Ind., Japan*, 1923, 26, 48—59).—A mixture of potassium chlorate 78.0, ferric oxide 7.0, ferrous carbonate 3.0, iron powder 5.0, silicon dioxide 2.0, magnesium oxide 0.3, magnesium chloride 0.0025, and water 5.0%, compressed by about 1,000 lb. per sq. in., and heated in a bomb, evolves oxygen of 98% purity. Ferrous carbonate may be replaced by nickel or cupric carbonate.

K. K.

System Sulphur Trioxide. I. A. SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1923, 26, 270—273).—A theoretical discussion of some of Le Blanc and Rüttele's results on sulphur trioxide (*Ber. Sächs. Akad. Wiss.*, 1922, 74, 106).

J. F. S.

The Formation of Sulphuric Acid by the Chamber Process. E. BRINER and M. ROSSIGNOL (*Helv. Chim. Acta*, 1923, 6, 647—655).—To study the influence of various factors on the gas reaction in the chamber process, a special apparatus was designed in which the reaction took place in a series of seven glass tubes, provision being made for the measurement of the acid formed in each. The concentration of the reacting gases was varied by varying the proportion of nitrogen. Increase of concentration increased the reaction in such a manner that the time needed to oxidise a given proportion of the sulphur dioxide varied inversely as the square

of the initial concentration. It follows from this relation that the reaction is of the third order. Increasing the pressure has the same effect as increasing the concentration. Increasing the concentration of nitrogen peroxide has an enormous effect on the reaction velocity. Thus increasing the proportion of nitrogen peroxide from 0.5 to 2.43% increased the reaction velocity about twelve times. The possible application of these results to the industry is discussed.

E. H. R.

Composition, Purification, and certain Constants of Ammonia. E. C. MCKELVY and C. S. TAYLOR (*U.S. Bur. Standards, Sci. Paper* 465, 1923, 655—693).—From an examination of fifteen carefully purified samples of ammonia, containing less than one part per million of non-condensing gases and less than 0.003% of water, the mean values of its physical properties were found to be as follows: Density of the solid at -79° , 0.817 g. per c.c.; at -185° , 0.836 g. per c.c.; freezing point, -77.7° ; vapour pressure at freezing point, 45.2 mm. [Cf. *J.S.C.I.*, 1923, Aug.]

A. R. P.

Specific Volume of Saturated Ammonia Vapour. C. S. CRAGOE, E. C. MCKELVY, and G. F. O'CONNOR (*U.S. Bur. Standards, Sci. Paper* 467, 1923, 707—735).—The specific volume of saturated ammonia vapour between -50° and $+50^{\circ}$ was measured by the pyknometer method and by measuring the refractive index. Above 0° , the values obtained by both methods agreed well with those calculated from the Clapeyron equation; below 0° , however, the pyknometer results are consistently lower and the optical results higher than the Clapeyron values. The following equation represents the results very closely: $\log_{10} \mu' = 300[6.46344/\theta - 0.106887 + 0.0356803 \log_{10} \theta] + 0.0862366 \sqrt{406.1 - \theta} + 0.002667(406.1 - \theta)$ where μ' is the specific volume of saturated ammonia vapour in c.c. per g. and θ is the absolute temperature.

A. R. P.

Ammonia and the Carbonates of the Potassium Group. H. PAULY (*Ber.*, 1923, 56, [B], 1454—1455).—If potassium, rubidium, or caesium carbonate is added to saturation to an aqueous solution of ammonia of any concentration at 20° , the mixture becomes divided into two layers; the upper one is a concentrated solution of ammonia containing only about 1% of the carbonate, whereas the lower one is a saturated solution of the carbonate containing about 1% of ammonia. A similar effect is not produced by sodium carbonate or by a number of freely soluble salts, such as potassium acetate, sodium iodide, or potassium cyanide.

If copper acetate is added to the system potassium, rubidium, or caesium carbonate-ammonia-water, the copper is retained almost exclusively by the solution of the carbonate. Cellulose dissolved in Schweitzer's reagent can therefore be caused to separate by the addition of potassium carbonate solution; the procedure has the advantage over other methods that the cellulose is precipitated slowly in a viscous, compact form.

H. W.

Monochloroamine, NH_2Cl . W. MARCKWALD and M. WILLE (*Ber.*, 1923, 56, [B], 1319—1325).—An extension of the work of Raschig (*A.*, 1909, ii, 232), involving the isolation of homogeneous chloroamine.

Well-cooled, approximately *N*-solutions of potassium hypochlorite and ammonia are mixed and the product is distilled under diminished pressure at 30—40°, the distillate being cooled in ice. It contains about 10—12% of chloroamine which suffers decomposition to a considerable extent during the distillation. Even at 0°, the solution soon commences to evolve nitrogen and to separate oily drops of nitrogen chloride. Its instability rapidly increases when it is preserved, decomposition being catalytically accelerated by the liberated acid. The course of the change is represented by the equations: $3\text{NH}_2\text{Cl} = \text{NH}_4\text{Cl} + 2\text{HCl} + \text{N}_2$, $\text{NH}_2\text{Cl} + 2\text{HCl} = \text{NH}_4\text{Cl} + \text{Cl}_2$, and $\text{NH}_2\text{Cl} + 2\text{Cl}_2 = \text{NCl}_3 + 2\text{HCl}$. Attempts to extract chloroamine from its aqueous solution by means of benzene, chloroform, carbon tetrachloride, or ether had only limited success, the last named solvent being the most suitable.

According to Raschig, the decomposition of chloroamine in alkaline solution proceeds smoothly in accordance with the equation: $3\text{NH}_2\text{Cl} + 3\text{KOH} = \text{NH}_3 + \text{N}_2 + 3\text{KCl} + 3\text{H}_2\text{O}$. This appears, however, only to be the case when dilute solutions of alkali are employed. With more concentrated solution the reaction takes place partly in accordance with the scheme: $3\text{NH}_2\text{Cl} + 3\text{KOH} \rightarrow 3\text{NH}_3 + 2\text{KCl} + \text{KClO}_3$.

The isolation of pure chloroamine has been rendered possible by the observations that its aqueous solutions are greatly stabilised by the presence of very small amounts of ammonia. Even under these conditions, however, the concentration of the 10—12% solutions cannot be effected by distillation, since violent explosions invariably occur which are obviously due to the formation of nitrogen chloride. The authors therefore have had recourse to the desiccation of the vapours of the 10—12% solution and condensation of the unabsorbed portions in a U-tube cooled in liquid air. For this purpose, calcium chloride and soda lime are unsuitable, since they influence the slight hydrolysis of chloroamine by water, $\text{NH}_2\text{Cl} + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{HClO}$, in such a manner that the condensate consists of chlorine monoxide. Better results are obtained with anhydrous potassium carbonate; *chloroamine* is thus obtained as a colourless, crystalline substance, m. p. -66° . It decomposes suddenly at about -50° into nitrogen, chlorine, ammonium chloride, and nitrogen trichloride, and frequently explodes violently, so that its physical properties could not be further investigated. H. W.

Molecular State at Low Temperatures of Dissolved Nitrogen Peroxide. PAUL PASCAL (*Bull. Soc. chim.*, 1923, [iv], 33, 539—548).—As complex additive products of nitrogen peroxide are known to exist, the question of the existence of this substance at low temperatures in a higher state of condensation than N_2O_4 was investigated by cryoscopic methods. The problem was complicated by the formation of mixed crystals of nitrogen peroxide with the

solvents. Solutions in bromoform presented a eutectic corresponding with 23·5% of bromoform and melting at $-13\cdot5^{\circ}$. The calculated mol. wt. of the peroxide was 96, corresponding with N_2O_4 . In carbon tetrachloride solution, the eutectic temperature was -49° for 8·15% of the dissolved substance. The mol. wt. found was 48, corresponding with NO_2 . In bromobenzene, the eutectic mixture melted at $-42\cdot5^{\circ}$, and the mol. wt. was 90. In chloroform, a eutectic mixture melting at -68° containing 8·5% of peroxide was formed, the mixed crystals constituting it being almost pure chloroform crystals with mixed crystals containing 46% of peroxide. The mol. wt. of the peroxide was 89. Even at this low temperature, therefore, the peroxide in solution retains the same constitution as in the liquid state. Solutions in chloropicrin and methyl iodide were also studied. The binary system nitrogen peroxide-camphor was also investigated from a concentration of 0—80% of the latter. Two definite compounds, $5\text{N}_2\text{O}_4\cdot 4\text{C}_{10}\text{H}_{16}\text{O}$, m. p. -52° , and $2\text{N}_2\text{O}_4\cdot 3\text{C}_{10}\text{H}_{16}\text{O}$, m. p. $-45\cdot5^{\circ}$, were indicated, and three eutectics, the first, m. p. -60° , formed of crystals of the former combination and mixed crystals containing 27% of camphor, the second, m. p. $-55\cdot5^{\circ}$, containing 65·5% of camphor, formed of pure crystals of the above two compounds, and the third, m. p. $-46\cdot5^{\circ}$, containing 74% of camphor and formed of pure camphor and the compound $2\text{N}_2\text{O}_4\cdot 3\text{C}_{10}\text{H}_{16}\text{O}$.

G. F. M.

The Preparation of Phosphoryl Chloride by the Simultaneous Action of Water and Chlorine on Phosphorus Trichloride. A. A. VANSCHIEDT and VADIM MICHAÏLOVITSCH TOLSTOPIATOV (*J. Russ. Phys. Chem. Soc.*, 1920, 52, 270—284).—The oxidation of phosphorus trichloride to the oxychloride can be effected by a number of reagents, such as ozone and potassium chlorate. These methods are, however, inconvenient because the reagents and vessels employed must be dry; a very satisfactory yield (about 90%) of phosphoryl chloride can, however, be obtained by passing a stream of chlorine through phosphorus trichloride and adding, drop by drop, an equivalent quantity of water; the end of the reaction is recognised by the formation of phosphorus pentachloride and the yellow coloration of the liquid. The heat of the reaction maintains the liquid at the boiling point until the end; the boiling is then continued artificially for about half an hour. A description is given of the apparatus used.

G. A. R. K.

Revision of the Atomic Weight of Boron. Analysis of Boron Trichloride. O. HÖNIGSCHMID and L. BIRCKENBACH (*Ber.*, 1923, 56, [B], 1467—1472).—The ratios, $\text{BCl}_3 : 3\text{Ag} : 3\text{AgCl}$, have been determined for three specimens of boron chloride purified by Stock and Kuss (following abstract), the values for the atomic weight of boron thus found being 10·840, 10·818, and 10·825, respectively. The slightly high value of the first series is probably attributable to the presence of a trace of silicon tetrachloride, derived from the action of boron trichloride on the glass with which it had

been in contact during four months. The authors adopt the mean value, $B=10.82$, which is in close agreement with the figure, 10.83 , obtained by Baxter and Scott (A., 1922, ii, 285). H. W.

The Preparation of Pure Boron Chloride and Boron Bromide for the Determination of the Atomic Weight of Boron. ALFRED STOCK and ERNST KUSS (*Ber.*, 1923, 56, [B], 1463—1466).—Boron chloride is agitated during twenty-four hours in sealed glass bulbs with pure mercury and distilled; the process is repeated a second time to ensure removal of free chlorine. The remaining impurities consist of silicon tetrachloride and hydrogen chloride. The product is distilled from a special, all-glass apparatus, and the distillate is collected in three receivers, cooled respectively to -90° to -85° , -120° to -115° , and in liquid air. The first receiver collects boron chloride and silicon tetrachloride, the second retains the purer fraction of boron chloride, and the third serves to condense the hydrogen chloride in addition to a little boron trichloride. The second fraction is distilled repeatedly until the condensates in each receiver have identical tensions. Lastly, the pure boron chloride is submitted to a control distillation and finally collected in small bulbs which are sealed.

Boron bromide is prepared from boron and "atomic weight" bromine, and is purified in the same manner as the chloride. In this instance, the homogeneity of the different fractions is judged by the melting point, -46.0° , since the tension at 0° is too small to permit a sufficiently accurate judgment to be made.

The materials thus prepared have been used by Hönigschmid and Birckenbach in determining the atomic weight of boron (preceding abstract). H. W.

Revision of the Atomic Weight of Iron. Analysis of Ferric Chloride. O. HÖNIGSCHMID, L. BIRCKENBACH, and R. ZEISS (*Ber.*, 1923, 56, [B], 1473—1481).—As mean value of twenty-five individual determinations of the ratios $\text{FeCl}_3 : 3\text{Ag} : 3\text{AgCl}$, the authors have determined the atomic weight of iron to be 55.85 . The preparation and the exact analysis of well-defined, sublimed ferric chloride are fully described in the original communication.

H. W.

The Appearance of Particles of Colloidal Carbon. HILARY LACHS (*Istny Zjazd Chemików Polskich*, 1923, 31—32).—Among other particles visible under the ultramicroscope in solutions of colloidal carbon are a number of scintillating particles, which continue to scintillate until the solution dries. These particles must be in the form of plates or prisms. Colloidal carbon solutions exhibit faint double refraction.

R. T.

Oxidation of Graphite by means of a Mixture of Silver Dichromate and Sulphuric Acid. L. J. SIMON (*Compt. rend.*, 1923, 177, 122—124; this vol., ii, 506).—Oxidation of Canadian graphite (99.9—100% purity) by means of this mixture gave a value for carbon percentage (c_1) of 101.3 — 102.7 , apparently owing to the presence of occluded hydrogen, which escapes oxidation.

After heating the graphite, the carbon percentage found was 99.6—100.5.

Sulphuric acid and chromic anhydride gave values for the carbon percentage (c_2) of 72.7—73.25. Oxidation is thus incomplete.

The oxidation of artificial (Niagara), schistous Canadian, Siberian, Madagascan, and laboratory-made graphites, and of plumbago, by the two different methods, gave a roughly constant c_2/c_1 ratio (0.66) for all the samples examined.

Diamond, wood-charcoal, coke, sugar-charcoal, anthracite, and natural coke are only partly oxidised by the silver dichromate method.
E. E. T.

Hydrofluosilicic Acid. Maximum Concentration of the Acid at Room Temperatures. C. A. JACOBSON (*J. Physical Chem.*, 1923, 27, 577—580).—Hydrofluosilicic acid is rarely put on the market in concentrations greater than 25%. The author finds that acid of this concentration (25%) can readily be obtained by passing silicon tetrafluoride into water. This solution can be concentrated to 40—45% by distilling in a double distillation flask at the ordinary temperature while a gentle stream of air is passed through the distilling liquid. Further concentration is effected by vacuum distillation at the ordinary temperature. For this purpose, two glass flasks of about 500 c.c. capacity with ground necks are connected by means of ground joints by a glass tube which is fitted with a side tube carrying a stopcock. A quantity (about 300 c.c.) of solution (41.41%) is placed in one flask, *A*, and the other flask, *B*, is placed in a freezing mixture, the whole exhausted (to 8 mm.) and kept at 20—22°, and periodically the concentrations of acid in *A* and *B* are estimated. The results show that the concentration of acid in *B* increases with the concentration in *A*, and that a maximum concentration of 60.92% is obtained in *A*. Acid of this concentration is stable for long periods of time, perhaps indefinitely.
J. F. S.

Influence of Neutral Salts on Silica Gels. S. GLIXELLI (*Compt. rend.*, 1923, 176, 1714—1716).—An augmentation of the acidity of silica gels under the influence of a neutral salt such as sodium, potassium or calcium chloride, sodium sulphate, etc., was indicated by titrating the gel with 0.01N-sodium hydroxide with phenolphthalein as indicator. The acid properties of silica increase, therefore, as do those of carbonic anhydride, in presence of uni- or bi-valent ions of a neutral salt. The effect can be explained by the adsorption of OH-ions by the silica particles, with which corresponds an increase in the negative charge of the colloidal particles.
G. F. M.

Decomposition of Potassium Chlorate. I. Spontaneous Decomposition Temperatures of Mixtures of Potassium Chlorate and Manganese Dioxide. F. E. BROWN, J. AUSTIN BURROWS, and H. H. McLAUGHLIN (*J. Amer. Chem. Soc.*, 1923, 45, 1343—1348).—When homogeneous, finely divided mixtures of potassium chlorate and manganese dioxide in various proportions

are rapidly heated, those containing more than one-sixteenth molecular equivalent and less than five molecular equivalents of manganese dioxide to one molecular equivalent of potassium chlorate undergo a spontaneous decomposition, accompanied by a rapid rise of temperature, at a temperature which is characteristic for each mixture. This acceleration is due to the exothermal nature of the decomposition. Pressure of oxygen exerts a marked effect on the decomposition of potassium chlorate. The decomposition temperature for mixtures containing 6 mol.% of manganese dioxide is 375°; 9%, 350°; 11%, 340°; 14%, 330°; 20%, 317°; 33%, 300°; with larger amounts of manganese dioxide up to about 60% the temperature does not fall much more, but above 60% it rises; thus with 84% of manganese dioxide the decomposition temperature is 315°.

J. F. S.

Oxidations with Fluorine. I. FR. FICHTER and K. HUMPERT (*Helv. Chim. Acta*, 1923, 6, 640—642).—The formation of potassium persulphate by the action of fluorine on a solution of potassium hydrogen sulphate was observed qualitatively by Brunner (A., 1921, ii, 45). Using the convenient method for preparing fluorine described by Meyer and Sandow (A., 1921, ii, 398), the observation has been confirmed. When the gas is passed into the cold saturated aqueous solution of potassium hydrogen sulphate for ten to twelve hours the persulphate crystallises out; after three recrystallisations from water, it is pure, having the composition $K_2S_2O_8$. Persulphates have previously only been obtained from hydrogen sulphates by electrolysis.

E. H. R.

The Influence of the Formation of Hydrates and Double Salts on the Reaction of Double Decomposition of Salts in Aqueous Solution, in the Case of the System Sodium Chlorate-Potassium Carbonate. VL. P. ILJINSKI (*J. Russ. Phys. Chem. Soc.*, 1923, 54, 29—59).—Solubility curves are constructed for the system sodium chlorate-potassium carbonate at 24.2° and at 40°. The solid phases of this system may contain the following salts at 24.2°: $KClO_3$; $NaClO_3$; $Na_2CO_3 \cdot 7H_2O$; $Na_2CO_3 \cdot 10H_2O$; $K_2CO_3 \cdot 2H_2O$; $K_2CO_3 \cdot Na_2CO_3 \cdot 6H_2O$. The solubilities of mixtures of sodium chlorate and carbonate are determined at 24.2° and at 40°, the solid phases at 24.2° being found to contain sodium chlorate, and the hepta- or deca-hydrates of sodium carbonate, and at 40° sodium chlorate and the monohydrate of sodium carbonate. The formation of the heptahydrate at a temperature below its transition point into the decahydrate is explained as being due to the extremely soluble sodium chlorate abstracting so much water from the solution as to cause a shortage of "solvent" water, thus rendering impossible the deposition of the more fully hydrated salt. The solubilities of mixtures of potassium and sodium carbonates are determined at 40°, 24.2°, 10°, and -6°. At 40°, the solid phases may consist of $Na_2CO_3 \cdot H_2O$, $Na_2CO_3 \cdot K_2CO_3 \cdot 6H_2O$, and $K_2CO_3 \cdot 2H_2O$; at 24.2° and at 10°, they may contain $Na_2CO_3 \cdot 10H_2O$, $Na_2CO_3 \cdot K_2CO_3 \cdot 6H_2O$, and $K_2CO_3 \cdot 2H_2O$, whilst at -6°, $Na_2CO_3 \cdot 10H_2O$, a new double salt hydrate, $Na_2CO_3 \cdot K_2CO_3 \cdot 24H_2O$, and a hydrate, $K_2CO_3 \cdot 3.75H_2O$,

may separate. Similar measurements are made at 40° and at 24.2° for mixtures of sodium and potassium chlorates, which are found to be the only constituents of the solid phases, although evidence is given for the formation of a double salt in solution. This is based on a new criterion for double salt formation, namely, that the solubilities of two salts increase at those concentrations at which the double salt appears, owing to the liberation of water "fixed" to the separate salts, thereby providing more solvent. Thus, the appearance of maxima of density of solutions may serve as an indication of double salt formation. The solubilities of mixtures of potassium chlorate and carbonate at 40° and at 24.2° are determined, the solid phases being $K_2CO_3 \cdot 2H_2O$, and $KClO_3$. From the results obtained, it is concluded that the most economical proportions of potassium carbonate and sodium chlorate to use for the preparation of potassium chlorate are 71 g. of the former and 67 g. of the latter per 100 g. of water. Using these proportions, potassium chlorate is precipitated quantitatively from the solution, the mother-liquor containing practically pure sodium and potassium carbonates.

The preparation by electrolysis of sodium chlorate from sodium chloride is examined. A steady current is allowed to pass for various intervals of time through a solution of sodium chloride, and the yields of chlorate are measured. It is found that using 6,565 ampere hours a yield of 93% of the total possible from the current is obtained, whilst using 13,195 ampere hours the yield is only 48% of theory.

R. T.

Constitution of the Insoluble Alkali Metaphosphates. PAUL PASCAL (*Compt. rend.*, 1923, 176, 1712—1714).—The insoluble alkali metaphosphates, as, for example, sodium metaphosphate prepared by the fusion of sodium dihydrogen phosphate at 850° , are not true metaphosphates, but are substances having the properties of colloids, of which certain transformations are irreversible. Sodium metaphosphate dissolves even in a dilute solution of sodium pyrophosphate, giving a viscous liquid, and its apparent molecular weight varies inversely with the dilution. The metaphosphate is precipitated from these solutions by the addition of a few drops of acetic acid as a colloidal mass which, after the removal of the greater part of the water, is as elastic as caoutchouc, and is dispersible in water, giving a liquid of extremely high viscosity which is no longer precipitable by acetic acid. If the insoluble metaphosphate is fused with sodium pyrophosphate, and the calcined product dissolved in water, the above-described phenomena are not reproduced, and the solution presents instead all the analytical characteristics of the true metaphosphates.

G. F. M.

Change of Reaction by the Conversion of Secondary and Primary Alkali Phosphates into Pyro- and Meta-phosphates. The Alkalinity of Borax Solutions. HANS MURSCHHAUSER (*Biochem. Z.*, 1923, 138, 6—12).—As a means of determining the relative changes in reaction when primary and secondary sodium phosphates are converted into meta- and pyro-phosphates, the effect

of these salts on the rate of mutarotation of dextrose was investigated. Equivalent quantities of the salts under comparison were dissolved in water, and 100 c.c. of this solution were used to dissolve 5 g. of dextrose in each experiment. 0.025N $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ gave a mutarotation constant of 24.9 at 20.4°, whilst the 0.025N $\text{Na}_4\text{P}_2\text{O}_7$, prepared from the disodium phosphate by heating, gave constants of 90.5 and 84.1. 1.0N $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ gave 26.3 and 24.9; after conversion to NaPO_3 , the value was 10.7. 0.1N $\text{Na}(\text{NH}_4)\text{HPO}_4 \cdot 4\text{H}_2\text{O}$ gave 40.4 and after conversion to NaPO_3 in 1.0N concentration 8.8. It is concluded that conversion of Na_2HPO_4 to $\text{Na}_4\text{P}_2\text{O}_7$ increases the alkalinity, whilst the change of NaH_2PO_4 to NaPO_3 lessens the acidity. $M/120 \text{ Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ gave, under similar conditions, a mutarotation constant of 27.8, $M/80$ gave 42.4, whilst with $M/12$ solution mutarotation was so rapid that five minutes after solution the $[\alpha]_D$ was +42.5, i.e., below the equilibrium value for aqueous solutions. This low value (which remains constant for some time) is ascribed, not to any change in the sugar, but to a specific action of borax.

J. P.

The Space Lattices of the Lithium Halides. HEINRICH OTT (*Physikal. Z.*, 1923, 24, 209—212).—Anhydrous lithium chloride, bromide, and iodide have been investigated by the Debye-Sherrer method. On account of their hygroscopicity, these substances were examined in cylinders of waxed paper made air-tight with paraffin wax. Corrections were necessary for the effect of the paper. To avoid the fogging of the plates by the L -radiation of iodine, the rod of lithium iodide was surrounded by aluminium foil. The three space lattices were found to be of the sodium chloride type, and from their dimensions, calculated values of the densities were obtained, which agreed closely with the experimental figures. The monohydrate of lithium chloride possesses a space lattice of the caesium chloride type.

W. E. G.

The Polysulphides of the Alkali Metals. IV. The Polysulphides of Ammonium. JOHN SMEATH THOMAS and RICHARD WILLIAM RIDING (*T.*, 1923, 123, 1726—1738).

Stability of Bleaching Powder. SHUICHIRO OCHI (*J. Chem. Ind. Japan*, 1923, 26, 348—385).—The author has studied the effects of water and other common impurities on the stability of bleaching powder, and investigated methods to prevent the decomposition. The decomposition of bleaching powder is greatly accelerated, not only by the uncombined water, but also by the water of crystallisation of the compound $\text{OCl} \cdot \text{CaCl}$. At elevated temperature, 45°, the decomposition is quicker and the effect of water is greater than at the ordinary temperature. The stability of bleaching powder is increased by drying at 100° under reduced pressure (50 mm.), without any appreciable loss of available chlorine. Sodium sulphate or soda lime also promotes stability, but is less effective. Calcium sulphate has little effect, and calcium chloride none. When a mixture of bleaching powder and calcium oxide is chlorinated again, a stable substance is produced containing

31—35% of available chlorine. On the decomposition involving loss of available chlorine, ferric oxide and manganese sesquioxide have a great effect, silicon dioxide a little, and aluminium oxide and magnesium oxide none. The decomposition of the completely dried powder may be represented as follows: $\text{Ca}(\text{OCl})\text{Cl} = \text{CaCl}_2 + \text{O}$; this decomposition is accelerated by admixture with ferric oxide or manganese sesquioxide, but not by aluminium, magnesium, or silicon oxides. Decomposition leading to the formation of chlorate arises from the presence of water; the more water, the more vigorous the decomposition; it may be almost entirely prevented by drying under reduced pressure or by mixing with calcium oxide, sodium sulphate, or soda lime. The evolution of chlorine may be represented as follows: $2\text{CaCl} \cdot \text{OCl} + (x+1)\text{H}_2\text{O} = \text{CaCl}_2 + \text{Ca}(\text{OH})_2 + \text{OCl}_2 + x\text{H}_2\text{O}$ and $\text{OCl}_2 = \text{O} + \text{Cl}_2$. The reaction $\text{Ca}(\text{OCl})\text{Cl} = \text{CaO} + \text{Cl}_2$ could not be realised. K. K.

Setting of Plaster of Paris. PIERRE JOLIBOIS and CHASSEVENT (*Compt. rend.*, 1923, **177**, 113—116).—From experiments on the solubility, etc., of calcium sulphate (baked at various temperatures) and of the hemi-hydrate, it is concluded that the setting of anhydrous calcium sulphate takes place in three stages: formation of solid hemi-hydrate, dissolution of the latter, and crystallisation of dihydrate. E. E. T.

The Analysis of Bubbles in Glass. RESEARCH STAFF OF THE GENERAL ELECTRIC CO., J. W. RYDE and R. HUDDART, LONDON (*Proc. Physical Soc.*, 1923, **35**, 197—198).—A small piece of glass containing bubbles is contained in one limb of an exhausted U-tube and mercury in the other. The glass is softened by heating, and then disintegrated by plunging the tube into cold water, the mercury being simultaneously thrown on to the glass. Gases liberated from the bubbles are examined spectroscopically in a capillary discharge tube attached to the U-tube. The presence of nitrogen indicates the introduction of air or furnace gases into the glass during ladling, stirring, or pouring. If nitrogen is absent, it is concluded that the bubbles are due to the generation of gas in the glass. J. S. G. T.

The Alkaline-earth Permanganates. M. CRESPI and E. MOLES (*Anal. Fis. Quím.*, 1922, **20**, 693—701; cf. this vol., ii, 161).—A study of the preparation and properties of the permanganates of calcium, strontium, and barium. The thermal behaviour of these permanganates resembles that of the permanganates of the alkali metals. It is shown that hydrates of calcium and strontium permanganates do not exist. G. W. R.

Equilibrium between Lead Iodide and the Iodides of Potassium and Ammonium in Aqueous Solution. (MME) N. DEMASSIEUX (*Compt. rend.*, 1923, **177**, 51—54).—By means of the solubility method, the author shows that, of the various double iodides of lead with potassium and ammonium, only those

($\text{PbI}_2 \cdot \text{KI} \cdot 2\text{H}_2\text{O}$ and $\text{PbI}_2 \cdot \text{NH}_4\text{I} \cdot 2\text{H}_2\text{O}$) described by Herty (A., 1896, ii, 474) and by Wells and Johnston (A., 1893, ii, 523) actually exist.
E. E. T.

Hydrous Oxides. V. Hydrous Cupric Oxide. HARRY B. WEISER (*J. Physical Chem.*, 1923, 27, 501—532; cf. A., 1922, ii, 575, 853).—After a discussion of the literature concerning hydrated copper oxides, the author describes a number of experiments on the stability of the granular hydrated oxide, and the action of salts on the precipitated forms of hydrated copper oxide. The results show that no definite hydrates of cupric oxide are known with certainty. Since a hydrated oxide having approximately zero vapour pressure approaches the composition $\text{CuO} \cdot \text{H}_2\text{O}$, it is usually concluded that a monohydrate exists. This conclusion is shown to be incorrect by the fact that the anhydrous oxide does not take up water at the ordinary temperature when in contact with water, but, on the contrary, the hydrated oxides lose water under these conditions. A crystalline hydrate has been described (A., 1895, ii, 267), but this has been found to consist of pseudo-crystals or granular particles which do not result from its own power of crystallisation. Loss of water takes place more readily from the gelatinous oxide than from the granular oxide, because of the compact structure of the latter. Highly dispersed hydrated cupric oxide is very light blue in colour. The gelatinous oxide in mass has a characteristic clear blue colour which alters slowly at the ordinary temperature, but rapidly at higher temperatures, passing through various shades of blue to green, brown, and finally to black. The continuous change in colour is due to agglomeration of the particles which accompany the spontaneous loss of water. Blue, gelatinous cupric oxide kept at 0° passes spontaneously to a denser and bluer granular product. It is thus possible to obtain any number of hydrated oxides which vary continuously in composition from $\text{CuO} + 20\text{H}_2\text{O}$ to $\text{CuO} + \text{H}_2\text{O}$. Hydrated cupric oxide adsorbs ions strongly. If shaken with solutions of neutral salts like sodium chloride or sulphate, hydrolysis takes place and the solution becomes distinctly alkaline owing to stronger adsorption of acid than of base. On account of the strong adsorption of hydrated cupric oxide for certain ions the presence of some salts frequently accelerates slightly the spontaneous loss of adsorbed water. Hydrated cupric oxide may be heated at 100° without darkening in the presence of very small amounts of salts, such as manganous, cobalt, aluminium, chromous, zinc, and copper sulphates, and zinc and cupric chlorides. The stability of hydrated cupric oxide at 100° in the presence of the above-named salts is not due to adsorption of the hydrated oxides of their metals as stated by Bancroft (A., 1914, ii, 250) and by Blucher and Farnau (A., 1914, ii, 841). The evidence against their stabilisation theory is, that hydrated cupric oxides adsorb acids more strongly than bases, that relatively high concentrations of the colloidal hydrated oxides are not effective, and that cupric sulphate is as effective as manganous and chromous sulphates. This latter observation is conclusive, since it is in-

conceivable that a substance should be stabilised by adsorbing some of itself. The absence of darkening cannot be due to the formation of basic cupric salts, since the effective concentration of electrolyte is so low that the ratio of oxide to sulphate in the salts could be no less than $20\text{CuO} : \text{SO}_4$, which is altogether improbable; and it is not due to the formation of a protecting film of basic salt, since alkali salts which give basic salts under certain conditions hasten rather than retard the blackening. Darkening of the hydrated oxide at 100° does not take place in the presence of suitable concentrations of certain salts owing to a change in the physical character from the highly gelatinous to the granular form of the oxide. Only those salts which hydrolyse appreciably are effective in low concentrations, since the slight solvent action of the hydrogen-ion destroys the gelatinous structure, and the denser granular modification which forms loses water and darkens less readily than the loose voluminous mass. J. F. S.

The System Copper Oxide, Copper Hydroxide, Cuprite, Sodium Hydroxide. ERICH MÜLLER [with MAX KAHLERT, GEORG WIEGAND, ILSE ERNST, and JOHANNES KEIL], (*Z. physikal. Chem.*, 1923, 105, 73—118).—An investigation of the system copper oxide, copper hydroxide, cuprite, and sodium hydroxide. It is shown that the blue cupric hydroxide is soluble in concentrated solutions of sodium hydroxide to form deep blue solutions, from which, if the hydroxide concentration does not exceed $17N$, dark brown precipitates separate after keeping for some time. The undissolved blue cupric hydroxide also turns brown on keeping. These dark-coloured substances are to be regarded as solid solutions of cupric oxide and cupric hydroxide, the hydroxide content being connected with the concentration of copper in the supernatant liquid. The dehydration of cupric hydroxide takes place through a series of these solid solutions. The solubility of cupric oxide and cupric hydroxide in sodium hydroxide increases with increasing alkali hydroxide concentration, but above a given concentration the solubility again decreases. The solubility of cupric hydroxide is considerably greater than that of cupric oxide. The rising branch of the solubility curve is represented by $C_{(\text{NaOH})}^2/C_{\text{Cu}}=K$ and the falling branch by $C_{(\text{NaOH})}^2 \cdot C_{\text{Cu}}=K'$. The maxima of the solubilities correspond with the transition point of $\text{CuO} + \text{H}_2\text{O} \rightleftharpoons \text{Na}_2\text{CuO}_2$ and $\text{Cu}(\text{OH})_2 \rightleftharpoons \text{K}_2\text{CuO}_2$, respectively. Hence cupric oxide and hydroxide on treatment with very concentrated alkali hydroxide are converted into cuprite. A sodium cuprite may be crystallised from aqueous alkali hydroxide solution; this substance has a cobalt blue colour and probably the formula Na_2CuO_2 . A diagram has been constructed which presents all the possibilities which may occur when cupric oxide or hydroxide is treated with alkali. The view that copper oxide is colloidally dissolved by alkali hydroxide can no longer be maintained. J. F. S.

Complexes in Solutions of Copper and Cobalt Salts. HENRY GEORGE DENHAM and STUART WORTLEY PENNYCUICK (*J. Amer. Chem. Soc.*, 1923, 45, 1353—1357).—Measurements of the *E.M.F.* of

cells of the type $\text{Co}|\text{CoCl}_2 + x\text{MCl}_y||\text{NH}_4\text{NO}_3(\text{sat})||\text{Hg}_2\text{Cl}_2, 0.1\text{N KCl}|\text{Hg}$ have been made at 25° , where the concentration of the cobalt chloride is kept constant, and where the nature of MCl_y varies as does also the concentration. The salt MCl_y is potassium chloride, magnesium chloride, aluminium chloride, or zinc chloride. The concentration of the cobaltous ion has been calculated in each case. Similar measurements have been made with cells of the type $\text{Cu}|\text{CuSO}_4 + \text{M}_x(\text{SO}_4)_y||\text{NH}_4\text{NO}_3||\text{Hg}_2\text{Cl}_2, 0.1\text{N KCl}|\text{Hg}$, where $\text{M}_x(\text{SO}_4)_y$ is potassium, aluminium, or zinc sulphate. A comparison of the results fails to reveal any striking difference between the behaviour of zinc and aluminium. Were the electro-affinities of zinc and aluminium the only factors in bringing about changes in the colours of solutions of copper and cobaltous salts, it would be expected that the depressions of the ionic concentrations of copper and cobalt would be more noticeable in the case of aluminium than zinc. The above experiments do not confirm this. In all cases, the effect of adding a zinc salt to a solution of a copper or cobalt salt is rather greater than that produced by an equivalent quantity of an aluminium salt, a result probably due to the increased ionisation of the zinc salt. The moving boundary experiments of Donnan and Bassett (T., 1902, **81**, 939), together with the quantitative migration experiments of Denham and Watkins (T., 1919, **115**, 1269; A., 1909, ii, 373), make it probable that the colour changes exhibited by solutions of copper and cobalt salts are intimately associated with complex formation. The results also indicate that still another factor, which may be hydration, also plays a part in the changes.

J. F. S.

Association of Mercuric Chloride. F. BOURION and E. ROUYER (*Compt. rend.*, 1923, **177**, 54—56).—From measurements of the boiling point of a number of aqueous solutions of mercuric chloride, it is concluded that the salt is associated to give treble molecules, which are given the extended formula $\text{Hg}[\text{HgCl}_3]_2$, to bring the compound into line with $\text{K}[\text{HgCl}_3]$.

E. E. T.

Double Decomposition in the Absence of Solvents. II. The Systems of Mercuric Iodide with the Nitrates of Thallium and Alkali Metals. A. G. BERGMANN (*J. Russ. Phys. Chem. Soc.*, 1922, **54**, 200—218).—A study of the system $\text{HgI}_2\text{--TiNO}_3$ shows that these compounds do not interact on melting, and the diagram of state is of a simple type, with a single eutectic point at 192° and a flat portion in the region 33—75 mol.% HgI_2 indicating miscibility of the components. The usual transition points for the modifications of thallium nitrate were observed, namely, 78.5° and 142.5° , m. p. 207° ; for mercuric iodide, 129.5° , and m. p. $257\text{--}258^\circ$, respectively.

The systems of mercuric iodide with the nitrates of ammonium, lithium, sodium, potassium, and rubidium, were not studied in great detail, because it was found that the mutual solubility of the components was very slight; no signs of interaction of the components could be observed. It is suggested that the higher the negative thermal effect of the double decomposition between the

components, the less is their miscibility in the liquid state; thus in the system $\text{AgNO}_3\text{--HgI}_2$ there is complete miscibility, whilst LiNO_3 and HgI_2 are practically immiscible; the thermal effects of their interaction are calculated at -54.48 cal. and -126.4 cal., respectively.

The theoretical views of van Laar (A., 1908, ii, 808), of Eggink (A., 1908, ii, 1043), and of Smits and Bokhorst (A., 1915, ii, 262) are discussed.

G. A. R. K.

Aluminium-Titanium Alloys and the Influence of Titanium on Aluminium. EUGEN VAN ERCKELENS (*Metall und Erz*, 1923, 20, 206—210).—Aluminium-titanium alloys containing up to 30.7% of titanium consist of a mixture of hard, needle-shaped crystals of Al_4Ti in a softer ground mass of aluminium. The compound Al_4Ti melts at 1325° and forms neither eutectic nor solid solution with aluminium. Addition of titanium, in amounts not exceeding 1%, to aluminium removes the combined nitrogen and oxygen and consequently improves the tensile properties; at the same time, the resistance of the metal to attack by salt solutions and by organic acids is appreciably increased. [Cf. *J.S.C.I.*, 1923, 721A.]

A. R. P.

Synthetic Aluminium Silicates and their Relationships to Kaolin. ROBERT SCHWARZ and ALBERT BRENNER (*Ber.*, 1923, 56, [B], 1433—1437).—The action of sodium silicate on aluminium chloride in aqueous solution has been investigated, the conditions being so chosen that the mixtures are neutral in reaction. The precipitates are filtered, dried on the water-bath, washed successively with water, alcohol, and ether, and subsequently analysed. The filtrates contain only traces of aluminium in addition to silicic acid and sodium chloride. The influence of concentration is such that the molecular ratio of silica to aluminium hydroxide diminishes with increasing dilution, but is always at least slightly in excess of the proportion 1.5:1, thus showing that silica is invariably adsorbed by the primary product, $2\text{Al}_2\text{O}_3.3\text{SiO}_2$. The proportion of silica in the product increases with increasing concentration of sodium silicate, although the latter never enters quantitatively into the reaction; when 6—10 molecular proportions of silicic acid are present, the compound $\text{Al}_2\text{O}_3.2\text{SiO}_2$ is invariably produced which corresponds in composition with natural kaolin, $\text{Al}_2\text{O}_3.2\text{SiO}_2.2\text{H}_2\text{O}$. A normal silicate, $\text{Al}_2(\text{SiO}_3)_3$, appears incapable of existence. The primary product of the action is the compound $2\text{Al}_2\text{O}_3.3\text{SiO}_2.x\text{H}_2\text{O}$, which absorbs silicic acid when left in contact with the solution and tends to pass into the compound $\text{Al}_2\text{O}_3.2\text{SiO}_2$. If the precipitate is heated in contact with the solution, the substance $\text{Al}_2\text{O}_3.2\text{SiO}_2.2\text{H}_2\text{O}$ (after desiccation at 110°) is obtained. Röntgen spectrographic investigation of the products proves that the primary product, $2\text{Al}_2\text{O}_3.3\text{SiO}_2.6\text{H}_2\text{O}$, is amorphous, and that from it there is formed in course of time a crystalline substance which is similar or closely related to natural kaolin in structure. The natural product loses its two molecular proportions of water continuously from 360° and becomes anhydrous at 640° . The artificial product loses one molecular pro-

portion up to 260° and the second proportion between 360° and 640° .

It appears, therefore, that in the neutral, aqueous system, $\text{Al}_2\text{O}_3, \text{SiO}_2 + \text{H}_2\text{O}$, a single compound, $\text{Al}_2\text{O}_3, 2\text{SiO}_2, x\text{H}_2\text{O}$, is capable of formation which is uninfluenced by the presence of an excess of silica or by the period of the reaction; this compound is formed with particular readiness when at least six molecules of silica are present for each molecule of aluminium oxide, as is the case with feldspar. H. W.

Permeability of Nickel to Hydrogen. VICTOR LOMBARD (*Compt. rend.*, 1923, 177, 116—119).—The volume of hydrogen passing in unit time through a given area of nickel (used in disks 0.3—0.4 mm. thick) is an exponential function of the temperature, and is proportional to the square root of the pressure. Temperatures of 370° to 693° and pressures of 11 to 775 mm. were used. E. E. T.

The Constitution of the Higher Oxide of Nickel. OWEN RHYS HOWELL (*T.*, 1923, 123, 1772—1783).

Chemistry of Hafnium. G. HEVESY (*Chem. News*, 1923, 127, 33—34).—Zirconium minerals all contain hafnium to the extent of from 1 to 30% of their zirconium content. Typical thorium minerals were found to be free from hafnium. Zirconium and hafnium are best separated by crystallisation of the potassium double fluoride, prepared by melting the zirconium mineral with potassium hydrogen fluoride. The zirconium and hafnium double fluoride are extracted with boiling water which dissolves 25% of potassium zirconifluoride. On cooling the solution, the hafnium salt concentrates in the mother-liquor, the solubility at 20° of the hafnium double fluoride in $N/8$ -hydrofluoric acid solution being about 3% and larger than that of the corresponding zirconium compound. Thus by crystallising a solution of 1000 g. of potassium zirconifluoride containing 6% of hydrofluosilicic acid from a 10% hydrofluoric acid solution, and repeating the process four times, the residual 750 g. of the double fluoride contained only 2% of the potassium salt. Alternatively, the crystallisation described may be replaced by crystallisation of the corresponding ammonium compound, or combined with the partial precipitation of zirconium-hafnium compounds with ammonia, or by boiling the solution with sodium thiosulphate. The phosphate of hafnium is appreciably less soluble in concentrated acids than zirconium phosphate, but separation along these lines is tedious. A preliminary determination, employing hafnium containing from 5 to 6% of zirconium, indicates that the atomic weight of hafnium is between 178.4 and 180.2.

J. S. G. T.

Germanium. V. Extraction from Germanium Bearing Zinc Oxide. Direct Preparation of Germanium Dioxide Free from Arsenic. Detection of Minute Amounts of Arsenic in Germanium Dioxide. L. M. DENNIS and E. B. JOHNSON (*J. Amer. Chem. Soc.*, 1923, 45, 1380—1391; cf. A., 1921, ii, 456; 1922, ii, 302).—A new method for the extraction of germanium

from crude zinc oxide is described. Like the earlier published methods for the extraction of germanium from this material, this new method is based on the volatility of germanium tetrachloride, but it is superior to the earlier methods in that it eliminates the necessity for the use of hydrogen sulphide and concentrates germanium by successive distillations with the aid of a column still of new design. By this process, 99% of the germanium in the crude material is recovered, and of this 83% is obtained directly as germanium dioxide, the remaining 16% is recovered indirectly by the return of residual materials to subsequent extractions. The germanium dioxide produced by this method is of exceptional purity. Spectroscopic examination of the material indicated that it contained less than 0.001% of iron and less than 0.0005% of arsenic.

J. F. S.

Germanium Oxide. E. L. NICHOLS (*Proc. Nat. Acad. Sci.*, 1923, 9, 248—251).—The intensity of the visible radiation from germanium oxide at temperatures between 837° and 1370° in the spectral regions $\lambda\lambda$ 0.65 μ , 0.52 μ , and 0.45 μ , and the departure of the radiation from that characterising a black body have been investigated, together with the production of luminescence in the substance by flame excitation. The melting point of germanium oxide, correct to within a few degrees, is 1400°.

J. S. G. T.

Preparation of Metallic Sulphides by Double Decomposition. Application to Cuprous Sulphide. (MLLE) GERMAINE MARCHAL (*Bull. Soc. chim.*, 1923, [iv], 33, 597—602).—The displacement of antimony from antimonious sulphide (stibine) by copper always results in the formation of cuprous sulphide, whatever the proportion of copper employed. The reaction, scarcely perceptible at 500°, occurs readily at 600—700°, and at that temperature is complete in about eight hours, the antimony having volatilised and condensed on the cooler portions of the experimental tube, whilst almost pure cuprous sulphide remains. When insufficient copper is used for the complete formation of cuprous sulphide no cupric sulphide is formed, but instead the compound $3\text{Cu}_2\text{S} \cdot \text{Sb}_2\text{S}_3$, which is only slowly decomposed at temperatures above 700°, antimony sulphide subliming without decomposition, leaving finally a residue of cuprous sulphide only. A similar reaction occurs between copper and zinc sulphide at temperatures of 950—1000°, and here again cuprous sulphide and metallic zinc are the only products.

G. F. M.

Mineralogical Chemistry.

Crystal Structure of Molybdenite. ROSCOE G. DICKINSON and LINUS PAULING (*J. Amer. Chem. Soc.*, 1923, **45**, 1466—1471).—The mineral molybdenite has been investigated by means of spectral and Laue photographs and with the aid of the theory of space

groups, the simplest structure capable of accounting for the X-ray data has been derived. This structure, which is of a new type, contains two molecules of molybdenum disulphide in a hexagonal unit having $d_{0001}=12.30$ Å. and an axial ratio 3.90. The molybdenum atoms are at $(1/3, 2/3, 1/4)$ and $(2/3, 1/3, 3/4)$ and the sulphur atoms at $(1/3, 2/3u)$, $(2/3, 1/3u)$, $(1/3, 2/3, 1/2-u)$ and $(2/3, 1/3, 1/2+u)$ where u is 0.621 ± 0.004 . In the structure found, each sulphur atom is equidistant from three molybdenum atoms, and each molybdenum atom is surrounded by six equidistant sulphur atoms at the corners of a small triangular prism the altitude of which is 3.17 ± 0.10 Å. and the edge of which is 3.15 ± 0.02 Å. The distance from the molybdenum atom to the nearest sulphur atoms is 2.41 ± 0.06 Å. The excellent basal cleavage of molybdenite is undoubtedly connected with the relatively great distance between the sulphur atoms.

J. F. S.

Cornish Torbernite. WILLY STEINKUHLER (*Bull. Soc. chim. Belg.*, 1923, **32**, 253—255).—A specimen of torbernite from Tincroft consisted of large spangles embedded in quartz. The crystals were quadratic tablets deep emerald in colour with vitreous lustre: hardness 2; d^{17} , 3.68; n , 1.594—1.600 (mean). Analysis gave:

H ₂ O.	P ₂ O ₅ .	UO ₃ .	CuO.	PbO.	Insoluble.	Fe ₂ O ₃ +Al ₂ O ₃ .
14.62	14.40	60.54	8.58	0.11	0.15	0.61

corresponding with the formula $\text{CuO}, 2\text{UO}_3, \text{P}_2\text{O}_5, 8\text{H}_2\text{O}$.

F. A. M.

Torbernite from Katanga ($\text{CuO}, 2\text{UO}_3, \text{P}_2\text{O}_5, 8\text{H}_2\text{O}$). WILLY STEINKUHLER (*Bull. Soc. chim. Belg.*, 1923, **32**, 270—271; cf. previous abstract).—Of three specimens of torbernite from Katanga, two only could be purified sufficiently for analysis; these were massive forms; d^{17} , 3.84—3.951; n , 1.600—1.618. All the specimens contained lead. Analysis gave:

H ₂ O.	Insol.	P ₂ O ₅ .	PbO.	UO ₃ .	Fe ₂ O ₃ +Al ₂ O ₃ .	CuO.	Te.	MoO ₃ .
14.31	0.18	14.42	2.95	60.35	0.88	7.15	0.63	100.87

The water content both here and the Cornish specimen approximates to that of metatorbernite, but the refractive index is intermediate between that for torbernite and metatorbernite, whilst the density differs considerably from either of these. The anomalies may be due in part to the lead content, as this element is present in much greater amount than has hitherto been recorded for torbernite.

F. A. M.

Natural Gases. IV. F. HENRICH and G. PRELL (*Ber.*, 1923, **56**, [B], 1259—1262; cf. A., 1922, ii, 858).—In continuation of previous work, analyses are now recorded of gases evolved from a number of springs the water of which is so constant in composition that they can be influenced but little or not at all by surface waters.

H. W.

Analytical Chemistry.

Sublimation as an Analytical Procedure. J. HORTVET (*J. Assoc. Off. Agric. Chem.*, 1923, 6, 481—489).—The use of a sublimator is described, whereby numerous organic substances may be estimated and separated from other substances which have different temperatures of sublimation. A. G. P.

A Trap for the Van Slyke Gas Analysis Apparatus. A. T. SHOHL (*J. Biol. Chem.*, 1923, 56, 125—126).—The trap is illustrated in the original. It consists of a tube attached to, and parallel with, the blood pipette, and carries a stop-cock at the top. Any gas or fluid adhering to the tubing of the apparatus after cleaning gradually collects in this trap, and may then be expelled from the apparatus through the stop-cock. E. S.

Method of Estimating the Available Chlorine in Bleaching Powder. SHUICHIRO OCHI (*J. Chem. Ind., Japan*, 1923, 26, 185—190).—Among the methods for estimating available chlorine in bleaching powder, Penot's arsenite method only is regarded as trustworthy, Wagner's iodine method being rejected as giving too high results. The author has improved the latter method by using 2—4 c.c. of dilute acetic acid (1 : 1) for 25 c.c. of the testing solution, the chlorate then being without influence. The arsenite method gives results lower than the true value, whilst the iodine method gives somewhat high figures; the difference is chiefly due to the difference of the application of indicator, *i.e.*, outside and inside indicators, the difference between the two methods being 0.2—0.3%. The accuracy of the two methods is of the same order, but when the testing solution or the standard solution is dilute, Wagner's method gives the more accurate result. K. K.

Use of Bromate in Volumetric Analysis. II. Influence of Mercuric Mercury on Bromic Acid Reactions. G. FREDERICK SMITH (*J. Amer. Chem. Soc.*, 1923, 45, 1417—1422; cf. this vol., ii, 504).—A number of experiments are described illustrating the use of mercuric mercury in causing bromate to be converted entirely into either bromide or free bromine in oxidation reactions. It is shown that mercuric mercury causes bromate to be reduced to bromide entirely in its action on chlorides, bromides, and iodides. In the presence of mercuric perchlorate the reactions between manganous nitrate, chromic nitrate, nitrous acid, and oxalic acid, respectively with bromic acid yield bromide entirely, whereas in the absence of the mercuric salt the reaction yields free bromine rather than the bromide. This action is not restricted to reactions with bromates; bromides in the presence of sufficient mercuric mercury are not decomposed by potassium permanganate in hot sulphuric acid solution. Further, the oxidation of sodium oxalate solution by potassium iodate in hot sulphuric acid, according to the equation $2\text{KIO}_3 + 5\text{Na}_2\text{C}_2\text{O}_4 + 6\text{H}_2\text{SO}_4 = \text{I}_2 + \text{K}_2\text{SO}_4 + 5\text{Na}_2\text{SO}_4 +$

$10\text{CO}_2 + 6\text{H}_2\text{O}$, is entirely prevented by the presence of sufficient mercuric perchlorate. Mercuric perchlorate is prepared by treating mercuric nitrate with a slight excess of 70% perchloric acid and heating to expel the nitric acid. The solution is then boiled until copious fumes of perchloric acid are evolved, allowed to cool, and the pasty mass centrifuged. This salt is preferable to mercuric sulphate or nitrate, since these salts are so readily hydrolysed and, in the case of the sulphate, difficult to obtain free from mercurous sulphate. The preventive action of mercuric mercury is shown to be due to the formation of slightly ionised mercuric halides. J. F. S.

The Distribution of Iodine between Chloroform and Starch Solution, with and without the Addition of Potassium Iodide. J. B. FIRTH and F. S. WATSON (*J. Soc. Chem. Ind.*, 1923, 42, 308—310r).—The authors find that starch solutions give an immediate blue coloration with solutions of iodine in chloroform of concentrations greater than $N/1000$. The amount of iodine transferred to the starch solution is proportional to the concentration of the starch, and is increased considerably by the presence of a small amount of potassium iodide, up to 0.192 g. per litre. Further additions of potassium iodide increase the amount of iodine transferred, but the increase is not proportional to the potassium iodide added. A starch solution containing 4 g. of starch and 0.384 g. of potassium iodide per litre will detect iodine in a solution of strength $N/20,000$. J. S. G. T.

Estimation of Iodine by Sodium Thiosulphate. F. O. RICE, MARTIN KILPATRICK, jun., and WILLIAM LEMKIN (*J. Amer. Chem. Soc.*, 1923, 45, 1361—1365).—In connexion with the estimation of iodine by titration with sodium thiosulphate, the authors have investigated the volatility of iodine solutions and the stability of solutions of sodium thiosulphate. It is shown that iodine solutions have an appreciable vapour pressure of iodine, and that this is reduced in 0.1*N*-solutions just as effectively by 2% of potassium iodide as by 4% of potassium iodide. Iodine may be estimated in acid solution if it is added to standard sodium thiosulphate solution in the presence of a buffer solution, which may be either the phosphate or boric acid buffer described by Washburn (*A.*, 1908, ii, 363). Standard thiosulphate solutions should be made up in the purest water obtainable; they may then be standardised and used immediately after preparation. The authors have devised a method of handling and estimating iodine solutions which is as follows. The stock-bottles containing the iodine and thiosulphate solutions are each fitted with a syphon terminating in a stop-cock, the tip of which is drawn out to be 15 cm. long, with internal and external diameters 0.5 and 1.5 mm., respectively. Portions of thiosulphate (10—30 g.) containing a little starch solution were weighed to 0.0005 g. in stoppered conical flasks. Before adding the iodine to the thiosulphate, the tip of the syphon was filled by adding a little iodine to a beaker of water, keeping the tip about 1 cm. below the surface of the water. The tip was then touched against the side of the beaker to remove adhering liquid and placed

in the thiosulphate solution to a depth of 1 cm. and iodine run in until a faint blue colour appeared. The flask was then removed, stoppered, and weighed. The slight excess of iodine added was corrected by means of blank experiments. J. F. S.

Estimation of Iodine in Thyroid Glands and in Thyroid Extracts. R. FABRE and H. PÉNAU (*Bull. Soc. Chim. biol.*, 1923, 5, 341—347).—The iodine in thyroid extract may be estimated by evaporating to dryness with an aqueous-alcoholic solution of potassium hydroxide, and calcining. The residue is dissolved in dilute sodium chloride solution, and filtered from carbonaceous matter. Permanganate is added to change all iodides to iodates, and the excess destroyed by the addition of alcohol. The iodate is then estimated in the usual way by the addition of iodide and acid and titration of the iodine set free. Thyroidin from pigs contained 0.3048% of iodine, from oxen 0.4127%, from sheep 0.399%, and from horses 0.290%. W. O. K.

Standardisation of Solutions used in Iodimetry. STEPHEN POPOFF and F. L. CHAMBERS (*J. Amer. Chem. Soc.*, 1923, 45, 1358—1360).—A number of experiments are described on the standardisation of solutions of sodium thiosulphate by iodine and by potassium permanganate, respectively. Ordinarily, the two methods do not give identical results, the former being about 0.1% higher than the latter. It is pointed out that the divergence between the two results is probably to be attributed to the fact that the one titration is carried out in acid solution and the other in neutral solution. The authors show that if both determinations are carried out under identical conditions the result is the same in both cases. The method of titration recommended is: *Iodine method*.—The usual procedure is followed except that the iodine solution, before titration, contains 140 c.c. of water, 10 g. of potassium iodide, and 15 c.c. of 1:5-sulphuric acid. *Permanganate method*.—To 100 c.c. of 10% potassium iodide solution containing 15 c.c. of 1:5-sulphuric acid a quantity of standard potassium permanganate is added sufficient to liberate about the same quantity of iodine as is normally used in the standardisation of sodium thiosulphate by the iodine method. The liberated iodine is then titrated in the usual way with sodium thiosulphate. Both methods have been used to standardise a given solution of thiosulphate; the iodine method gives the normality of the solution as 0.10053, whilst the permanganate method gives 0.10052. J. F. S.

Estimation of Sulphur in Iron. TERUO ASHIDA (*J. Chem. Soc. Japan*, 1923, 44, 483—491).—Amongst the methods for the estimation of sulphur in iron or steel, the hydrogen sulphide method gives lower values than the gravimetric method, but takes a shorter time. By the following modification, however, accurate results may be obtained: 2—3 g. of the granulated sample are placed in an Erlenmeyer's flask with about 10 g. of amalgamated zinc (prepared from 8 g. of mercuric chloride and 500 g. of granulated zinc), and hydrochloric acid (d 1.15—1.2) is gradually added. When

the reaction becomes feeble, the flask is heated and the gas washed out with hydrogen. The evolved hydrogen sulphide, after washing with 60 c.c. of hot water, is led into a wash bottle (A) containing 40 c.c. of water, and then into an absorption bottle containing 10 c.c. of ammoniacal cadmium chloride solution (prepared from 120 g. of cadmium chloride, 1500 c.c. of water, and 600 c.c. of aqueous ammonia) diluted with 50 c.c. of water. The cadmium sulphide produced is filtered, washed, and titrated with *N*/50-iodine and about *N*/50-sodium thiosulphate solutions. Hydrogen sulphide absorbed in A is estimated and the amount added to the previous figure. The result is identical with that obtained by the gravimetric method, whilst the time required is about thirty minutes only. K. K.

Volumetric Estimation of Tellurium by the Dichromate Method. VICTOR LENHER and H. F. WAKEFIELD (*J. Amer. Chem. Soc.*, 1923, 45, 1423—1425).—It is shown that the potassium dichromate titration can be applied successfully to the volumetric estimation of tellurium. Tellurium dioxide in hydrochloric acid solution is oxidised quantitatively to tellurium trioxide by potassium dichromate. Certain very definite steps in the procedure are essential. The weight of tellurium dioxide should be less than 0.3 g. and the solution should contain 2.0% of free hydrochloric acid. The volume of the solution should be approximately 200 c.c. The titration is carried out as follows. To the acid solution of tellurium dioxide an excess of 0.1*N*-potassium dichromate solution is added, followed in half an hour by a known excess of standard ferrous sulphate solution, the excess of which is subsequently titrated by dichromate, using ferricyanide as an outside indicator. J. F. S.

Estimation of Amino-nitrogen in Compounds Reacting Slowly with Nitrous Acid. D. WRIGHT WILSON (*J. Biol. Chem.*, 1923, 56, 183—190).—Using Van Slyke's apparatus, the amount of nitrogen evolved, when various substances, mainly purine and pyrimidine derivatives, react slowly with nitrous acid, has been measured. The estimations were carried out at temperatures of from 21—26°; the times of reaction varied from three minutes to five hours. Guanosine, guanylic acid, guanine, and cytosine gave amounts of nitrogen which corresponded with more than the theoretical one amino-group; the amount from allantoin corresponded with nearly two such groups; adenine and adenine nucleotide gave the theoretical amount for one amino-group; xanthine, hypoxanthine, guanidine, and methylguanidine yielded small amounts of gas; none was produced by uric acid, thymine, uracil, uridine, brucine, betaine, or sarcosine.

In the estimation of amino-nitrogen in urine by Van Slyke's method, one-third of the blank may be due to the presence of creatinine. E. S.

Estimation of Free Amino-nitrogen in Proteins. D. WRIGHT WILSON (*J. Biol. Chem.*, 1923, 56, 191—201).—A comparison of the methods of Van Slyke and of Sørensen has led to

the conclusion that the latter is more accurate. Van Slyke's method may give high results owing to slow hydrolysis of the proteins, or low results due to precipitation. E. S.

A Characteristic Reaction for Hydroxylamine. W. N. HIRSCHER and J. A. VERHOEFF (*Chem. Weekblad*, 1923, 20, 319—320).—An ammoniacal solution of diacetylmonoxime in presence of hydroxylamine condenses to dimethylglyoxime, which in presence of nickel gives the well-known red precipitate. A concentration of 1 mg. per c.c. of hydroxylamine gives the precipitate at once in the cold; for small quantities, it is necessary to boil, cool, and neutralise with acetic acid, and in this way 0.01 mg. can be detected.

Care must be taken in preparing the diacetylmonoxime solution, since this partly hydrolyses with warm water, yielding free hydroxylamine, which forms dimethylglyoxime when the solution is made alkaline. S. I. L.

Detection of Nitrates in Vegetable or Animal Material. TH. SABALITSCHKA and C. SCHMIDT (*Ber. Deut. pharm. Ges.*, 1923, 33, 181—184).—The conditions are given for the application of the diphenylamine test for nitrates in presence of organic matter, bromide, iodide, chromate and chloride together, etc. [See *J.S.C.I.*, 1923, Aug.] T. H. P.

A New Gravimetric Estimation of Nitric Acid. H. RUPE and F. BECHERER (*Helv. Chim. Acta*, 1923, 6, 674—676).—Di-(α -naphthylmethyl)-amine, prepared by catalytic reduction with hydrogen of α -naphthonitrile, forms an extraordinarily sparingly soluble nitrate and can be used for the estimation of nitric acid. A hot 10% solution of the base in 50% acetic acid is added to a boiling, very dilute solution of the nitrate, and when the solution is allowed to cool, the di(α -naphthylmethyl)amine nitrate separates in glistening leaflets which can be readily filtered and washed with cold water. The only acids which form readily soluble salts with the new base are sulphuric acid and phosphoric acid; other acid radicles interfere with the determination of nitrate by this method. The solubility of the nitrate per 100 c.c. of water is 0.00004 g. at 24° and 0.0795 g. at 100°; in 100 c.c. of alcohol, 0.0446 g. at 21°. The solubility of the hydrochloride is 0.0972 g. per 100 c.c. of water at 21°. As a qualitative reagent, the new base gives a distinct precipitate with a 1 : 100,000 solution of potassium nitrate. The nitrate of di(β -naphthylmethyl)amine has a higher solubility, 0.026 g. per 100 c.c. of water at 20°. E. H. R.

The Estimation of Nitrates in Soils by the Phenol-Di-sulphonic Acid Method. C. T. GIMINGHAM and R. H. CARTER (*J. Agric. Sci.*, 1923, 13, 60—62).—In the estimation of nitrates in soil extract by the phenoldisulphonic acid method, using aluminium hydroxide as a decolorising agent (*Emerson, Soil Sci.*, 1921, 12, 413) untrustworthy results may be obtained where the extracts are filtered through certain kinds of filter-paper. It is shown that with a standard solution containing sodium nitrate equivalent to four

parts of nitrogen per million the most satisfactory agreement is obtained where a coarse filter-paper is used. It is suggested that retention by filter-paper may affect the accuracy of estimations in other methods.

G. W. R.

The Quantitative Separation of Arsenic, Antimony, and Tin. G. LUFF (*Chem. Ztg.*, 1923, 47, 601—602).—The mixed sulphides obtained in the ordinary course of analysis are dissolved in 5 g. of the purest sodium hydroxide dissolved in a little water, and the solution is treated with hydrogen peroxide until colourless, boiled for one hour, and evaporated to 100 c.c. After cooling, the solution is neutralised with hydrochloric acid, treated with twice its bulk of the same acid, and saturated with hydrogen sulphide whilst keeping the vessel cooled in ice. Next day, the precipitate of arsenic sulphide is collected on a Gooch crucible, washed with 2 : 1 hydrochloric acid, then with warm water and dissolved in ammonia and hydrogen peroxide. The solution is boiled, exactly neutralised with acetic acid, and treated with ammonium nitrate and silver nitrate, and the silver arsenate is collected on a Gooch crucible, dried at 120°, and weighed. The filtrate from the arsenic sulphide is evaporated to 100 c.c. and its acidity adjusted so that it contains 14 c.c. of hydrochloric acid per 100 c.c.; after adding 5 g. of ammonium chloride per 100 c.c., the antimony is precipitated by hydrogen sulphide, the precipitate collected in a Gooch crucible, washed, dried, heated at 270° in carbon dioxide, and weighed. Tin is estimated in the filtrate from the antimony sulphide by any convenient method.

A. R. P.

New Volumetric Method of Elementary Analysis. L. HACKSPILL and G. DE HEECKEREN (*Compt. rend.*, 1923, 177, 59—60).—The substance to be analysed is heated with cupric oxide in an exhausted silica tube. Combustion, to give carbon dioxide, nitrogen, and water, is complete in about three hours. The products formed are readily estimated. Water is removed by cooling to -80°, etc., subsequently treating with calcium hydride, and measuring the hydrogen produced. Nitrogen and carbon dioxide are measured in the usual manner.

E. E. T.

Two Analytical Figures of Interest with regard to Illuminating Gas: "Combustible Power" and Percentage of Nitrogen. MAURICE NICLOUX (*Bull. Soc. chim.*, 1923, [iv], 33, 823—835).—The "combustible power" of a gas is defined as the number of volumes of air necessary for the complete combustion of 100 volumes of the gas. The author describes a simple method for the determination of this figure, using only small quantities of gas (of the order of 50 c.c.), and quotes figures for the gas supply of Paris and of Strasbourg. Determinations of the percentage of nitrogen in the gas show that this figure is larger at the present time than before the war.

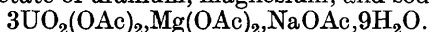
H. H.

Estimation of Carbon Monoxide in the Air. MAURICE NICLOUX (*Bull. Soc. chim.*, 1923, [iv], 33, 818—822).—The air, deprived of oxygen, is passed through ox blood containing alcohol

as a preservative and the volume of air necessary for the production of the absorption bands of carboxy-hæmoglobin noted. It is claimed that by adhering strictly to the method of procedure and always using the same apparatus set up in the same way, accurate and comparable results can be obtained.

H. H.

[Micro]-estimation of Sodium. A. BLANCHETIÈRE (*Bull. Soc. chim.*, 1923, 33, [iv], 807—818).—Sodium can be estimated in small quantities of biological materials (blood, fæces, etc.) by precipitation as the triple acetate of uranium, magnesium, and sodium,



The author has investigated the conditions under which this method is applicable. [Cf. *J.S.C.I.*, 1923, Aug.]

H. H.

A Method for the Analysis of Alkali Phosphotungstates. R. MELLET (*Helv. Chim. Acta*, 1923, 6, 656—661).—A sample is ignited in a platinum crucible to estimate water or, in the case of ammonium salts, water and ammonia. To estimate phosphoric oxide, the residue is fused with a mixture of four to five times its weight of mixed sodium and potassium carbonates and, after dissolution, the phosphorus is precipitated as magnesium ammonium phosphate in the usual way. A second precipitation is advisable, and the result obtained is generally 1 to 1.5% too low.

The best method available for estimating the tungsten is to precipitate the phosphotungstate as insoluble quinoline phosphotungstate, and to estimate the phosphoric oxide in the residue obtained by igniting the quinoline salt, the tungstic oxide being obtained by difference. The quinoline salt is precipitated at 60° with a solution containing 20 g. of quinoline in 50 g. of glacial acetic acid. The precipitate must be well washed with a dilute solution of quinoline acetate, and even then it adsorbs a small quantity of alkali. The quinoline precipitates stable complex acids completely, but when the complex is unstable, part of the phosphoric acid may remain in solution. The ignition of the quinoline phosphotungstate requires care to prevent reduction of the tungstic oxide to the blue oxide; if this is formed, it can sometimes be reoxidised with nitric acid. Some complex salts, however, cannot be ignited without reduction of part of the tungstic acid to metallic tungsten which, during the alkaline fusion, adheres to the bottom of the crucible as a tungsten-platinum alloy. Its amount is given by the gain in weight of the crucible.

The alkali metal can be determined as chloride in the solution obtained after precipitation of the quinoline phosphotungstate. In such cases where the precipitation of the phosphoric acid is incomplete, the alkali metal can only be estimated by difference. Ammonia is estimated by the usual distillation process.

E. H. R.

The Titration of Silver- and Chlorine-ions in Presence of Protective Colloids. W. D. TREADWELL, S. JANETT, and M. BLUMENTHAL (*Helv. Chim. Acta*, 1923, 6, 513—518).—Silver nitrate can be titrated electrometrically with sodium chloride in presence

of a protective colloid such as gelatin without appreciable loss of sharpness at the end-point. From the titration curve, it is calculated that the solubility of the colloidal silver chloride is about 2×10^{-2} millimols. per litre, which is about twice the solubility of ordinary silver chloride. The colloidal silver chloride particles introduce no error through adsorption of chlorine- or silver-ions, although such errors are observed in the titration of silver with sulphide. The electrometric titration with chloride is applied in the estimation of ionic silver in a number of pharmaceutical preparations containing silver. [Cf. *J.S.C.I.*, 1923, Aug.] E. H. R.

New Gravimetric Method for the Estimation of Zinc. G. SPACU (*Bul. Soc. Ştiinţe Cluj*, 1923, 1, 361—364; from *Chem. Zentr.*, 1923, ii, 508).—An excess of ammonium thiocyanate, either solid or in concentrated solution, is added to a neutral solution of a zinc salt. Pyridine is then added with agitation (3 drops to each 0.1 g. of zinc sulphate) until present in excess. The precipitate, which has the composition $\text{Zn}(\text{C}_5\text{NH}_5)_2(\text{CNS})_2$, is collected and washed with an aqueous solution containing 0.3% of ammonium thiocyanate, 0.2% of ammonium sulphate, and 0.2% of pyridine. The precipitate is dried, ignited over a Teclu burner, and weighed as zinc oxide. The results are in good agreement with those obtained electrolytically. G. W. R.

The Estimation of Metallic Sulphides by Ignition in Hydrogen Sulphide. L. MOSER and E. NEUSSER (*Chem. Ztg.*, 1923, 47, 541—543, 581—582).—Lead sulphide is stable in an atmosphere of hydrogen or of hydrogen sulphide up to 350° . It begins to volatilise in the latter gas at 570° . Lead oxide, sulphate, carbonate, and chloride may all be converted into sulphide quantitatively by ignition in hydrogen sulphide. For the estimation of lead in solution by this process, it is first precipitated from a solution containing a little nitric acid by a current of hydrogen sulphide, and the precipitate is collected on a Gooch crucible, washed, and heated in an air-bath at 300 — 400° in a current of the gas. Bismuth may be similarly estimated, but the heating is conducted at 270° . Higher temperatures or an atmosphere of hydrogen decompose the compound. Bismuth oxychloride or the precipitated metal, but not the ignited oxide, are quantitatively converted into sulphide by ignition in hydrogen sulphide at 270° . For the estimation of thallium by the process, hydrogen sulphide is passed into the neutral solution of the thallium salt and ammonia is then added to give a distinct alkaline reaction. The precipitate, collected on a Gooch crucible, is ignited in a current of the gas at 300° and weighed as thallous sulphide. To obtain accurate results air must be excluded from the apparatus. Antimony sulphide, precipitated in either the black or red modification, is converted into pure trisulphide at 270° in hydrogen sulphide, whilst tungsten trioxide, especially if freshly precipitated, is converted quantitatively into disulphide at 500° in a current of the same gas. The process is inapplicable to molybdenum, nickel, cobalt, and tin. A. R. P.

The Molybdo-manganimetric Micro-estimation of Copper.

GEORGES FONTÈS and LUCIEN THIVOLLE (*Bull. Soc. chim.*, 1923, [iv], 33, 840—844).—The copper salt may be treated with an alkali to precipitate the hydroxide, which is then dissolved in glycerol and reduced to cuprous oxide with dextrose or formaldehyde. The cuprous oxide is then dissolved in the phosphomolybdic reagent, and the blue oxides of molybdenum so produced are titrated with potassium permanganate. The authors, however, recommend one of the following methods. The copper may be deposited electrolytically on a platinum gauze spiral, the copper dissolved in the phosphomolybdic reagent (warmed gently if necessary), and the titration carried out as before. The second method consists of the precipitation of the copper as a compound with nitroso- β -naphthol, incinerating this to copper oxide which can be reduced in a current of hydrogen, dissolved in the phosphomolybdic reagent as before, and titrated with potassium permanganate. This method is inapplicable in the presence of iron or cobalt.

H. H.

Separation of Copper from Selenium. A. ANGELETTI (*Gazzetta*, 1923, 53, i, 339—341).—When copper and selenium occur together, the former may be precipitated by means of “cupferron,” treatment of the filtrate with sulphur dioxide then resulting in precipitation of the selenium. [Cf. *J.S.C.I.*, 1923, 746A.] T. H. P.

Estimation of Copper and its Separation from Cadmium.

P. WENGER and N. DÜRST (*Helv. Chim. Acta*, 1923, 6, 642—647).—When copper is estimated as oxide by precipitation with sodium hydroxide in a porcelain or glass vessel, the silica should always be estimated in the precipitate and a correction applied. The classical cuprous sulphide method is accurate when proper precautions are taken. The method of Girard, which consists in precipitating the copper with sodium hyposulphite and estimating as cuprous sulphide, is very good for copper alone, but not so good in presence of cadmium, as a second precipitation is necessary. The method of Dallimore (A., 1909, ii, 833), which consists in precipitating the copper with hypophosphorous acid as metallic copper and weighing as such, or as oxide, is very accurate and easy to carry out and is always to be recommended for the separation of copper and cadmium. Other methods described in the literature are not recommended.

E. H. R.

The Influence of Alkali on the Titration of some Metals with Ferrocyanide. II. W. D. TREADWELL and D. CHEVRET (*Helv. Chim. Acta*, 1923, 6, 550—559).—See this vol., i, 764.

Estimation of Praseodymium. PAUL H. M.-P. BRINTON and H. ARMIN PAGEL (*J. Amer. Chem. Soc.*, 1923, 45, 1460—1465).—The effect of heating praseodymium oxalate in air, oxygen, and a vacuum has been investigated. It is shown that heating the oxalate in air gives a residue of constant weight in crucibles of platinum, porcelain, or alundum. This oxide when heated for sixty minutes in hydrogen at 900—950° loses 3.10% of its weight, but on again

heating in air at the same temperature it regains its original weight exactly. Heating the oxide in oxygen causes a slight increase in weight, but this increase is lost on again heating the oxide in air. These results show that the completely reduced oxide is the sesquioxide, Pr_2O_3 , whilst the oxide obtained by ignition in the air is Pr_6O_{11} , and not Pr_4O_7 , as stated by Welsbach. A volumetric method is described for the estimation of praseodymium. This consists in adding concentrated nitric acid to the sample, 1 c.c. for 0.1 g. of oxide, and heating to effect solution. About 100 c.c. of water are added and the solution is heated at $60\text{--}70^\circ$ and an excess of 0.1N-oxalic acid added slowly with constant stirring. The mixture is kept warm for about an hour. The excess of nitric acid is now gradually neutralised with ammonium hydroxide, which is added a few drops at a time at intervals of several minutes until the liquid shows only a faintly acid reaction. The oxalate precipitate is filtered and washed, and the excess of oxalic acid heated at 80° and titrated with potassium permanganate solution after the addition of 10 c.c. of 1:1-sulphuric acid. The results for pure praseodymium and for praseodymium with less than 1% of cerium are very satisfactory, but if lanthanum is present they are too high.

J. F. S.

An Improvement in the Colorimetric Estimation of Manganese in Carbon Steels. H. FORESTIER (*Bull. Soc. chim.*, 1923, [iv], **33**, 659—660).—In the estimation of manganese in carbon steels the oxidation method with persulphate can be used successfully colorimetrically with mean errors of only 0.5% on the manganese content if the light employed in the colorimeter is sensibly complementary to that traversing the solutions under examination. In this case, white, diffused light is filtered through a solution of nickel sulphate, and a neutral tint is thus obtained at the eye-piece which is very sensitive to the least variation of luminous intensity. The sources of possible error in the Proctor Smith method—incomplete oxidation of the manganese, and subsequent incomplete reduction—are eliminated by the colorimetric method, as an excess of persulphate can be used to ensure complete oxidation of the manganese to permanganate.

G. F. M.

The Reaction Between Ferric Salts and Alkali Thiocyanates. J. F. DURAND and K. C. BAILEY (*Bull. Soc. chim.*, 1923, [iv], **33**, 654—659).—On shaking ferric chloride with silver thiocyanate in anhydrous ether a red coloration due to ferric thiocyanate, $\text{Fe}(\text{CNS})_3$, is produced; but if the ethereal solution is then shaken with water, practically the whole of the coloration is transferred to the water. The violet-red colour which is extracted from the aqueous solution by ether or amyl alcohol in the usual test for iron or thiocyanates where the alkali thiocyanate is in excess, cannot therefore be due to ferric thiocyanate, and it is also shown that if the ferric salt is present in excess the coloration is scarcely transferred to the ethereal layer at all. The addition of a further quantity of alkali thiocyanate, or even of an alkali chloride, determines the solubility

of the coloured substance in ether or amyl alcohol. For this reason, the colorimetric method proposed by Lachs and Friedenthal for the estimation of iron (A., 1911, ii, 542) cannot be used conversely for the estimation of a thiocyanate. The solubility or otherwise of the red coloration in ether or amyl alcohol cannot be regarded as a specific test for the presence or absence of a thiocyanate, as not only is the thiocyanate colour not always soluble in the organic solvents, but, on the other hand, ferric chloride gives with potassium iodide an intense orange-red colour not destroyed by hydrochloric acid, and soluble in amyl alcohol and ether, and with alkaline acetates the colour is likewise soluble in amyl alcohol, although not in ether.

G. F. M.

A New Gravimetric Method for the Estimation of Iron and for the Separation of Iron and Manganese. BOGDAN SOLAJA (*Chem. Ztg.*, 1923, 47, 557).—Iron may be precipitated quantitatively from solutions of ferric salts by addition of so-called infusible white precipitate (NH_2HgCl). The precipitate obtained is dense, filters readily, and is easily washed; on ignition, it leaves a residue of ferric oxide. The method may be used to separate iron from manganese.

A. R. P.

Molybdo-manganimetry and its Applications. II. Micro-estimation of Iron. Application to the Estimation of Iron in the Blood. G. FONTÈS and L. THIVOLLE (*Bull. Soc. Chim. biol.*, 1923, 5, 325—340; cf. this vol. ii, 264).—The principle of the micro-method described is as follows. The iron is reduced to the ferrous state with copper and phosphoric acid, the phosphomolybdate reagent is added, and the blue colour produced is titrated with permanganate. For very small quantities a modification is preferred in which the iron is precipitated with nitroso- β -naphthol. The precipitate is then ignited and reduced to the metallic state in a current of hydrogen. The phosphomolybdate reagent is added and the blue colour titrated. For the estimation of iron in blood, the iron may be precipitated combined with the hæmoglobin by picric acid, and the whole ignited. The iron is then reduced to the metallic state and estimated as above. Alternatively, the organic matter may be destroyed by heating with sulphuric and nitric acids. The mean error by these methods is 2—3%.

W. O. K.

The Molybdo-manganimetric Micro-estimation of Iron. GEORGES FONTÈS and LUCIEN THIVOLLE (*Bull. Soc. chim.*, 1923, [iv], 33, 844—849; cf. this vol., ii, 581).—Two methods are proposed. First, a ferric salt is reduced to the ferrous state by means of metallic copper in the presence of phosphoric acid, and the copper in the filtrate estimated as previously described (*loc. cit.*). In the second method, the iron is precipitated by means of nitroso- β -naphthol, incinerated to the oxide, reduced to the metallic state, and estimated as in the case of copper. The second method is inapplicable in the presence of copper or cobalt, but small amounts of phosphates do not interfere.

H. H.

Dinitrosoresorcinol as a Reagent for the Estimation of Cobalt in the Presence of Nickel and other Metals of the Iron Group. W. R. ORNDORFF and M. L. NICHOLS (*J. Amer. Chem. Soc.*, 1923, **45**, 1439—1444).—When an aqueous solution of dinitrosoresorcinol is added to a solution of cobalt sulphate or chloride, a brownish-red precipitate is formed, which, when dry, has the composition $(C_6H_3O_4N_2)_2Co$. This can be collected in a Gooch crucible and dried to constant weight at 125—130°, when it has the composition given above; at 160—161°, the compound decomposes. The quantitative precipitation is effected as follows. A solution containing about 0.03 g. of cobalt sulphate or chloride is diluted to 50 c.c. and 1 c.c. of hydrochloric acid (*d* 1.17) added. This is warmed and 300 c.c. of a hot aqueous solution of dinitrosoresorcinol (1 g. per litre) are added. A deep red colour but no precipitate is produced. Then, whilst the mixture is stirred, 10 c.c. of a solution of sodium acetate (10 g. of crystallised salt in 100 c.c. of water) are added slowly. A colloidal precipitate is formed; the solution is digested for fifteen minutes over a flame and stirred once after five minutes' heating. A voluminous, brownish-red precipitate is formed which settles after a short time, leaving a clear, reddish-yellow solution. The precipitate is filtered, with gentle suction, in a Gooch crucible, washed with 0.5—1.0% hydrochloric acid until the filtrate is colourless, and dried at 125—130° until of constant weight. This requires about two hours. The results are accurate to about $\pm 1\%$. In the presence of small quantities of nickel, cobalt is estimated as follows. The cobalt is precipitated as above and allowed to settle; the clear supernatant liquid is then decanted through a weighed Gooch crucible. A very small amount of precipitate collects on the filter, which is washed with 50 c.c. of 0.085*N*-hydrochloric acid. This same acid is then transferred to the precipitate in the beaker and the whole digested for thirty minutes over a low flame. The precipitate is then filtered through the same Gooch crucible and thoroughly washed with 0.5—1.0% hydrochloric acid and the estimation completed as described above. Neither zinc nor manganese forms a precipitate with dinitrosoresorcinol, and experiment shows that in the presence of relatively large quantities of these metals cobalt may be estimated by the method as originally described. Copper is precipitated to some extent by dinitrosoresorcinol, and the precipitate is not dissolved by digesting with hydrochloric acid, so that to estimate cobalt if copper is present the latter element must be removed first. This is accomplished as follows. The solution containing 0.0200 g. of cobalt and 0.06 g. of copper is acidified with sulphuric acid and electrolysed to remove the copper, then neutralised with 1:1-ammonium hydroxide and 1 c.c. of hydrochloric acid (*d* 1.17) added. The cobalt is estimated as before. Iron forms a green precipitate with dinitrosoresorcinol which is not dissolved by digesting with hydrochloric acid. To estimate cobalt in the presence of iron, the solution is treated with 5 c.c. of hydrochloric acid (*d* 1.17) and evaporated to 25 c.c., and extracted with ether, which removes most of the iron. The aqueous solution is boiled to remove ether

and treated with dilute ammonia to precipitate the iron, the precipitate is dissolved in acid and reprecipitated, and the combined filtrates are evaporated to 50 c.c., neutralised with dilute hydrochloric acid, 1 c.c. of hydrochloric acid ($d\ 1.17$) is added, and the cobalt estimated as before. J. F. S.

New Volumetric Method for the Estimation of Nickel. G. SPACU and R. RIPAN (*Bul. Soc. Ştiinţe Cluj*, 1922, **4**, 325—331; from *Chem. Zentr.*, 1923, ii, 380).—The method depends on the action of potassium or ammonium thiocyanate on nickel salts in the presence of pyridine, whereby the nickel is precipitated as a blue compound, $[\text{Ni}(\text{C}_5\text{NH}_5)_4](\text{CNS})_2$. The excess of thiocyanate may be determined volumetrically by standard silver nitrate solution. A good agreement is shown with electrolytic estimations. G. W. R.

New Gravimetric Method for the Estimation of Nickel and Thiocyanates. G. SPACU (*Bul. Soc. Ştiinţe Cluj*, 1922, **1**, 314—320; from *Chem. Zentr.*, 1923, ii, 380; cf. preceding abstract).—The method is based on the reaction of nickel salts with ammonium thiocyanate in the presence of pyridine. The complex nickel pyridine thiocyanate, $[\text{Ni}(\text{C}_5\text{NH}_5)_4](\text{CNS})_2$, is washed with 5% aqueous pyridine solution and after ignition weighed as nickel oxide. In the estimation of thiocyanate by the reverse method, a portion of the nickel forms a soluble blue compound, according to the equation $2\text{NH}_4\text{CNS} + 6\text{C}_5\text{NH}_5 + 2\text{NiSO}_4 + 2\text{H}_2\text{O} = [\text{Ni}(\text{C}_5\text{NH}_5)_4](\text{CNS})_2$ (precipitate) + $[\text{Ni}(\text{H}_2\text{O})_2(\text{C}_5\text{NH}_5)_2]\text{SO}_4$ (soluble compound) + $(\text{NH}_4)_2\text{SO}_4$. G. W. R.

The Analytical Value of the "Molybdenum-blue" Reaction. F. FEIGL (*Chem. Ztg.*, 1923, **47**, 561).—The solution used for the test for tin described by Hüttig (this vol., ii, 437) has a distinctly oxidising effect on stannous chloride solutions owing to the presence of nitrates. The most sensitive solution for carrying out the test is made by dissolving 1 g. of molybdenum trioxide in a little sodium hydroxide solution, acidifying with hydrochloric acid, and diluting to 200 c.c. The test may be made very sensitive by shaking the solution with a little amyl alcohol, which extracts the blue compound, giving a blue upper layer (cf. Feigl and Neuber, this vol., ii, 508). The blue colour is more stable in the presence of phosphoric or arsenic acid; the actual blue compound appears to be a derivative of molybdenum pentahydroxide, possibly the molybdate, in a colloidal form. In support of this, it is shown that the best conditions for the formation of the colour are a low acidity, absence of neutral salts, and a low temperature. A. R. P.

Detection of Small Quantities of Antimony and Bismuth in Biological Liquids. CAILLE and E. VIEL (*Compt. rend.*, 1923, **176**, 1759—1761).—The reaction recently described (this vol., ii, 443) for the detection of alkaloids by the precipitation of their iodoantimonates by means of a potassium iodide-antimonious chloride reagent may be used conversely for the detection of small amounts of antimony. The most satisfactory reagent for this purpose contains 1 g. of antipyrine and 2 g. of potassium iodide in

30 c.c. of water. This reagent is stable and can be kept indefinitely. It gives a golden-yellow precipitate with an antimony solution to which one-fifth of its volume of hydrochloric acid has been added, and as little as 0.025 mg. of antimony can be detected in this way. By using it as a microchemical reaction the sensibility is raised to 1 in 200,000. Under similar conditions, bismuth gives a brick-red precipitate. To apply the reaction for the detection of antimony and bismuth in biological fluids, the samples must be freed from blood and other organic matter by ignition and subsequent solution of the ash in nitric acid, followed by evaporation to dryness. The white ash is then dissolved in hydrochloric acid and the reagent added. G. F. M.

Combustion of Methane in the Presence of Glowing Platinum. J. W. WHITAKER (*Fuel*, 1923, 2, 201—202).—In estimating methane in mine gases by slowly burning it in contact with a heated platinum spiral, the latter must be raised to a white heat and the gas exposed to the action of it for three to four minutes, otherwise the methane is not completely oxidised. Such incomplete oxidation may be recognised by the value of C/A obtained (C , contraction in volume after combustion; A , amount of subsequent absorption in potassium hydroxide solution), which in place of the theoretical value 2.0 may approach 4.1 or more. In such cases, the gas should be re-exposed to the action of the hot wire, and this treatment repeated until the ratio total C /total A is very nearly 2. The results obtained are usually slightly higher than those of explosion analysis (cf. Hansen and Nielsen, *ibid.*, 115). T. S. W.

Analysis of Gas Mixtures containing Methyl Chloride. RALPH H. MCKEE and STEPHEN P. BURKE (*Ind. Eng. Chem.*, 1923, 15, 578—579).—In estimating methyl chloride in mixtures containing other components soluble in organic solvents, the acetic acid absorption method (Allison and Meighan, A., 1919, ii, 527) is supplemented by burning the gas mixture, in a measured excess of oxygen, over a strong solution of potassium hydroxide in a combustion pipette. The alkaline solution and washings are filtered to remove, as mercurous oxide, the small amount of mercury which goes into solution during the combustion, the filtrate is neutralised, and the chloride in it estimated. The quantity of methyl chloride found can be checked by the volume of oxygen consumed, if the nature and amount of any other combustible components are known. A discrepancy between the two results indicates the presence of a higher chlorinated compound or of some combustible gas not taken into consideration. The experimental error is less than 0.7%. If ethylene is present, its volume may be estimated approximately by shaking with bromine water under standard conditions, the amount of methyl chloride reacting with the bromine being inappreciable. W. T. K. B.

Examination of Methyl Alcohol. Frequency of the Occurrence of Impurities acting on Potassium Iodide and Iodine, and on Potassium Permanganate. F. RICHARD (*J. Pharm. Chim.*, 1923, [vii], 27, 456—458).—Although commercially pure

methyl alcohol should give no iodoform with potassium iodide, iodine, and sodium hydroxide (absence of acetone, etc.) and should not within fifteen minutes discharge the violet coloration produced by one drop of *N*/10-permanganate, it is difficult to find since the war samples which respond to these tests, and amounts of acetone varying from 4 to 37 g. per litre have been found in various specimens of methyl alcohol examined. G. F. M.

Estimation of Phenols in Blood. NORRIS W. RAKESTRAW (*J. Biol. Chem.*, 1923, 56, 109—119).—The method is a modification of that of Folin and Denis (*A.*, 1912, ii, 1011; cf. also Pelkan, *A.*, 1922, ii, 399) and is applicable to tungstic acid blood filtrates. Uric acid is precipitated by the addition of zinc chloride and sodium carbonate according to Morris and McLeod's method (*A.*, 1922, ii, 328), and is separated by centrifuging or filtering. Free phenols are then estimated colorimetrically in the filtrate, using a phosphotungstic-phosphomolybdic reagent (phenol reagent) and employing phenol as a standard; conjugated phenols are given by the difference between this result and one obtained after hydrolysis with hydrochloric acid. The precipitate may be used for the estimation of uric acid. E. S.

The Detection of Ethylenic Derivatives in Official Anæsthetic Ether. F. RICHARD (*J. Pharm. Chim.*, 1923, [vii], 27, 448—455).—The mercurial reagent for the detection of ethylenic compounds in ether, specified by the French codex and consisting of a mixture of a solution of mercuric chloride and a solution of potassium hydrogen carbonate is very unsatisfactory, as it is very unstable and forms an opalescent or cloudy solution even before it can be used, such opalescence being readily mistaken for that produced by ethylenic derivatives. A more satisfactory reagent is that recommended by Denigès prepared by dissolving 50 g. of mercuric oxide in a mixture of 200 c.c. of concentrated sulphuric acid and 1,000 c.c. of water. On shaking this reagent with an equal volume of ether and setting aside for one hour no opalescence should be produced in the aqueous layer. In presence of ethylenic derivatives, a white opalescence passing eventually into a yellow precipitate is obtained. G. F. M.

Investigation of Abnormal Components of Urine: Dextrose. I. G. INGHILLERI (*Boll. Chim. Farm.*, 1923, 62, 225—227).—Fehling's solution is reduced by creatine, creatinine, uric acid, asparagine, theobromine, caffeine, the urine of patients undergoing "salvarsan" treatment, etc. In none of these cases, however, is reduction observed if the sodium hydroxide of the Fehling's solution is replaced by sodium carbonate and the Rochelle salt by sodium citrate, the reagent being then specific for dextrose. The reagent, which is stable towards light and is stored as a single solution, is prepared by dissolving 185 g. of crystallised sodium carbonate and 160 g. of sodium citrate in about 500 c.c. of water, the solution being heated, cooled, and filtered; 16 g. of crystallised copper sulphate are dissolved in water in the original vessel and the solutions mixed and made up to 1000 c.c.

Two c.c. of the urine is heated to boiling with 6—8 c.c. of the reagent in a test-tube. Excepting with a large proportion of dextrose, when cuprous oxide is precipitated at once, it is necessary to leave the liquid to cool or to rub the sides of the tube with a glass rod. The precipitate or turbidity obtained in presence of dextrose is orange-yellow and readily visible in artificial light. In cases of pronounced uricæmia, the treated urine develops a precipitate or turbidity of the colour of Turnbull's blue if left overnight; thus, the reagent serves also for the detection of uric acid.

T. H. P.

Estimation of Starch Content in the Presence of Interfering Polysaccharides. GEORGE PELHAM WALTON and MAYNE R. COE (*J. Agric. Res.*, 1923, **12**, 995—1006).—The estimation of the starch content of certain materials by a diastase method is rendered impossible by the presence of mucilages, pectins, and similar carbohydrates. In the method proposed, the material is successively extracted on a filter with ethyl ether, 25—35% ethyl alcohol, 95% ethyl alcohol, and finally ether. The material is then gelatinised by boiling with water, and the starch converted by digestion with malt extract. The interfering polysaccharides are precipitated with 60% ethyl alcohol, and after filtration and removal of alcohol from the filtrate by evaporation the starch conversion products are hydrolysed by dilute hydrochloric acid. The resulting solution is defecated by addition of phosphotungstic acid and the dextrose estimated gravimetrically by copper reduction.

G. W. R.

A New Titrimetric Method for Estimating Formic Acid. L. UTKIN-LJUBOVZOV (*Biochem. Z.*, 1923, **138**, 205—208).—For the estimation of formic acid in distillates from urine, tissues, and culture media, existing methods were found to be unsatisfactory. A titrimetric modification of the gravimetric Skala method was adopted. The mercurous chloride formed by reduction of the mercuric salt by the formic acid, as in the Skala method, is filtered from the acidified solution, washed and oxidised with a known excess of 0.1*N*-iodine, in the presence of 10% potassium iodide. The excess of iodine is estimated by back titration with 0.1-, 0.02-, or 0.01*N*-thiosulphate, according to the amount of formic acid present. Comparison with other methods of estimation gives good results.

J. P.

Estimation of Acetic Anhydride. G. C. SPENCER (*J. Assoc. Off. Agric. Chem.*, 1923, **6**, 493—497).—0.3—0.4 G. of the acetic anhydride is weighed out in a stoppered capsule, which is then transferred to and opened in a 100 c.c. stoppered Erlenmeyer flask containing a cooled mixture of 15 c.c. chloroform and 1 c.c. of aniline. The flask is immediately stoppered, well shaken, and placed in a refrigerator for not less than an hour. The mixture is washed into a 125 c.c. Squibb separating funnel containing 15 c.c. of 10% sulphuric acid and 15 c.c. of water. Ten c.c. of chloroform are used for the transference. The chloroform layer is drawn

off into a second separating funnel containing 15 c.c. of water, shaken, and the chloroform layer drawn off into a flask. A further 10 c.c. of chloroform are added to the liquid in the first separating funnel, shaken, and drawn off into the second funnel, shaken, and drawn off into the flask. The chloroform washings are repeated with 7 c.c. of chloroform. The united chloroform extracts are evaporated nearly to dryness, and the remaining chloroform is removed with an air blast. Ten c.c. of 10% sulphuric are added to the residual crystals and evaporated on a water-bath to about half the volume. Ten c.c. of water are added, and the evaporation is repeated. The acetanilide must be thoroughly hydrolysed, but the acid must not become sufficiently concentrated to decompose the aniline sulphate. The residue is dissolved in 60 c.c. of water, 5 c.c. of concentrated hydrochloric acid are added, and the liquid is titrated with potassium bromide-bromate solution until a slight permanent yellow coloration is obtained. The bromide-bromate can be made with the requisite amounts of the two substances or by dissolving 13.3 c.c. [40 g.] of bromine in a solution of 28 g. of potassium hydroxide which is subsequently boiled. The accuracy of the method is 1%.
A. G. P.

Micro-estimation of the Volatile Acidity of Wines. PH. MALVEZIN (*Bull. Soc. chim.*, 1923, [iv], 33, 849—852).—The wine under examination is distilled with or without the addition of tartaric acid and the distillate is titrated with *N*/100-sodium hydroxide, using phenolphthalein as indicator. The former method gives the total volatile acid, the latter the free volatile acid.

H. H.

Estimation of Mucic Acid. E. O. WHITTIER (*J. Amer. Chem. Soc.*, 1923, 45, 1391—1397).—Mucic acid may be estimated in acid solution by oxidation with an excess of standard potassium permanganate solution at the boiling temperature, followed by a back titration with standard oxalic acid solution and the standard permanganate solution. The same method may be applied to tartaric acid and to racemic acid. A mixture of oxalic and mucic acids may be precipitated quantitatively as calcium salts, the whole filtered, dissolved in sulphuric acid, and the acids estimated in the presence of each other by first titrating the oxalic acid at 50° with standard permanganate and then applying the above method for mucic acid. Tartaric and racemic acids cannot be titrated with any degree of accuracy in the same solution with oxalic acid. Other combinations of organic acids could in all probability be estimated by this method. The fact that the relationships between these dibasic oxy-acids and potassium permanganate are not stoichiometric under the conditions employed is shown to be due to the production of formic acid, which is further oxidised only to a slight extent under the conditions of the titrations. J. F. S.

The Cryoscopy of Milk. E. M. BAILEY (*J. Assoc. Off. Agric. Chem.*, 1923, 6, 429—434).—The depression of the freezing point of milk increased regularly with the acidity, the increase approximating closely to 0.003° per 0.01% acidity. Correction for acidity,

outside the range of "normal" milks, should be applied when cyoscopic methods are used to detect added water in milk. A. G. P.

Estimation of Fat in Milk. A. ZEGA and LILLI ZEGA (*Chem. Ztg.*, 1923, **47**, 405).—Five c.c. of milk, 2 c.c. of a weakly ammoniacal solution of ammonium citrate (d 1.036—1.040), and 10 c.c. of a mixture of 55 parts of ether and 45 parts of alcohol are successively introduced into a graduated tube sealed at one end and of 20—25 c.c. capacity. The tube is corked and the contents are mixed by agitation. The milk dissolves and on keeping the contents separate into two layers. The volume of the ether-alcohol layer is read off and 1—2 c.c. are removed with a pipette, evaporated, dried, and the fat weighed. The temperature of the liquids should not be below 20° when they are mixed or solution of the milk will not be complete. The graduated tubes are easily cleaned with water and need not be dried before use. H. C. R.

Estimation of Formaldehyde in Paraformaldehyde. P. BORGSTROM and W. G. HORSCH (*J. Amer. Chem. Soc.*, 1923, **45**, 1493—1497).—The iodometric method for the estimation of formaldehyde in paraformaldehyde (Romijn, A., 1897, ii, 166), based on the equation $\text{CH}_2\text{O} + \text{I}_2 + 3\text{OH}^- = \text{H}\cdot\text{CO}_2^- + 2\text{I}^- + 2\text{H}_2\text{O}$; the peroxide method (Blank and Finkenbeiner, A., 1899, ii, 188), consisting in the oxidation of formaldehyde to formic acid by means of hydrogen peroxide in alkaline solution, and titration of the excess of alkali; the neutral sulphite method (Doby, *Z. angew. Chem.*, 1907, **20**, 353), depending on the reaction $\text{H}_2\text{O} + \text{CH}_2\text{O} + \text{Na}_2\text{SO}_3 = \text{CH}_2\text{OH}\cdot\text{SO}_3\text{Na} + \text{NaOH}$; and the oxidation of paraformaldehyde by means of potassium dichromate or potassium permanganate in hot sulphuric acid solution, and estimation of the carbon dioxide evolved (Messinger, A., 1889, 80), all give results in substantial agreement with the figures obtained by the estimation of carbon and hydrogen in the Liebig combustion apparatus, but the fixed alkali method (Smith, A., 1899, ii, 188), based on the reaction $2\text{CH}_2\text{O} + \text{NaOH} = \text{MeOH} + \text{H}\cdot\text{CO}_2\text{Na}$, gives results about 0.8% low. The last reaction may also occur if, when using the peroxide or iodometric methods, the hydrogen peroxide or iodine is not added sufficiently soon after the alkali. W. S. N.

The Lautenschläger Process for the Estimation of Aldehydes. L. ROSENTHALER and K. SEILER (*Z. anal. Chem.*, 1923, **62**, 385—388).—The estimation of piperonal and of vanillin by Lautenschläger's process (*Arch. Pharm.*, 1918, **256**, 81), involving condensation of the aldehyde and hydrazine to form an aldazine followed by iodometric estimation of the excess of reagent, was found to give results that were much too low. No better results were obtained by effecting the condensation with hydrazine sulphate and determining the liberated acid alkalimetrically; in this case the results were high. A. R. P.

The Error in the Urea-Hypobromite Method. B. M. MARGOSCHES and HEINRICH ROSE (*Biochem. Z.*, 1923, **137**, 542—561).—The cause of the nitrogen deficit in the hypobromite method

for the estimation of urea has been studied; the main error is not due to the solubility of the nitrogen in the hypobromite solution, to oxide formation, or to formation of cyanate, but is due to undecomposed urea. The authors' alkalimetric hypobromite method (this vol., ii, 348) being carried out in warm solution overcomes the difficulty.

H. K.

Estimation of Urea alone and in the Presence of Cyanamide by Means of Urease. E. J. FOX and W. J. GELDARD (*Ind. Eng. Chem.*, 1923, 15, 743—745).—An accurate and direct method is given for the estimation of urea, based on its conversion into ammonium carbonate by the action of urease and the subsequent titration of the ammonia. The velocity of the reaction is nearly doubled for each 10° rise of temperature between 10° and 50°, and the activity of the enzyme is destroyed at 80°. Experiments were carried out to determine the safe limits as to time of digestion and concentration of urea and urease. Most salts have a depressing effect on the action of the urease, and those of barium and calcium must be removed. Details are given of the methods of estimating urea alone and in presence of cyanamide and phosphates. The method appears to be of quite general application.

H. C. R.

A Microchemical Method of Estimating Hydrocyanic Acid. L. ROSENTHALER and K. SELER (*Z. anal. Chem.*, 1923, 62, 388—389).—Hydrocyanic acid in small quantities in very dilute solution may be estimated by titration with iodine under the following conditions: the solution is placed in a small flask with a narrow neck and treated with a measured amount of a saturated solution of calcium carbonate, 2 to 3 c.c. of light petroleum are added, and the liquid is titrated with *N*/1000-iodine until a faint permanent brown colour is observed in the petroleum layer which should extend up the neck of the flask. One c.c. of the iodine solution corresponds with 0.0135 mg. of hydrocyanic acid.

A. R. P.

The Iodometric Estimation of Small Quantities of Cyanides and Thiocyanates. E. SCHULEK (*Z. anal. Chem.*, 1923, 62, 337—342).—The cyanogen group in cyanides and thiocyanates is completely converted into cyanogen bromide by treatment with bromine in slightly acid solution, and the bromide may be estimated iodometrically. The process is carried out as follows: 50 c.c. of a solution containing 0.1 to 40.0 mg. of hydrocyanic acid or 0.3 to 90.0 mg. of thiocyanic acid are treated with 5 c.c. of 20% phosphoric acid and a slight excess of bromine; 30 to 40 drops of a 5% solution of phenol are added, and the mixture is left for fifteen minutes in the dark. 0.5 G. of potassium iodide is dropped into the solution, and, after half an hour in the dark, the liberated iodine is titrated with thiosulphate. Half the molecular weight of either of the acids under examination is the equivalent weight in this process. If it is desired to estimate each acid in the presence of the other, the solution is first distilled with 1 g. of crystallised boric acid, which decomposes cyanides only. The distillate is

collected in weak sodium hydroxide solution and the cyanide content of this is determined as described above, the thiocyanate being estimated similarly in the residue in the distillation flask.

A. R. P.

Detection of Quinine in Presence of Antipyrine and Pyramidone. DOMENICO GANASSINI (*Boll. Chim. Farm.*, 1923, 62, 321—322).—The red coloration given by chlorine water and ammonia with a mixture of quinine and antipyrine is obtained only when these two substances are present in about equal proportions. The disturbing effect produced by small quantities of antipyrine or pyramidone on the colour reactions of quinine may be obviated by treating the residue of the ethereal extract several times with cold water, which dissolves the antipyrine and pyramidone almost completely and leaves nearly pure quinine.

T. H. P.

An Unambiguous Macro- and Micro-chemical Test for Histidine in Protein. HERMANN BRUNSWICK (*Z. physiol. Chem.*, 1923, 127, 268—277).—The diazo-reaction is given both by histidine and by tyrosine, so that if the latter is present, as shown by a positive Millon's reaction, a modification is necessary in testing for histidine. The substance should first be nitrated by warming with dilute nitric acid (20—50%) and then made alkaline with sodium carbonate. Tyrosine no longer gives the diazo-reaction, so that, under these conditions, this test is specific for histidine. It may be applied quantitatively, using a colorimeter, or micro-chemically, on a microscope slide.

W. O. K.

Rapid Method for Estimating Theobromine in Cocoa. TRIFON UGARTE (*J. Pharm. Chim.*, 1923, [vii], 27, 420—423).—The cocoa is heated in a dry Kjeldahl digestion flask until the theobromine is sublimed and the cocoa completely carbonised. The theobromine is extracted with hot water, filtered, and the filtrate evaporated to dryness on the water-bath. The residue is purified by extraction with absolute alcohol, treated with aqueous ammonia, and dissolved in chloroform. The chloroform solution is filtered and evaporated to dryness, the residue extracted three times with 3 c.c. of hot water, filtered, and the filtrate evaporated to dryness on a watch glass, dried at 100—105°, and weighed. The whole estimation takes about two and a half hours. The percentage of theobromine in various samples of commercial cocoa varied from 0.45% to 1.17%.

H. C. R.

A New Optical Instrument for the Estimation of Hæmoglobin. H. S. NEWCOMER (*J. Biol. Chem.*, 1923, 55, 569—574).—The instrument is a modified Duboscq colorimeter. For the estimation of hæmoglobin, the whole blood is mixed with 1% hydrochloric acid and the solution of acid hæmatin thus obtained compared with a standardised yellow glass (cf. A., 1919, ii, 179) which is incorporated in one of the plungers of the hæmoglobino-meter. The instrument is calibrated to read percentage of hæmoglobin.

E. S.

General and Physical Chemistry.

Refraction Equivalents of Ions and the Structure of Compound Ions. JARL A. WASASTJERNA (*Soc. Sci. Fennica Com. Phys.-Mat.*, 1923, **1**, No. 37, 1—7).—From previously published data (A., 1922, ii, 1, 2, 491), the author has calculated the ionic refractivities of several uni- and bi-valent ions. The following new values are recorded: $F''=2.20$; $Mg''=0.44$; $O''=4.06$; $S''=15.0$; $Br'=11.84$; $I'=18.47$; the atomic refractivities of the inert gases have also been calculated and the values $Ne=1.01$, $A=4.23$, $Kr=6.42$, and $X=10.56$ obtained. It is shown that Cuthbertson's rule, which connects the atomic refractivity with the atomic weight of gaseous elements, is approximately followed by the ions of the alkali and alkaline-earth metals and also by the halogen-ions. But in the latter case the refraction equivalent increases rather more slowly than is required by Cuthbertson's rule. The constitution of compound ions, such as NO_3' , SO_4'' , PO_4''' , CO_3'' , has been discussed in connexion with the refraction values of these ions. The values calculated for these ions on the basis of the accepted structure of the ions are found to be of much the expected dimensions. It is shown that in the determination of constitution of inorganic ions, the interaction between the central sustaining ion and the electron systems of the surrounding ions is a matter which in all probability cannot be neglected generally. J. F. S.

Radii of Ions. JARL A. WASASTJERNA (*Soc. Sci. Fennica Com. Phys.-Mat.*, 1923, **1**, No. 38, 1—25).—A theoretical paper in which the connexion between ionic radii and refraction equivalents is discussed. The ionic radii of the metals of the alkalis and alkaline-earths, and of the halogens and members of the oxygen group, have been calculated from the refraction equivalents previously obtained (cf. preceding abstract). The values of the ionic radii thus obtained are discussed and compared with similar values found by Bragg (A., 1920, ii, 537), by Fajans and Herzfeld (A., 1920, ii, 174), and by Grimm (A., 1922, ii, 127). J. F. S.

The Optical Constants of certain Liquids for Short Electric Waves. J. D. TEAR (*Physical Rev.*, 1923, **21**, 611—622).—The refractive indices of water, glycerol, methyl alcohol, and ethyl alcohol for short electric waves, λ 4 to 27 mm., have been computed from measured values of absorption and reflection coefficients, some values also being obtained by utilising the phenomenon of interference in thin films. The values of n for λ 0.42 cm. and λ 2.7 cm., respectively, are abstracted as follows: Ethyl alcohol, 1.84, 2.27; methyl alcohol, 2.10, 3.3; glycerol, 1.98, 2.53; water, 5.33, 8.45. A. A. E.

Spectrochemical Investigations: [Unsaturated γ -Lactones, Hydroxy-aldehydes, Hydroxy-ketones and Acetals]. K. VON AUWERS [with H. WISSEBACH] (*Ber.*, 1923, **56**, [B], 1672—1682).—

From a consideration of the molecular refractive and dispersive powers of the isomeric and substituted angelicalactones, the conclusion is drawn that it is possible to distinguish Δ^1 - from Δ^2 -lactones by refraction measurements alone. It is also shown that Δ^1 -lactones show smaller exaltations of molecular refractive power than do the corresponding unsaturated open-chain ketones, thus conforming to the general rule that ring-closure tends to diminish exaltations of refractive and dispersive power.

The method of exaltations of molecular refractive and dispersive power is also applied to the determination of the structure of hydroxy-aldehydes and ketones, and it is claimed that by exercising great care in the purification of the compound and the determination of its optical constants, it is possible to distinguish between open-chain and cyclic structures. For example, the spectrochemical evidence is in favour of the cyclic structure $O < \begin{matrix} \text{CHMe} - \text{CH}_2 \\ | \\ \text{CH(OH)} \cdot \text{CH}_2 \end{matrix}$ for γ -hydroxy-valeraldehyde. This tendency to ring formation is more marked in the case of hydroxy-aldehydes than with hydroxy-ketones.

Spectrochemical evidence is in favour of the normal structure for diphenylacetaldehyde, and not of the isomeric diphenylvinyl alcohol. H. H.

The Doublet Separations of Balmer Lines. J. C. McLENNAN (*Nature*, 1923, **112**, 166).—Results obtained by the author and G. M. Shrum confirm Sommerfeld's theory of the structure of the lines of the Balmer series. A. A. E.

The Secondary Spectrum of Hydrogen under Various Excitations. MASAMICHI KIMURA and GISABURO NAKAMURA (*Japan. J. Phys.*, 1923, **1**, 85—95).—The authors have examined the effects of various modes of excitation on the secondary spectrum of hydrogen. The results indicate that lines of the secondary spectrum between H_α and H_β are very sensitive to a variation of the mode of excitation, whilst those in the region between H_β and H_γ are generally less affected. One group of lines was emitted strongly in a fine capillary of a discharge tube, whilst another was intense in the wider part of the tube. The intensities of the former were much increased by the application of a heavy condensed discharge or a strong magnetic field, or by increasing the gas pressure. In the light emitted from a glowing cylindrical cathode, lines in the region λ 5000 to λ 5700 were enhanced compared with their intensities in the positive column. Lines included between λ 5700 and 5950 were similarly enhanced by the electrodeless discharge. Assuming the secondary spectrum to be emitted by molecules, the authors consider that lines of the spark type are emitted by ionised molecules whilst those of the arc type originate in neutral molecules. J. S. G. T.

The Band Spectra and the Electronic Configuration of Nitrogen and Carbon Monoxide Molecules. HANTARO NAGAOKA (*Japan. J. Phys.*, 1922, **1**, 49—57).—A comparison of the

respective band and line spectra of carbon monoxide and nitrogen confirms the suggestion of a resemblance in the electronic configurations of the molecules of these gases, derived from measurements of other physical constants. The author considers that the fourteen electrons associated with the oxygen and carbon atoms in the molecule of carbon monoxide, or with two atoms of nitrogen, are symmetrically arranged in a face-centred cube, whilst the positive nuclei occupy the centre of the cube and are in rapid motion, and give rise to band spectra by reacting on the electrons. Moreover, the transition between stationary orbits is greatly influenced by the molecular motions. The greater complexity of the band lines in the spectrum of carbon monoxide is attributable to the asymmetry of the central nuclei in the molecules of this gas. The configuration described conforms with results deduced from the kinetic theory of gas, on the assumption that two atoms have two electrons in common.

J. S. G. T.

Combination Relations and Terms in the Band Spectrum of Helium. A. KRATZER (*Z. Physik*, 1923, 16, 353—366).—From an analysis of the wave-lengths of the lines contained in the band spectrum of helium in the regions $\lambda\lambda$ 6400, 4546, and 5730 Å. as determined by Curtis (A., 1922, ii, 330) the existence of a number of combination relations between wave-lengths in the respective systems classified by Curtis is definitely established. This result is in accord with the author's theory of the emission of band spectra and contrary to the conclusion of Curtis on this matter. The analysis indicates that the bands $\lambda\lambda$ 6400 and 4546 probably originate in the same system of electrons, the initial conditions of these, in the two cases, being characterised by different oscillation quantum numbers, the higher number being associated with the 4546 band. The band λ 5730 Å. belongs to a different system, characterised by the same end-term as that associated with the two other bands. The various terms are calculated by a general method. It is shown that the moment of inertia of the helium molecule about the line joining the electrons with the nucleus is extremely small, and certainly less than $0.1\hbar/2\pi$.

J. S. G. T.

The Crossed-orbit Model of Helium. LUDWIK SILBERSTEIN (*Nature*, 1923, 112, 53; cf. this vol., ii, 400).—An examination of certain regularities observed on application of the spectrum formula previously proposed for helium.

A. A. E.

Determination of Spectroscopic Standard Wave-lengths in the Short Wave-length Region. SISIR KUMAR MITRA (*Ann. Physique*, 1923, [ix], 19, 315—339).—Employing the interferometer method devised by Fabry and Perot, the author has determined the following wave-lengths in the arc spectrum of copper below λ 2374 Å., where standard determinations have hitherto been lacking: 2369.891, 2303.134, 2276.261, 2242.622, 2218.107, 2189.631, 2148.897, 2126.047, and 2112.105 Å. In addition, the standard line λ 2334.816 in the arc spectrum of tin has been determined. In general, experimental values differed from the respective mean

values given by less than $\pm 0.002 \text{ \AA.}$ and never by more than $\pm 0.003 \text{ \AA.}$

J. S. G. T.

The Mass-spectrum of Copper. F. W. ASTON (*Nature*, 1923, **112**, 162).—The masses ascribed by Dempster (this vol., ii, 640) to the isotopes of copper are improbable, since (a) no case is yet known of an element of odd atomic number consisting of more than two isotopes, and (b) except in the case of nitrogen; with such elements the more abundant of the two constituents, or both, are of odd atomic weight. By the use of cuprous chloride, the mass-spectrum of copper is found to contain lines at 63 and 65, having the expected intensity ratio of about 2.5:1, and not showing any deviation from the whole-number rule. Dempster's lines are possibly due to the presence of zinc as an impurity.

A. A. E.

An Experimental Verification of the Theory of Röntgen Ray Spectra, due to a Multiple Atomic Ionisation. A. DAUVILLIER (*Compt. rend.*, 1923, **177**, 167—169).—The spectrum of iron shows Hjalmar's line $K\beta'$ and the line $K\gamma$ (due to two superficial electrons of iron, N_8 and N_9), but not the doublet $K\alpha_3\alpha_4$, when excitation is produced, not by direct bombardment, but by fluorescence (cf. this vol., ii, 243, and Wentzel, this vol., ii, 249).

E. E. T.

Structure of the Spectrum of the Neutral Molybdenum Atom. MIGUEL A. CATALÁN (*Anal. Fis. Quím.*, 1923, **21**, 213—235).—The flame, arc, and spark spectra of molybdenum are composed of two classes of lines attributable respectively to the neutral and ionised atoms. The lines of the first class, which are fully described, consist of three systems of triplets, with lines of intercombination, and five multitruplets with lines of intercombination between these and the first three systems. A close similarity is shown between the spectra of chromium and molybdenum.

G. W. R.

Regularities in the Arc Spectrum of Titanium. C. C. KIESS and HARRIET K. KIESS (*J. Washington Acad. Sci.*, 1923, **13**, 270—275).—The arc spectrum of titanium has been analysed with the object of ascertaining the regularities of this spectrum. It is shown that two different sets of multiplets of six or seven lines occur. These sets have respectively the differences 170.1 and 216.7 and are similar to the multiplets of the alkaline-earth metals. There are also multiplets of eleven to thirteen lines with differences 42.0, 62.3, 81.7, and 100.2, similar to the multiplets of manganese, chromium, and molybdenum. The majority of the lines classified belong to King's temperature classes I and II, although a few belong to the classes III and IV (*Astrophys. J.*, 1914, **39**, 139). About 10% of the arc lines of titanium are thus classified. Long tables of the classification are given in the paper.

J. F. S.

The Absorption Spectrum of Arsenic Sulphide Sols. A. BOUTARIC and M. VUILLAUME (*Compt. rend.*, 1923, **177**, 259—261).—The experimental values obtained for the absorption spectrum of a solution of arsenic trisulphide made by passing hydrogen

sulphide through a solution of arsenious acid containing 5 g. per litre do not seem to be consistent with any of the theoretical laws. There appears to be an absorption by diffusion which itself accords with Rayleigh's law, but it is accompanied by selective absorption which is probably caused by the reflection of incident rays from the surface of the particles. The latter absorption should, therefore, vary with the extent of the total surface, diminishing for a constant weight of the sulphide when the number of particles decreases with consequent increase in their size. This was verified by experiment, the absorption curve showing less variation from the theoretical value with progressive ripening of the sol. H. J. E.

The Absorption Spectra of the Vapours of Various Quinones.
JOHN EDWARD PURVIS (T., 1923, 123, 1841—1849).

Fluorescence and Photochemistry. R. LEVAILLANT (*Compt. rend.*, 1923, 177, 398—401).—An investigation of the photochemical reduction or oxidation of fluorescent and other dyes, in very dilute solutions. Uranine in glycerol solution (0.01%) is decolorised under the influence of light, owing to photochemical reduction, the colour reappearing on leaving the solution in contact with air, but not doing so if air is excluded. More concentrated solutions (*e.g.*, 0.2%) are not decolorised in this way.

This phenomenon is fairly general with dilute solutions of colouring matters in polyhydroxy-alcohols (ethylene glycol, glycerol, erythritol, mannitol) or with solutions also containing neutral tartrates, dextrose, etc. Eosin, erythrosin, thiazines, and Meldola's blue show the effect well; but pyronin is much less sensitive. Similarly, the reappearance of the colour, on leaving, is observed in the case of thiazines, eosin, etc., but is less marked with Rose-Bengal and Magdala-red. The reappearance of colour depends to some extent on the solvent used and the final colour is not necessarily identical with the original one.

Many acids (acetic, oxalic, lactic, malic, tartaric, citric, etc.) play the same part as alcohols. Thus a solution of methylene-blue in acetic acid is slowly decolorised, whilst in 0.02% aqueous solutions, in presence of oxalic acid, decolorisation is rapid owing to reduction of the colouring matter (M): $\text{H}_2\text{C}_2\text{O}_4 + \text{M} = \text{MH}_2 + 2\text{CO}_2$. Hydroxylamine and phenylhydrazine hydrochloride play the same part as the above acids.

Photochemical oxidation may also occur, uranine being oxidised in aqueous solution in presence of air, irreversibly, to give a brownish-red decomposition product. In absence of air, an aqueous solution of uranine is not affected by light.

Light is supposed to be absorbed by a molecule of the fluorescent substance, which is raised to the critical state. Simple reversion may occur (with light emission), or the substance, in the highly active state, may undergo reduction (or oxidation). A non-fluorescent substance should be less sensitive to light. In fact, fuchsine, tartrazine, malachite-green, and indigo-carmin, in glycerol solution, are unaffected by light although indigo carmin in aqueous solution, in presence of oxalic acid, is partly reduced and

the rhodamines, although fluorescent, are practically unaffected by light, in glycerol solution. The same lack of generality applies to results obtained on the sensitiveness to heat of solutions of colouring matters of the two types.

E. E. T.

Phosphorescence caused by Active Nitrogen. H. KREPELKA (*Nature*, 1923, **112**, 134; cf. Lewis, this vol., ii, 361; Jevons, this vol., ii, 451).—A bright green phosphorescence was observed when aluminium chloride, freshly prepared from aluminium and chlorine in a tube through which nitrogen had been passed, was gradually cooled in nitrogen. In the case of aluminium bromide, phosphorescence was not observed. The phenomenon is ascribed to the activation of some of the nitrogen by the violent reaction of the chlorine left in the tube with the aluminium.

A. A. E.

The Minimum Concentration of Luciferin to give a Visible Luminescence. E. NEWTON HARVEY (*Science*, 1923, **57**, 501—503; cf. A., 1915, i, 628; 1917, i, 365, ii, 436; 1918, i, 89).—On oxidation in presence of luciferase, the light emitted from a solution of 1 part of dry *Cypridina* in 4×10^8 parts of sea-water can just be detected by the unassisted eye. This corresponds with a concentration of luciferin between 1 in 4×10^9 and 1 in 4×10^{10} . Attention is directed to the degree and tenacity of the adsorption on glass vessels of substances at such dilution.

A. A. E.

The Molecular Scattering of Light in Benzene, Vapour and Liquid. K. R. RAMANATHAN (*Physical Rev.*, 1923, **112**, 564—572).—The intensity of the light scattered by benzene, as liquid or vapour, at right angles to the incident beam has been compared with that scattered by ethyl ether. The results, together with the measurements of the degree of polarisation of the scattered light, are held to confirm the general validity of Raman's views (A., 1922, ii, 603).

A. A. E.

Optical Rotation and Atomic Dimension. D. H. BRAUNS (*Physica*, 1923, **3**, 69—75).—The optical rotations of chloro-, bromo-, iodo-, and fluoro-acetyldextrose, -acetylcellose, and -acetylxylose have been compared, and the differences between the specific rotations for the fluoro- and chloro-, chloro- and bromo-, and bromo- and iodo-compounds are found to be nearly proportional to the differences in the atomic diameters found by Bragg. The atomic dimensions thus form an additive element in the rotation.

CHEMICAL ABSTRACTS.

The Kinetics of Photochemical Reactions. P. P. LAZAREV (*Bull. Acad. Sci. Russ.*, 1919, 239—254; cf. A., 1915, ii, 719).—A mathematical study of reversible, non-reversible, and pseudo-reversible photochemical reactions under different conditions of light.

CHEMICAL ABSTRACTS.

Photo-decomposition of Nitrosyl Chloride. A. KISS (*Rec. trav. chim.*, 1923, **42**, 665—674).—The formation and decomposition of nitrosyl chloride in white light has been investigated at 0.1°, 18°, 38°, 48°, 58°, and 78° by the method previously employed

(this vol., ii, 237). The results show that the rate of formation of nitrosyl chloride is the same whether the mixture is illuminated or preserved in the dark. The decomposition of nitrosyl chloride under the influence of white light is strictly unimolecular. The temperature coefficient of the velocity constant over the range 0° to 78° is unity.

J. F. S.

Spectral Sensitiveness of Silver Bromide and the Influence of Adsorbed Substances on the Sensitiveness. W. FRANKENBURGER (*Z. physikal. Chem.*, 1923, 105, 273—328).—The photo-decomposition of silver bromide has been investigated in respect of its dependence on various factors and an attempt is made to explain the mechanism of the decomposition on the basis of the quantum hypothesis and the modern views on crystal structure. The view of Fajans (A., 1921, ii, 386), that the primary process in the ion lattice of the silver bromide consists in the transference of an electron from a bromine-ion to a silver-ion with the formation of free bromine and silver, is accepted as a working hypothesis. Every change in the normal lattice energy (electrical) must affect the electron transference and consequently the sensitiveness of the silver bromide to a greater or less extent. With the object of confirming and extending these views, the photochemical behaviour of preparations of silver bromide of variously constituted surface have been investigated. The surface has been varied by the adsorption of various substances on it. It has been found necessary to distinguish between chemical sensitisation, which consists in the combination of the liberated bromine by acceptors and so preventing it from setting up the reverse reaction with the liberated silver, and optical or spectral sensitiveness, which consists in the change of the lattice energy brought about by the adsorption of foreign substances on the surface. The following cases have been examined. Pure silver bromide free from moisture in the presence of mercury vapour as acceptor has a spectral sensitiveness commencing between 435 and $410\ \mu\mu$. Silver bromide under an excess of silver nitrate solution, which is to be regarded as silver bromide coated with silver-ions, commences to be sensitive to light at $>620\ \mu\mu$, presumably in the ultra-red. The bromine acceptor in this case is the silver nitrate solution itself. The strong sensitisation here is due to the fact that the adsorbed silver-ions, on electrostatic grounds, are more active acceptors of electrons than the silver-ions from pure silver bromide. Silver bromide under an acid solution of potassium bromine begins to be sensitive to light between 435 and $410\ \mu\mu$. In this case, the silver bromide is coated with excess of bromine-ions and hydrogen-ions, and the bromine acceptors were sulphurous acid and phenylpropionic acid. From silver bromide under alkaline solutions, a different type of photosensitive system is produced, for here the electron passing to the silver-ion comes, not from the bromine-ion, but from the adsorbed hydroxyl- or oxygen-ion. The decomposition commences here at $>620\ \mu\mu$, possibly in the ultra-red. The great sensitisation in this case is due to the decomposition of the very sensitive silver oxide on the surface. For all preparations

of silver bromide, prepared by any of the methods stated, the decomposition of silver bromide commences between $620\ \mu\mu$ and $560\ \mu\mu$ if silver nuclei are formed. The limiting values of the sensitiveness have been compared with thermochemical data, whereby an explanation of the action of the silver nucleus has been obtained. It is pointed out that certain empirical processes used in the photographic practice bring about an increased sensitiveness of the emulsions by means of a modification of the silver bromide grains. These changes are similar to those mentioned above. As a whole, the results found in the present work with substances free from binding materials are confirmed by those obtained with emulsions.

J. F. S.

Electrostatic Recalculation [on the Photochemical Behaviour of Silver Bromide]. K. F. HERZFELD (*Z. physikal. Chem.*, 1923, 105, 329—332).—A mathematical treatment of the energy relations of the transference of an electron from a bromine ion to a silver-ion in the photo-decomposition of silver bromide, as put forward by Frankenburger (cf. preceding abstract). J. F. S.

Photochemical Reduction of Zinc Sulphide. ANDRÉ JOB and GUY EMSCHWILLER (*Compt. rend.*, 1923, 177, 313—316).—The darkening of zinc sulphide is due to the formation of free zinc. In order that a specimen should be sensitive to light, it must be phosphorescent and hygroscopic; it is more sensitive the more these conditions are satisfied. The darkening is due to the following series of changes. The preparation of the sulphide, involving ignition, affords a metastable product. Incident radiation raises the metastable molecules to a critical state, and, if the sample be dry, it simply emits radiation and reverts to the previous, metastable, condition. When, however, it has deliquesced slightly, hydrolysis occurs, producing hydrogen sulphide and zinc hydroxide. During illumination, a critical molecule of the sulphide reacts with the hydroxide, giving zinc and sulphurous acid, which with hydrogen sulphide affords sulphur, zinc pentathionate also being produced. The main products are thus zinc and sulphur.

E. E. T.

Temperature Coefficients of Reactions in Tropical Sunlight. NILRATAN DHAR (T., 1923, 123, 1856—1861).

Action of Ultra-violet Light on Diketones. C. W. PORTER, H. C. RAMSPERGER, and CAROLYN STEEL (*J. Amer. Chem. Soc.*, 1923, 45, 1827—1830).—Under the influence of ultra-violet light, benzil is decomposed at temperatures above 200° into carbon monoxide and benzophenone; diacetyl vapour gives carbon monoxide and ethane, but an aqueous solution of diacetyl yields acetic acid and acetaldehyde. In dilute alcoholic solution, in the absence of air, benzil is partly hydrolysed to benzoic acid and benzaldehyde, but part of it is reduced by the alcohol to benzoin. In aqueous alcohol, in contact with air, it is converted into benzoic acid, which is partly oxidised to salicylic acid. Benzilic acid or its decomposition products, namely, benzpinacol in the absence of air,

together with benzophenone in the presence of air, are never found in exposed solutions of benzil. W. S. N.

A Method of Photographing the Disintegration of Atoms and of Testing the Stability of Atoms by the Use of High-speed Alpha Particles. WILLIAM D. HARKINS and R. W. RYAN (*Nature*, 1923, 112, 54—55).—The high-speed α -particles from thorium-*C'* have been employed in Wilson's photographic method. Collisions showing an α -particle deflection up to 165° have been observed, as well as the formation of three branches at the point of collision, a characteristic to be expected if the bombarded atom disintegrates. A. A. E.

Secondary β -Rays produced in a Gas by X-Rays. PIERRE AUGER (*Compt. rend.*, 1923, 177, 169—171).—A study of secondary and tertiary β -rays produced as a result of the incidence of X-rays on various gases diluted with hydrogen (to produce longer rectilinear initial β -ray trajectories). In the case of nitrogen, the β -rays have an angle of 80 — 100° (for the most part) with the X-rays. With heavier gases (*e.g.*, chlorine), the concentration of secondary rays round the perpendicular direction is less marked. A highly ionised path is seen to start from the same origin as a β -ray, the direction being different. This is due to the less violent loss of a second electron (observed with argon, chlorine, and iodine). The speed of the tertiary ray so produced depends on the nature of the gas, and varies only slightly (about a mean value) with the frequency of the X-rays used. E. E. T.

Some Cases of Analogous Action of Radiation and Ozone on Chemical and Colloidal Reactions. A. FERNAU (*Kolloid Z.*, 1923, 32, 89—92).—A number of cases are enumerated and discussed in which radiation (ultra-violet, α -ray, X-ray) brings about the same reaction as treatment with ozonised air. Sucrose in neutral, acid, or alkaline solution is inverted when subjected to ultra-violet light; egg-albumin, when exposed to the radiation from radium, is coagulated and ceric hydroxide sols are similarly coagulated. These actions are also brought about when the substances concerned are treated with ozone or hydrogen peroxide. The mechanism of the change is discussed. J. F. S.

Chemical Action of Penetrating Radium Rays. XV. The Dependence of this Action on the Fraction of the Rays absorbed. Reduction of Potassium Persulphate. ANTON KAILAN (*Monatsh.*, 1923, 44, 35—47).—The decomposition, by penetrating radium rays, of hydrogen peroxide, in acid, neutral, and alkaline solution, and of potassium iodide in acid solution, has been measured in vessels of various shapes and sizes, using different ray-filters. The conclusion previously drawn (A., 1922, ii, 466, etc.), that the action depends on the primary β - and the γ -rays in proportion to the number of ion-pairs produced (or producible) by the fraction of these rays absorbed, is now confirmed, as is also the supposition that the fraction of γ - or secondary rays produced from them is of con-

siderable importance (cf. A., 1922, ii, 106) in connexion with the amount of action produced.

With similarly-shaped vessels, quadruplication of the reaction space is accompanied by an increase of action by 30–40%, owing to secondary effects.

In passing from a neutral solution of hydrogen peroxide to one containing sodium carbonate (present to give a *N*/1-solution), the decomposition effected solely by the rays is not increased in amount. In the reduction of potassium persulphate, the number of molecules reduced is of the same order as that of the ion-pairs produced (or producible) by the absorbed rays. The decomposition of persulphate under these conditions is a direct process, and is not due to interaction with hydrogen peroxide formed (cf. Price and Denning, A., 1904, ii, 247).
E. E. T.

Chemical Reactions under the Influence of X-Rays. N. P. PESKOV (*Bull. Inst. Polytech. Ivanovo-Voznesensk*, 1923, 7, 119–120).—The chemical action of X-rays on organic compounds is very slight as a rule, owing to the fact that the electrons which cause such reactions are very readily absorbed. It is suggested that the activity of X-rays could be greatly increased if the radiation were generated throughout the mass of the reacting substance; such a generation of X-rays occurs when the substance is mixed with the salts of heavy metals and then exposed to the radiation. Thus the action of X-rays in diminishing the activity of diastase is increased twenty times by adding an insoluble barium salt to the diastase solution; the decomposition of *o*-nitrobenzyl alcohol is similarly affected. Colloidal solutions of platinum, bismuth hydroxide, and stannic oxide also have such a sensitising effect.
G. A. R. K.

Carrying-down of Polonium with Bismuth Hydroxide in Soda [Sodium Hydroxide] Solution. ESCHER (*Compt. rend.*, 1923, 177, 172–173).—When an acid solution containing bismuth and polonium is treated with an excess of sodium hydroxide, the polonium partly remains in solution and is partly adsorbed by the bismuth hydroxide precipitated. This distribution of polonium between the solid and liquid phases is dependent on the proportion existing between the concentrations of bismuth and sodium hydroxide.
E. E. T.

Ionisation of Nitrogen by Electron Impact. H. D. SMYTH (*Proc. Roy. Soc.*, 1923, [A], 104, 121–133).—The method of investigating ionisation potentials previously used for mercury has been improved and extended to gases. The results obtained with nitrogen show that the ordinary ionisation potential at 16.9 volts corresponds with the production of singly charged molecular ions, N_2^+ ; doubly charged atomic ions, N^{++} , are produced at 24.1 ± 1.0 volts and singly charged atomic ions, N^+ , at 27.7 ± 0.8 volts. These results are interpreted as corresponding with the transitions $N_2 \rightarrow N_2^+$; $N_2 \rightarrow N^{++} + N(\text{or } N^-)$ and $N_2 \rightarrow N^+ + N^+$. This leads to the values of 11 and 18 volts for the first and second ionisation potentials of atomic nitrogen. Further results at higher voltages show the

variation of the relative intensity of the different types of ion with the voltage. In particular, there is a very sharp increase in the proportion of atomic ions between 350 and 400 volts, corresponding roughly with the *K*-limit of 375 volts found by Foote and Mohler ("Origin of Spectra," 1922, p. 195). It was found possible to produce negatively charged molecular ions, but only in very small quantities. No negatively charged atomic ions were observed.

J. F. S.

Ionisation Produced by the Hydration of Quinine Sulphate.

(MILE) CHAMIE (Compt. rend., 1923, 177, 181—184).—In continuation of previous work, with improved apparatus (cf. this vol., ii, 113), the author has studied the hydration of quinine sulphate (the maximum hydration corresponding with a hydrate containing 4.81% of water), using two methods, carried out under the same conditions: increase of weight and decrease in current passing in an enclosed space. It is found that the curves of the diminution of the ionisation current (at points near that of saturation) are symmetrical with those of weight-increase with respect to the same time axis.

E. E. T.

Luminescence of Mercury Vapour under the Action of Low-velocity Electrons. V. I. PAVLOV (Bull. Acad. Sci. Russ., 1918, 127—150).—Under the experimental conditions, the minimum *E.M.F.* necessary for visible luminescence of mercury vapour was 8.25 volts. A definite amount of electronic energy was found to be necessary for the excitation of each line of the luminescence spectrum, the lines at $546\mu\mu$ and $576.9\text{--}579.0\mu\mu$ being produced by 8.25 volts and 11.75 volts, respectively. A minimum volumetric density of the electrical energy of the discharge is necessary to start visible luminescence.

CHEMICAL ABSTRACTS.

The Relation between the Visible Luminescence and the Ionisation of Mercury Vapour under the Action of Electrons.

V. I. PAVLOV (Bull. Acad. Sci. Russ., 1918, 1931—1954).—The increase of the initial ionisation by the action of the field of electrical discharge (secondary ionisation) does not present an indispensable part of the luminous discharge. It can be totally suppressed, without influencing the increase of ionisation in the field of the visible luminescence. A variation in the initial ionisation as brought about by different means, although necessary to start a visible luminescence and anomalously to ionise the gas, is not necessary for maintaining the luminosity. A constant mechanism of ionisation of a gas may produce a quite different degree of ionisation, after the first stage of luminescence is reached, when all ionisers develop a far larger efficiency. A working hypothesis concerning the cause of the latter phenomenon is developed.

CHEMICAL ABSTRACTS.

The Electrical Conductivity of Molybdenite. A. T. WATERMAN (Physical Rev., 1923, 21, 540—549).—When a current was passed through a strip of molybdenite perpendicularly to the crystallographic *c*-axis, the relation $i = KV^be^{-k/T}$, where i is the current, V the applied *E.M.F.*, T the absolute temperature, and

b , k , and K are constants, was found to be approximately valid. The value of b is generally about 1.6 and of k , 3000. Two forms of molybdenite, of widely differing conductivity, may possess different structures.

A. A. E.

Design and Use of Conductivity Cells for Non-aqueous Solutions. J. LIVINGSTON R. MORGAN and OLIVE M. LAMMERT (*J. Amer. Chem. Soc.*, 1923, **45**, 1692—1705).—A study has been made of the errors inherent in the design and use of conductivity cells containing non-platinised electrodes, when employed for non-aqueous solutions, and the following general conclusions have been drawn. In order to make accurate electrical conductivity measurements of dilute non-aqueous solutions, some comparison solution other than the very dilute aqueous solutions needed should be used, since the latter cannot be kept as free from contamination as the non-aqueous solutions which are to be measured. A solution of potassium chloride diluted with alcohol is suggested as the most convenient comparison solution. The change in resistance with a change in frequency from 500 to 1000 cycles has been measured throughout a wide range of resistances with a number of different cells and types of solutions. The results of Taylor and Acree (A., 1917, ii, 7, 8) have been confirmed, but the difference in resistance for small electrodes does not decrease continuously with an increase in resistance, but passes through a minimum between 5,000 and 10,000 ohms. There is not, as Taylor and Acree state, a minimum resistance above which a cell may be used with accuracy, but an optimum range which may or may not give results sufficiently accurate, depending on the accuracy required and the size of the electrodes, since as the size of the electrodes increases, the range and possible accuracy within the range increase. So choosing the cells that the resistance in them is large is not equivalent experimentally to increasing the size of the electrodes. Cells are designed with the aid of Washburn's equations (A., 1917, ii, 10), which do not change in resistance with a change in frequency and which with the Washburn type A cell cover the range from 2×10^{-3} to 2×10^{-7} reciprocal ohms. The method of cleansing and drying the electrodes has been found to be of far greater importance than any of the other factors involved, the errors from this source alone often being as high as 2—3%. The usual method of cleansing and drying seemed to make the cell, filled with its solution, not a resistance and a capacity, but a voltaic cell which gives the effect of an abnormally high resistance. A method is given for cleansing the cells which has for its underlying principle the production of two electrodes having as nearly as possible the same contact potential when immersed in the same solution; it involves scrubbing the electrodes after any treatment with an acid cleaning mixture and keeping the electrodes short-circuited during all the process of cleaning, drying, and bringing the cell to temperature equilibrium. It is believed that the difference in the potential developed by different electrodes when subjected to the same treatment accounts for the change in resistance with a change in the impressed voltage, and for the fact

that some observers have not been able to eliminate the change by cleansing them thoroughly whilst others have. The term "clean" applied to electrical conductivity cells should be more rigidly defined, if comparable values are to be obtained by different workers.

J. F. S.

Ionisation Potentials of Copper and Silver. A. G. SHENSTONE (*Nature*, 1923, **112**, 100).—Low voltage arcs have been obtained in the vapours of copper and silver. For copper, a voltage of 7·8 was found; for silver, the value was 6·0 volts, with indications of a resonance potential at 3·1 volts.

A. A. E.

The Hydrogenation Potential of the Alloxantins. EINAR BILMANN and HAKON LUND (*Ann. Chim.*, 1923, [ix], **19**, 137—144; cf. A., 1921, ii, 372).—Alloxantin being considered as chemically analogous to quinhydrone, an attempt was made to use it for electrochemical purposes in a similar manner. In measuring the potentials of alloxantin electrodes against hydrogen electrodes, it was found practicable to measure the hydrogenation potential of alloxantin and of tetramethylalloxantin. Details of the experimental work are given; the results obtained show for the former substance a value of 0·3696 volt and for the latter 0·3657 volt, the measurements being made at 18° and under a hydrogen pressure of 760 mm. The influence on the hydrogenation potential of the replacement of hydrogen by methyl is greater in the quinhydrone series than for the alloxantins, but the authors point out that in the case of quinhydrone a transformation of the ring structure is involved.

H. J. E.

Critical Potentials of Thallium Vapour. F. L. MOHLER, PAUL D. FOOTE, and A. E. RUARK (*Science*, 1923, **57**, 475—477; cf. A., 1919, ii, 42).—A recalculation of the previous results, the 1·55 volts collision now being regarded as the first resonance point, gives a value of 6·12 volts instead of 7·3 volts as the ionisation potential of thallium. This potential has been redetermined by Lenard's method, with suitable correction of the applied potentials, and a weighted mean of $6\cdot04 \pm 0\cdot1$ volts obtained, in agreement with 6·08 volts corresponding with $2p_2=49264$. A peculiar type of resonance potential (0·96 volt, corresponding with the experimental figure, 1·07 volts) is noted, the resonance collision not being followed by the emission of the corresponding single-line spectrum; a metastable form of thallium is produced. Ionisation potentials of aluminium, gallium, indium, and thallium are predicted, respectively, as follows: $2p_2$:—5·960, 5·973, 5·761, 6·082; $2p_1$:—5·946, 5·871, 5·488, 5·120 volts. Resonance potentials are predicted as follows: $2p_2-2s$:—3·129, 3·060, 3·009, 3·269; $2p_2-3d$:—4·004, 4·294, 4·06, 4·47 volts; $2p_2-2p_1$:—0·014, 0·102, 0·273, 0·962 volt. A. A. E.

Forces at Phase Boundaries. EMIL BAUR and P. BUECHI (*Rec. trav. chim.*, 1923, **42**, 656—664).—The potential differences existent at the boundary of two immiscible liquids, such as amyl alcohol and water, are discussed in connexion with the published researches of Baur and Kronmann (A., 1917, ii, 231) and Wild

(this vol., ii, 53). Measurements of a number of complicated cells containing immiscible liquids are described and the potential set up at the boundary of immiscible liquids is evaluated.

J. F. S.

The Electromotive Polarisation of Platinum. A. V. PAMFILOV (*Bull. Inst. Polytech. Ivanovo-Voznesensk*, 1923, 7, 68—79).—The anodic polarisation of platinum and platinised electrodes in normal and decinormal sulphuric acid was studied at different current densities (0.01 to 0.12 ampere per sq. cm.).

With the platinum anode, which was a loop of wire 25 mm. long and 0.4 mm. in diameter and was kept rotating at 300 to 500 r.p.m., the electrode potential rose quickly in the first five minutes, then more slowly, reaching a maximum in ten to twenty minutes at a current density of 0.04 to 0.1 ampere, and two and a half to three hours at 0.01 ampere. After a short interruption of the polarising current, a different potential is observed and in general the numerical values obtained are not constant in different experiments, although the general character of the curves is the same. These numerical values appear to depend greatly on the previous treatment of the electrode under observation (action of oxidising or reducing agents, cathode polarisation, etc.).

With a platinised electrode the maximum is attained more slowly and the results are more constant; short interruptions of the current appear to have no effect on the electrode potential. The difference between the potential of the platinised and the solid electrode is found to be 0.1 to 0.2 volt, not 0.4 to 0.6 as observed by Foerster (A., 1909, ii, 962).

It is suggested that the results are best explained by the interaction of the surface of the electrode with the gas generated in the process of electrolysis, the metal suffering a change from which it recovers only after some time; the question of whether an oxide of platinum or a solid solution of the gas in platinum is formed is left open.

G. A. R. K.

Electromotive Force Measurements with a Saturated Potassium Chloride Bridge or with Concentration Cells with a Liquid Junction. GEORGE SCATCHARD (*J. Amer. Chem. Soc.*, 1923, 45, 1716—1723).—A theoretical paper in which it is shown that the proof of Fales and Vosburgh (A., 1918, ii, 424) that the saturated potassium chloride bridge eliminates liquid junction potentials depends on the assumption that in hydrochloric acid solution the activities of the two ions are equal; the proof of Corran and Lewis (A., 1922, ii, 691) depends on incompatible formulæ for the *E.M.F.* at the two electrodes. An analysis of experimental results indicates that the liquid junction potential with saturated potassium chloride is not more than 0.001 volt for solutions less than 0.1*M*, but that it increases rapidly with the concentration for hydrochloric acid. There is some theoretical confirmation for the assumption that the liquid junction potential with a saturated potassium chloride bridge is independent of the sucrose concentration if the concentration of electrolyte remains constant, but

this substantiation cannot be extended to solutes in general. The ordinary thermodynamic formula for the *E.M.F.* of a concentration cell with transport ignores the transport of water. If this be taken into account, the transport number involved is the true and not the Hittorf number. Emphasis is laid on the fact that activity measurements give the activity of the unhydrated ion. An increase in the fraction of ions not hydrated gives the simplest explanation of the increase of activity coefficients in concentrated solutions. J. F. S.

Effect of Sucrose on the Activities of certain Ions. J. W. CORRAN (*J. Amer. Chem. Soc.*, 1923, **45**, 1627—1636).—By means of *E.M.F.* measurements of potassium chloride concentration cells without transport, containing sucrose, the conclusion drawn in a previous paper (Corran and Lewis, A., 1922, ii, 691), that the potassium- and chloride-ions are soluble in the water of hydration of sucrose has been verified. It has been shown that whereas the transport number of the potassium-ion in sucrose solutions remains constant up to a concentration of 50% sucrose, it appears to increase slightly in 60% and 70% solutions. From a survey of Harned's results (A., 1920, ii, 664), it has been shown that the chloride-ion is soluble in the water of hydration of accompanying kations. This conclusion is therefore analogous to that reached in connexion with sucrose. Measurements of the mean activities of barium chloride, in the presence of sucrose, by means of the cell without transport, have shown that the barium-ion, as well as the potassium- and chloride-ions, is soluble in the water of hydration of sucrose. Since the solubility or otherwise of an ion in water of hydration is of primary importance in determining its true concentration in terms of available water, Harned's extension to any ion of MacInnes' postulate regarding the independent activity of the chloride-ion in solutions of univalent chlorides of the same concentration, is only valid for those ions which are soluble in the water of hydration of secondary solutes (either ions or non-electrolytes) (A., 1919, ii, 385). J. F. S.

Behaviour of Cadmium Amalgam in Relationship to the Weston Normal Element. ALFRED SCHULZE (*Z. physikal. Chem.*, 1923, **105**, 177—203).—The diagram of condition of cadmium amalgam for the concentration range 8% to 15% cadmium, which is of importance for the Weston element, has been subjected to a revision. The situation of the liquidus curve is confirmed by the thermal method and then the composition of the liquid phase is confirmed by analysis. The solidus curve could not be determined by the thermal method, for apparently too little heat is rendered latent in this change, nor was the determination possible by the dilatometric method, which is contrary to the experience of Bijl (A., 1903, ii, 6), nor by means of electrical conductivity determinations. On the other hand, the electromotive behaviour of the amalgams allowed the branching point to be definitely fixed in the temperature region 0° to 25°. These results are in excellent agreement with the *E.M.F.* measurements of Bijl at 25—75°, but at variance with his dilatometric measurements. In agreement with

Smith (*National Phys. Lab.*, Collected Researches, 1910, 6, 137), it is shown that the branching temperature, in the concentration range examined, lies considerably lower than Cohen has assumed (A., 1920, ii, 581). It is important that this fact is found whether the temperature is rising or falling. According to this, the branching point of the 12.5% amalgam used in the Weston cell lies below 0° so that the assertion of Cohen (*loc. cit.*) with regard to the metastability of the normal element is incorrect. The present result is in keeping with the bulk of the data obtained for the Weston element by the various controlling laboratories. Electrolytic amalgams lead to the same results. Divergences of the *E.M.F.* of elements containing strongly cooled amalgams, as obtained by Smith, can be explained by chemical analysis, for the liquid phase of the strongly cooled amalgams has a different composition from that of the slowly cooled amalgams. Measurements of the electrical conductivity of the 14.07% amalgam in the temperature region where the amalgam consists of two phases, show a remarkably large temperature coefficient. The change in resistance per degree is about 2%, whilst for most other metals it is about 4%.
J. F. S.

A Simple Model of a Micro-electrode for Estimation of P_H . GUNTHER LEHMANN (*Biochem. Z.*, 1923, 139, 213—215).—A micro-electrode is described and figured suitable for the determination of the P_H of a drop of fluid. It works as rapidly as the large electrode and gives values in agreement with the \bar{U} electrode of Michaelis.
H. K.

Gas Electrode. M. KNOBEL (*J. Amer. Chem. Soc.*, 1923, 45, 1723—1724).—A very convenient form of hydrogen or other gas electrode which reaches the equilibrium value very quickly is described. It consists of a piece of graphite rod 3 mm. in diameter and about 3—4 cm. long which is bored axially to within 6 mm. of the bottom. This is connected with a copper tube of the same diameter by a short length of rubber and electrical connexion between the two made by a copper spiral. The graphite is platinised in the usual way. The measurement is made by leading hydrogen at $\frac{1}{2}$ —1 atm. pressure into the tube, when it slowly bubbles from the graphite surface, thus constituting an extremely good electrode. The equilibrium value is reached in one and a half minutes and remains constant and is entirely independent of the pressure outside.
J. F. S.

The Action of Silica on Electrolytes. ALFRED FRANCIS JOSEPH and JOHN STANLEY HANCOCK (T., 1923, 123, 2022—2025).

Electrical Properties of Silicic Acid Sols. W. GRUNDMANN (*Koll. Chem. Beihefte*, 1923, 18, 197—222).—The change in silicic acid sols has been investigated by means of determinations of the amount of silicic acid carried by an electrical current and by determinations of the reduction of the electrical conductivity of hydrochloric acid in presence of varying quantities of the sol. It is shown that the charge of the silicic acid particles in an hydrochloric acid solution of silicic acid changes when the solution is kept for some

time. In the first few days, the charge becomes more negative and after five to ten days reaches a maximum, after which it becomes more positive. In the case of solutions from 0.0002 to 0.0004*N*-hydrochloric acid, the charge changes its sign twice. The maximum is reached earlier the smaller the concentrations of acid. The sol without the addition of acid exhibits a change toward the positive side. The diminution of the electrical conductivity increases steadily with time and after five to ten days a value is reached which remains steady for weeks if no coagulation takes place. When coagulation commences, the diminution increases very much. The diminution of the electrical conductivity depends on the concentration of the silicic acid, the concentration of the hydrochloric acid, the age of the sol, and the purity of the sol. With increasing age of the sol, the adsorption in concentrated sols decreases slowly, but increases in dilute sols and after a few days a dilute sol may show a larger diminution than a concentrated sol. J. F. S.

Electro-diffusion (Ionic Migration). ALFRED GILLET (*Compt. rend.*, 1923, **177**, 261—263).—Electrolysis of sodium sulphate solution containing sufficient gelatin to form a stiff jelly was effected and after some time the jelly was cut into sections parallel with the electrodes. Each portion was then analysed and the following conclusions were drawn from the results obtained. The current appears to be carried by the kation only, and towards the anode there is a movement, not only of sulphate-ions, but of all the molecules present in the solution. A species of equilibrium is established in which one molecule of sodium sulphate is equivalent to two of sulphuric acid at the anode and three molecules of sodium hydroxide to one of sodium sulphate at the cathode. Numerous secondary effects occur, but it is stated that none of these is sufficient to affect the conclusions to any serious extent.

H. J. E.

A Cataphoretic Apparatus for Small Quantities. A. VON SZENT-GYÖRGYI (*Biochem. Z.*, 1923, **139**, 74—76).—A cataphoretic apparatus is pictured and described suitable for small quantities of liquid. It is based on the Landsteiner-Pauli-Michaelis macro-apparatus. H. K.

Magnetic Properties of Gadolinium Ethyl Sulphate at Low Temperatures. L. C. JACKSON and H. KAMERLINGH ONNES (*Compt. rend.*, 1923, **177**, 154—158).—Gadolinium ethyl sulphate, $\text{Gd}(\text{SO}_4\text{Et})_3 \cdot 9\text{H}_2\text{O}$, is an example of a strongly diluted paramagnetic substance. At temperatures from the ordinary one to 14.56°K , the Curie Law ($K_m T = \text{const.}$) is obeyed. The susceptibility is independent of the field applied, so that the substance is purely paramagnetic. Further, crystals of gadolinium ethyl sulphate are magnetically isotropic. E. E. T.

Paramagnetism and Atomic Structure. A. DAUVILLIER (*Compt. rend.*, 1923, **176**, 1802—1805).—The author has interpreted the results obtained by Cabrera (A., 1922, ii, 469), assuming that paramagnetism is due to two causes acting singly or together,

(a) the presence of surface electrons, and (b) of internal electrons in incompletely furnished layers. Such elements as silicon, sulphur, germanium, selenium, tin, and tellurium, although possessing the same surface structure as those of the titanium and chromium type, are diamagnetic by reason of their electro-negative character. In the cases of scandium and copper, agreement with Cabrera's magnetic moments is good, whilst for the rare earths the two symmetrical magnetic moment curves (cerium-europium and samarium-lutecium) are in accordance with the fact that internal dissymmetry is at a maximum in neodymium and dysprosium.

H. J. E.

A Rapidly-constructed, Cheap, Internally-wound Electric Furnace. HUBERT FORESTIER (*Bull. Soc. chim.*, 1923, [iv], **33**, 999—1000).—About 4 m. of nichrome wire are wound on a metal tube, 3—4 cm. diameter, and the coil is covered with a layer of alundum cement 1—2 mm. thick. This is dried, placed in the axis of an asbestos mould about 10—12 cm. diameter, and the annular space filled with quick setting cement. The whole is then surrounded with a layer of about 3—4 cm. of asbestos wool, the metal tube is withdrawn, and the furnace is ready for use. The furnace described may be heated to 1000° in thirty minutes, and cools to 100° in one and a half hours. Its power consumption is about $\frac{1}{2}$ kw. (4.5 amperes at 110 volts).

H. H.

Thermoregulator for Electric Furnaces. JEAN SOLARI (*Bull. Soc. chim.*, 1923, [iv], **33**, 1000—1004).—The apparatus described consists essentially of a differential air thermometer with mercury as the moving liquid. One bulb is maintained at a constant temperature and the other is placed in a small auxiliary furnace of copper tube connected in series with the main furnace. The tube containing the mercury is provided with three platinum contacts so arranged in connexion with a resistance and a swinging commutator that automatic regulation of the current passing through the furnace is secured. If Q be the thermal capacity, R the radiating power, and C the conductivity of the tube carrying the heating coil of the main furnace, and q , r , and c the same constants for the small one, then temperature control to within $\pm 5^\circ$ may be obtained by making Q/q very large, R/r very small (but r must not be too great), and C/c very small (c may be very large).

H. H.

Theory of the Temperature Variation of the Specific Heat of Hydrogen. E. C. KEMBLE and J. H. VAN VLECK (*Physical Rev.*, 1923, **21**, 653—661).—New empirical formulæ for specific heats between 300° and 2300° K are: for hydrogen, $c_v = 4.87 + 0.539 \times 10^{-3}t + 0.146 \times 10^{-6}t^2$; for water vapour, $c_v = 6.03 + 4.2 \times 10^{-3}t - 4.07 \times 10^{-6}t^2 + 1.95 \times 10^{-9}t^3$. The following constants of the hydrogen molecule are computed: nuclear spacing, 0.488×10^{-8} cm.; moment of inertia, 1.975×10^{-41} gm.cm.²; wave-length corresponding with normal vibration, 2.05μ . A corrected calculation of the rotational and vibrational specific heat of an elastic model of a diatomic gas molecule is presented.

A. A. E.

Some Solidification Curves of Binary Systems. MICHELE GIUA (*J. Amer. Chem. Soc.*, 1923, **45**, 1725—1727; JAMES M. BELL (*ibid.*, 1727).—Polemical; Giua answers Bell's criticism of his interpretation of solidification curves of binary systems (cf. Giua, A., 1914, i, 817; Bell, A., 1921, i, 330); to this Bell replies.

J. F. S.

Cryoscopic Measurements with Nitrobenzene. HUGH MEDWYN ROBERTS and CHARLES R. BURY (*T.*, 1923, **123**, 2037—2043).

Sintering : Its Nature and Cause. ROBERT CHRISTIE SMITH (*T.*, 1923, **123**, 2088—2094).

Application of Thermodynamical Principles to the Time Rates of Chemical Changes and Vaporisation. SHIZUWO SANO (*Japan. J. Phys.*, 1922, **1**, 59—69).—By the use of thermodynamic potential functions, a mathematical expression is derived for the law of mass action in a form applicable to the case of concentrated solutions in which electrolytic ions may be present. In the case of the evaporation of a liquid, when the flux of kinetic energy and the effect of viscosity are taken into account, the assumption that the pressure of the vapour evaporating from the liquid is equal to that of the saturated vapour in equilibrium with the liquid phase appears to contradict thermodynamic principles.

J. S. G. T.

Vapour Tensions of Mixtures of Hydrochloric Acid and Water. N. YANNAKIS (*Compt. rend.*, 1923, **177**, 174—175; cf. (Lord) Rayleigh, A., 1903, ii, 59; Bates and Kirschman, A., 1920, ii, 88).—A determination of the boiling-point isotherm (50°) for the above mixtures. Pressures were measured by Regnault's method, as modified by Zawidsky (A., 1901, ii, 6). The composition of liquid and gaseous phases was determined in each case, eleven different mixtures being examined, of hydrogen chloride percentage 0 to 28·7.

E. E. T.

The Analytical Study of Vaporisation. DAMIENS (*Ann. Chim.*, 1923, [ix], **19**, 179—185).—A description of the experimental methods used in the work previously published (this vol., ii, 316). The results obtained show different types of vaporisation phenomena in the cases studied, (a) no intermediate compound is formed as in the system tellurium tetraiodide-tellurium, (b) one intermediate compound is formed as in the systems tellurium tetrabromide-tellurium and tellurium tetrachloride-tellurium. Here the mean composition of the vapour is that of the intermediate substance, but only when the mixtures heated are within definite composition limits. The rate of vaporisation is at a maximum in the neighbourhood of the point corresponding with the composition of the intermediate compound, but somewhat displaced in the direction of the more volatile of the original substances. The general conclusion is drawn that in a binary system in equilibrium in the solid state, if endothermic reaction between the two original

substances can take place, the vapour given off may have the composition of the resulting substance with or without that of the more volatile of the two original substances. H. J. E.

An Electrical Fuse for a Calorimetric Bomb. P. V. ZOLOTAREV (*Bull. Inst. Polytech. Ivanovo-Voznesensk*, 1923, 7, 117—118).—The usual method of firing the combustible material in the bomb has been improved by using a platinum wire 5 cm. long and 0.5 mm. in diameter fixed in such a way that the flame of the burning substance does not impinge upon it during the process of combustion. A current of known strength is passed through the wire, allowing the necessary correction to be made; a second wire, of the same dimensions, is inserted into the outer circuit of the calorimeter and serves to indicate when a suitable temperature has been attained. It is found that a fuse of this kind does not melt and can be used almost indefinitely. G. A. R. K.

Heat of Formation of Solid Solutions. G. BRUNI (*Bull. Soc. chim.*, 1923, [iv], 33, 907—908).—A reply to Landrieu (this vol., ii, 535). H. H.

Elevation of the Critical Solution Temperature by the Addition [of other Substances]. CARL DRUCKER (*Rec. trav. chim.*, 1923, 42, 552—555).—The elevation of the critical solution temperature of aniline-hexane by the addition of various quantities of water, urethane, benzil, benzamide, and thiocarbanilide has been determined. The same quantity has been determined for the binary system carbon disulphide-methyl alcohol by the addition of water, diphenylamine, carbamide, succinic acid, potassium chloride and bromide, sodium iodide, mercuric chloride, and barium chloride. The results show that the molecular elevation of the critical solution temperature is specific for each of the added substances. Reasons for the absence of colligative relationships in this property are discussed. J. F. S.

Special Case of Fictitious Volume Change in Solution Equilibria. ERNST COHEN, WILHELMA A. T. DE MEESTER, and A. L. TH. MOESVELD (*Rec. trav. chim.*, 1923, 42, 779—783).—In the determination of the fictitious volume change, which occurs in the solution equilibrium of the system tetrachloroethane-naphthalene, using the methods previously described (this vol., ii, 537), it has been found that the specific volume is a linear function of the concentration. Such a relationship has not hitherto been observed. The fictitious volume change has been determined in several ways and in this case it is shown to be independent of the solvent employed. J. F. S.

Upper Range of the Quartz Fibre Manometer. ALBERT SPRAGUE COOLIDGE (*J. Amer. Chem. Soc.*, 1923, 45, 1637—1643).—A form of bifilar quartz fibre manometer is described, from which troublesome harmonic vibrations are eliminated. A method is described by which the instrument may be read up to pressures

of 0.1 to 1 mm., depending on the gas used. The method involves calibration over the whole range with a permanent gas and a McLeod gauge at relatively high pressure, or a knowledge of the viscosity of the gas. So extended, the range of the instrument overlaps that of the McLeod gauge, even with easily condensible vapours. It is suggested that the manometer may be used to determine molecular weights of gases at very low pressures.

J. F. S.

The Coefficient of Viscosity of Helium and the Coefficients of Slip of Helium and Oxygen by the Constant Deflection Method. M. N. STATES (*Physical Rev.*, 1923, **21**, 662—671).—For helium, $\eta^{23}=1962.3 \times 10^{-7}$ (probably $\pm 0.1\%$). The coefficients of slip of helium and oxygen, respectively, are, for the unpolished silver oxide surface, $\zeta^{76}=123 \times 10^{-7}$, 61.1×10^{-7} ; for the polished surface, 160×10^{-7} , 64.5×10^{-7} .

A. A. E.

Measurements of the Viscosity and Surface Tension of Viscous Liquids at High Temperatures. EDWARD W. WASHBURN (*Rec. trav. chim.*, 1923, **42**, 686—693).—The author describes methods whereby the viscosity and surface tension of very viscous liquids (glasses) may be determined at high temperatures. Viscosity is measured by a modification of Margules's method of rotating cylinders. The cylinders employed were made of hard, dense porcelain, and the apparatus was standardised by means of very viscous solutions of dextrose. It is shown that the viscosity is given by the usual formula $\eta = KW/S$, where W is the weight required to give the rotating cylinder S revolutions per minute, and K is a constant. This constant is only strictly constant up to viscosities of 1,000 poises but for higher viscosities it varies with the viscosity. A curve has been constructed to express this variation by plotting $\log \eta$ against W/S , from which the viscosity can be read directly when the value of W/S is known for any glass. The errors arising from variations of the two cylinders have been discussed and evaluated. The results for a number of glasses are expressed as a series of curves made by plotting $\log \eta$ against the temperature. From the projection of curves from a solid model, a series of *isokoms* (*iso*, equal, *kommi*, gum) are produced for a series of glasses, which give the compositions having the same viscosity.

A new method is described for the measurement of surface tension; this consists in suspending a cylinder of platinum foil by means of a sensitive spiral spring above the surface of the molten glass. The position of a pointer attached below the spring is read by means of a cathetometer. The furnace is then raised by means of a screw until the surface of the glass just touches the cylinder, which is immediately drawn into the glass by the force of surface tension until these forces are balanced by the extension of the spring. The position of the pointer is again read. A constant of the apparatus is required before the results can be evaluated, and this is obtained by means of liquids of known surface tension, such as water, benzene, and specially prepared viscous liquids. The surface tension is plotted on solid diagrams and the curves

are projected to give a series of *isoeipitatic* lines. A set of such curves obtained from a series of molten glasses is given in the paper.
J. F. S.

Surface Phenomena in Sucrose Solutions. RAYMOND RENARD BUTLER (T., 1923, 123, 2060—2065).

Gibbs's Theorem of Surface Tension applied to Sodium Abietate Solutions. RUDOLF LORENZ (*Kolloid Z.*, 1923, 33, 15—18).—The measured surface tension of solutions of sodium abietate, which have been aged for five hours, have been compared with the calculated surface concentration of freshly diluted solutions of the same salt, obtained according to Gibbs's principle and a remarkable parallelism between the two sets of values obtained.
J. F. S.

Temperature Coefficient of the Molecular Surface Energy of some Substances with Very Long Carbon Chains. RUDOLF SCHENCK and MARIA KINTZINGER (*Rec. trav. chim.*, 1923, 42, 759—764).—The authors have discussed the temperature coefficient of the molecular surface energy and show that the measurement of this quantity does not allow conclusions to be drawn as to the degree of association of the substances concerned. A normal value for this factor (2.12) allows the conclusion that the substance concerned is normal, but a high value does not necessarily mean that the substance is associated. It is shown that the geometrical form of the molecule, presence of tautomerides, and many other causes in addition to the temperature have a strong influence on the molecular surface energy. The surface tension of *n*-hexacosane, *n*-myricyl alcohol, and *n*-hexacontane has been determined at a series of temperatures from 91.7° to 190.6° by the capillary rise method and the molecular surface energy and the temperature coefficient have been calculated. The following data are recorded: *n*-hexacosane $d^{91.7}$ 0.7560, γ (dynes) 24.79, $\gamma (M/d)^{2.3}$ 1529.6 ergs, k (mean) 3.91 ergs; *n*-myricyl alcohol $d^{95.3}$ 0.7773, γ 26.17, $\gamma (M/d)^{2.3}$ 1787.0, k (mean) 4.21; *n*-hexacontane $d^{115.4}$ 0.7465, γ 6.366, $\gamma (M/d)^{2.3}$ 2621.8, k (mean) 5.46. The high values of k are discussed in connexion with the long carbon chains of these compounds. According to the Baeyer theory these three compounds must be constructed as spirals with 5, 6, and 12 turns, respectively, numbers which are in the same order as the values of k .
J. F. S.

Density of Accumulation in the Adsorption of Silver-ions by Silver Bromide. K. FAJANS and W. FRANKENBURGER (*Z. physikal. Chem.*, 1923, 105, 255—272).—The adsorption of silver-ions from a solution of silver nitrate of fixed concentration by silver bromide has been investigated by determining the total surface of the silver bromide from the number of particles in a colloidal solution shortly before its coagulation and the amount of adsorbed silver-ions from the divergence between the Mohr and the Gay-Lussac titration methods. It is shown that in the adsorption

equilibrium with a silver-ion solution of the concentration 1.8×10^{-5} mol./litre in the presence of potassium nitrate, approximately every fourth to every tenth bromine-ion of the silver bromide surface adsorbs one extra silver-ion.

J. F. S.

Adsorption. I. Adsorption of Ions by Freshly Precipitated and Air-dried Manganese Dioxide. N. G. CHATTERJI and N. R. DHAR (*Kolloid Z.*, 1923, **33**, 18—29).—The adsorption of silver nitrate, copper sulphate and chloride, ferric sulphate and chloride, calcium chloride and nitrate, strontium chloride, barium chloride, uranium nitrate, nickel nitrate, potassium alum, aluminium sulphate, zinc sulphate and chloride, magnesium sulphate and chloride, cadmium chloride and sulphate, cobalt chloride, manganese sulphate and chloride, cerium nitrate, and thorium nitrate from solution by hydrated manganese dioxide has been investigated under varying conditions. The results show that the larger the valency of the kation the smaller is the adsorption; thus the atomic adsorption is silver 0.0015, barium 0.00033, zinc 0.00023, iron and aluminium 0.0001. These facts are in keeping with the Hardy-Schulze rule. It is also shown that for a given amount of electrolyte the adsorption increases with the dilution, but the adsorption is the same whether a dilute solution is taken or a concentrated solution containing the same amount of dissolved electrolyte and diluted after equilibrium is set up. The adsorbed quantity is not directly proportional to the amount of adsorbent. The influence of time and temperature is exceedingly small. The effect of the addition of a neutral salt on the adsorption is small, but measurable; thus *N*-sodium chloride has no effect on the adsorption of copper, but ammonium chloride reduces the adsorption. The adsorption of ions is discussed generally.

J. F. S.

Adsorption. II. Adsorption of Compounds and Qualitative Analysis. R. DHAR, K. C. SEN, and N. G. CHATTERJI (*Kolloid Z.*, 1923, **33**, 29—31; cf. preceding abstract).—The adsorption of salts by various precipitates used in qualitative analysis has been investigated. It is shown that strontium sulphate adsorbs iron in large quantities, aluminium and chromium to a smaller extent, nickel, cobalt, and copper still less, and mercury not at all. Barium and calcium sulphates adsorb notable quantities of iron; iron, aluminium, and chromium phosphates adsorb detectable quantities of calcium; aluminium, chromium, and ferric hydroxides adsorb measurable quantities of cobalt, nickel, zinc, and cadmium, but do not adsorb silver. Calcium, barium, and strontium carbonates carry down with them magnesium salts whether the precipitation is effected hot or cold. The addition of barium nitrate to a solution of lead sulphate in ammonium acetate gives a precipitate of barium sulphate containing much lead sulphate. The addition of freshly precipitated copper hydroxide to ferric chloride or potassium alum causes the precipitation of iron or aluminium hydroxide with solution of the copper hydroxide, but the precipitate contains some copper. The oxalates of calcium,

strontium, and barium carry down with them iron and magnesium. Iron is carried down by both calcium citrate and calcium benzoate.

J. F. S.

Nature of the Adsorption Process. I. A. FODOR [with R. SCHOENFELD] (*Koll. Chem. Beihefte*, 1923, **18**, 77—128).—From observations on sols of Congo-rubin, Congo-red, night-blue, and alkali-blue it is shown that analogously to the proteins two kinds of cataphoric transference take place side by side, and consequently two types of carriers of electric charges must be present. Of these, one is the enhydrone, the characteristic of which is its migration under a potential drop against water. The other carriers are those which migrate against solutions of electrolytes but not against water; these constitute the ekhydones. Both kinds may be present in definite concentrations. These latter carriers have an increased power of adsorption on charcoal over the first type. J. F. S.

Effect of Hydrogen-ion Concentration on Adsorption of Dyes by Wool and Mordants. O. REINMUTH and NEIL E. GORDON (*Ind. Eng. Chem.*, 1923, **15**, 818).—The adsorption of Orange II and other dyes by alumina and similar mordants is considerably affected by small changes in the hydrogen-ion concentration; there is also sometimes a marked change in colour. In the example quoted, adsorption decreases rapidly as P_H rises from 3.6 to 5.4. The results obtained with wool confirm those given by Briggs and Bull (this vol., ii, 58).

E. H. R.

The Physico-chemical Bases of Vital Permeability. III. R. BRINKMAN and A. VON SZENT-GYÖRGYI (*Biochem. Z.*, 1923, **139**, 274—279; cf. this vol., i, 974).—The authors have studied the spreading of capillary active substances on the surface of water in connexion with the theory of nerve conduction. For this purpose, a horizontal tube 1.25 m. long and 2 cm. wide is half filled with pure water of surface tension 74.5. A platinum ring attached to a torsion balance touches the water at one end and the torsion is adjusted to 72.5, so that when the surface tension is lowered by 2 dynes the platinum ring and water become separated. At various distances along the tube, quantities of 0.0001 to 0.001 c.c. of capillary active substances can be dropped on to the water surface by means of a fine pipette operated by a rubber membrane. Records are taken electrically. It was found that methyl or ethyl alcohol, ether, light petroleum, paraffin, glycerol, pyridine, or alkaloids did not spread on the surface in such a way as to free the ring. Hexoic, decoic, oleic, and α -hydroxybutyric acids and sodium oleate spread over the surface with constant velocity and released the ring. Using an alcoholic solution of oleic acid, the minimum quantity of oleic acid required to free the ring was found and this corresponded with a film on the whole surface of $0.2 \mu\mu$ thickness, or one molecule thick.

H. K.

Improvements in the Mode of Measurement of Osmotic Pressure. ARTHUR GROLLMAN and J. C. W. FRAZER (*J. Amer. Chem. Soc.*, 1923, **45**, 1710—1716).—A number of improvements

in the preparation of cells for the measurement of osmotic pressure are described. The pores of cells are filled with some insoluble material which gives additional support for the membrane. The filling material, which is generally magnesium silicate, is produced *in situ* by diffusion of the necessary solutions or electrolytically, and, after washing, the cell is baked at 1000—1450°. The most rapid results are obtained when the membrane is deposited by a modification of the Pfeiffer method instead of by electrolysis. This is carried out by filling the air-free cell with *M*-copper sulphate, and placing it in a beaker of water until the electrolyte has diffused through the walls. It is then washed on the outside and the water replaced by a *M*-solution of potassium ferrocyanide and the arrangement left over-night. A cell so prepared will give the equilibrium osmotic pressure in a very few minutes after introducing the solution. It is also shown that a water interferometer serves as the most suitable pressure gauge for the measurement of osmotic pressure. A number of modifications in the construction of such a gauge are described (cf. Adams, A., 1915, ii, 478; Cohen and Bruins, this vol., ii, 118).

J. F. S.

Kinetic Theory of the Laws of Osmotic Pressure of Strong Electrolytes. P. DEBYE (*Rec. trav. chim.*, 1923, 42, 597—604).—A theoretical paper in which on the basis of the kinetic theory, the author has deduced expressions for the osmotic pressure of strong electrolytes.

J. F. S.

Aqueous Solutions. Origin of Osmotic Effects. CAMILLE GILLET (*Compt. rend.*, 1923, 177, 257—258).—The author claims priority over Armstrong (this vol., ii, 542) and Kling and Lassieur (this vol., ii, 543), but points out that the results obtained by these workers, independently in each case, have considerable corroborative value. He gives a summary of his views and mentions results to which they have led, enumerating researches based on them (cf. A., 1909, ii, 388; 1910, ii, 381; 1912, ii, 1043).

H. J. E.

Mutual Solubility Curve of Two Liquids in the Region of the Critical Solution Point. J. E. VERSCHAFFELT (*Rec. trav. chim.*, 1923, 42, 683—685).—A theoretical paper, in which, making use of the experimental results of Michels (A., 1922, ii, 486) on the mutual solubility of isobutyl alcohol and water, the author has shown that the mutual solubility in the region of the critical solution temperature can be represented by an equation of the same type as has previously been employed to express the change of density near the critical point. The formula in the present case has the form $\log(x_2 - x_1) = 1.330 + 0.315 \log(t_e - t)$, where x_2 and x_1 are the concentrations of the two co-existing phases at temperature t and t_e is the critical solution temperature.

J. F. S.

Investigation of the Molecular Form by Means of Crystalline Liquids. D. VORLÄNDER (*Z. physikal. Chem.*, 1923, 105, 211—254).—A résumé of fifty-four dissertations published at Halle since 1902. It is shown that the formation of supercooled liquids, in the case of organic compounds, is favoured by those

constitutive influences which oppose the formation of liquid crystals, namely, branched chains, uneven number of side-chain groups, and meta- and ortho-substitution. If the properties of crystalline liquids be taken as the manifestation of molecular arrangement, then in all probability the phenomena of supercooling of amorphous liquids may be taken as being characteristic of a lack of molecular regularity. If the molecules of an amorphous melt are regarded as in motion, then it must follow that linear or symmetrical molecules must more easily produce a space lattice than those containing branched chains or in general an unsymmetrical structure. Other conditions may have an influence on the crystalline arrangement, but the molecular form is of greatest importance in the supercooling phenomena. J. F. S.

Molecular and Crystal Symmetry. T. V. BARKER (*Nature*, 1923, 112, 96; cf. this vol., ii, 388).—A reply to Shearer and Astbury (this vol., ii, 468). A. A. E.

Historical Development of the Idea of the Universality of the Colloidal Condition, together with some Data from the History of the Extension of the Conception Colloidal Condition in Reference to its Compass and Contents. P. P. VON WEIMARN (*Koll. Chem. Beihefte*, 1923, 18, 165—196).—An historical discussion of the extent of the domain of colloid chemistry. J. F. S.

Myricyl Alcohol Jellies. E. H. BUCHNER (*Rec. trav. chim.*, 1923, 42, 787—789).—The solubility of myricyl alcohol in amyl alcohol and chloroform has been determined at a number of temperatures and the solubility curve constructed. It is shown that the solubility curves after rising rapidly to 40° and 60°, respectively, then rise toward the melting point of myricyl alcohol and do not show anything approaching an horizontal part. This proves that in the liquid state myricyl alcohol is completely miscible with chloroform and amyl alcohol. Consequently, the evidence in favour of the emulsion theory of jelly structure is lost. The experiments show that the jelly of myricyl alcohol is a conglomerate of very fine crystals which retains a large quantity of liquid in the meshes. J. F. S.

Electrolytic Dissociation of Ionisable Colloids. A. GYEMANT (*Kolloid Z.*, 1923, 33, 9—15).—A theoretical paper in which hypotheses concerning the characteristic properties of the dispersed particles of ionisable colloids are put forward, which enable the connexion between the size of the particles and the quantity of the adsorbed ions, and also the electric charge, to be determined. On the basis of this hypothesis, the law of mass action has been applied to weak colloidal acids and bases and the divergence of the dissociation relationships of these substances compared with those of molecular dispersed electrolytes. J. F. S.

Protective Colloids. XIII. *Semen ceratoniæ siliquæ* as Protective Colloid. I. General Colloid Chemical Investigation of Carob Bean Extract. A. GUTBIER, E. LOCHER, and K. KREIDL (*Kolloid Z.*, 1923, 33, 37—39).—A stable extract of

carob beans may be prepared by crushing the beans, washing repeatedly with cold water, and then extracting 30 g. of the material for two to three days with a litre of water saturated with chloroform, at 50—60°. The extract is amber-coloured and is comparatively stable; an aqueous extract, however, is not at all stable. The extract has powerful reducing properties and decreases in viscosity on keeping. The viscosity increases with increasing concentration, and decreases with increasing temperature; it is unchanged by the addition of dilute hydrochloric acid (0.29%) and by sodium hydroxide (0.29%). The addition of 0.29% of sodium chloride causes a slight increase in viscosity. The colloid is negatively charged and under a potential of 110 volts it migrates to the anode. J. F. S.

Protective Colloids. XIV. Norgine as Protective Colloid.

A. GUTBIER, E. SAUER, and G. KRÖNER (*Kolloid Z.*, 1923, **33**, 92—98).—The properties of norgine and its suitability as a protective colloid have been investigated. Norgine is the ammonium sodium salt of laminaric acid and is obtained from seaweed (*Laminaria digitata* and *Saccharinus digitatus*). A full account of the colloidal properties of the substance is given. J. F. S.

Emulsions of Mineral Oil with Soap and Water: The Interfacial Film. EDWARD L. GRIFFIN (*J. Amer. Chem. Soc.*, 1923, **45**, 1648—1657).—Emulsions of kerosene in solutions of sodium and potassium oleate, palmitate, and stearate have been investigated. The quantity of soap in the interface and in each liquid phase has been determined. The results show that, in an emulsion of a mineral oil with soap and water, part of the soap is hydrolysed, the fatty acid being dissolved by the oil droplets and the free alkali remaining in the aqueous solution. The fatty acids may be prevented from dissolving in the oil by the addition of an excess of alkali. Part of the soap forms unimolecular films round the oil droplets. The average areas occupied by each molecule of sodium oleate, potassium stearate, and potassium palmitate were found to be 48, 27, and 30×10^{-16} sq. cm., respectively. These areas agree rather closely with those found for the corresponding fatty acids in unimolecular films on the surface of water (Langmuir, A., 1917, ii, 19, 525). In the case when sufficient soap is not present to form a unimolecular film, the emulsion is not stable. When an excess of soap is used, this remains in the aqueous solution. J. F. S.

Adhesion Forces in Solutions. II. Coagulation of Coarse Suspensions. SERGIUS WOSNESSENSKY (*Kolloid Z.*, 1923, **33**, 32—34; cf. A., 1922, ii, 350).—The sedimentation of suspensions of kaolin, antimony trioxide, and aluminium hydroxide in the presence of a number of electrolytes and mixtures of electrolytes has been investigated. The experiments show that the coagulation of coarse suspensions can only be brought about by the simultaneous action of bi- or ter-valent metals and an alkali hydroxide. The adsorption of the electrolytes on the surface of the suspended particles causes the formation of difficultly soluble hydroxides,

whereby the properties of the suspended particles are entirely changed and this can bring about a change in the cohesive and adhesive forces. The presence of substances which hinder the hydroxide formation disturbs the coagulation. J. F. S.

Rhythmic Banded Film Precipitates on the Surface of Liquids. II. A. JANEK (*Kolloid Z.*, 1923, **33**, 86—89; cf. this vol., ii, 395).—The formation of film precipitates on the surface of semi-solid solutions of gelatin containing potassium dichromate by silver nitrate has been investigated. It is shown that the band formation is independent of the concentration within the limits of the concentration used, 0.03 to 0.30 g. of potassium dichromate in 30 c.c. of 3.3% gelatin solution. The band formation has a definite structure and its thickness increases with the thickness of the gelatin layer on which it is formed, but in thicker layers it is shown to form only on the surface of the gelatin layer.

J. F. S.

The Significance of Displacement of Equilibrium. ALBERT COLSON (*Compt. rend.*, 1923, **177**, 184—186).—This law (that of Opposition of Reaction to Action), as far as solubility relationships are concerned (cf. this vol., ii, 543) cannot be verified when the solubility or the heat of solution is small. With concentrated solutions difficulties have arisen owing to the tendency to ignore the volume of the dissolved solute, for this volume may be of the same order as that of the solvent. The classical law can be applied in the case of solutions of ice in alcohol at low temperatures, but fails when the contraction volume (due to ice passing into water) becomes of the same order as that of the alcohol. The author concludes that in a saturated solution the variation of the concentration is neither always, nor exclusively, controlled by the heat of solution, even at a fixed pressure.

E. E. T.

The Mass Law and Statistical Equilibrium. WORTH H. RODEBUSH (*Science*, 1923, **57**, 358—359).—It is as fallacious to apply the mass law to too dilute solutions as to too concentrated solutions (cf. Neuhausen, this vol., ii, 396. The precipitated mercuric sulphide probably being in statistical equilibrium with the solution, the absolute number of mercuric- and sulphide-ions per c.c. must be very great). Since ions are shown to exist as such in a crystal, the mechanism of reaction between solids and solutions does not differ from reaction in solution.

A. A. E.

The Trajectories of Crystallisation in Chemical Equilibrium Diagrams. N. S. KURNAKOV and S. F. SHEMTSCHUSHNI (*Bull. Acad. Sci. Russ.*, 1918, 1855—1858).—In connexion with results obtained by other authors in experimental work covering the isothermic crystallisation of the mutual system: $2\text{NaCl} + \text{MgSO}_4 = \text{Na}_2\text{SO}_4 + \text{MgCl}_2$ from aqueous solutions at 25°, it is stated that both the isothermic and isotonic diagrams of equilibrium, together with all derived diagrams representing the correlations between composition and properties, may be considered as polyhedra

to which the rule of Euler: $\alpha_0(\text{corners}) - \alpha_1(\text{edges}) + \alpha_2(\text{faces}) - 2 = 0$, is generally applicable. Polyhedra of this type can be reduced to an open complex tree by removing n lines, where n equals $\alpha_1 - \alpha_0 + 1$, and this reduction may be pushed further until the simple tree of crystallisation of two phases (or two salts) is left. They can also be projected upon the surface of a globe, by drawing lines from the centre of the globe through the corners of the polyhedron. These axes form the invariants of each system, whilst the polyhedral systems projected by them can be treated by means of the theory of algebraic groups.

CHEMICAL ABSTRACTS.

Equilibrium in the System of the Four Components Sulphuric Acid, Ammonium Sulphate, Lithium Sulphate, and Water at 30°. G. C. A. VAN DORP (*Rec. trav. chim.*, 1923, 42, 765—774).—The four three-component systems made up from the four components named in the title have been investigated by Schreinemakers and Cocheret (A., 1906, ii, 424) and van Dorp (A., 1914, ii, 114). The results of these investigations together with some new solubility determinations with the four components are combined and the complete equilibrium diagram of the system is constructed.

J. F. S.

Equilibrium between Water, Potassium Chloride, Potassium Nitrate, Calcium Chloride, and Calcium Nitrate. JEAN BARBAUDY (*Rec. trav. chim.*, 1923, 42, 638—642).—The heterogeneous equilibrium $\text{Ca}(\text{NO}_3)_2 + 2\text{KCl} \rightleftharpoons 2\text{KNO}_3 + \text{CaCl}_2$ has been investigated. Solubility equilibria of the ternary systems $\text{H}_2\text{O}-\text{KCl}-\text{KNO}_3$, $\text{KCl}-\text{CaCl}_2-\text{H}_2\text{O}$, $\text{H}_2\text{O}-\text{KNO}_3-\text{Ca}(\text{NO}_3)_2$, and $\text{H}_2\text{O}-\text{CaCl}_2-\text{Ca}(\text{NO}_3)_2$ have been determined at 30° and tabulated and the quaternary equilibria $\text{KCl}-\text{Ca}(\text{NO}_3)_2-\text{H}_2\text{O}$ and $\text{CaCl}_2-\text{KNO}_3-\text{H}_2\text{O}$ investigated by the synthetic method at the same temperature. The whole of the results have been combined in an equilibrium diagram.

J. F. S.

Equilibria of Tungsten and Tungsten Oxides with Hydrogen and Water Vapour. W. REINDERS and A. W. VERVLOET (*Rec. trav. chim.*, 1923, 42, 625—631).—The authors have investigated the equilibria $\text{WO}_2 + 2\text{H}_2 \rightleftharpoons \text{W} + 2\text{H}_2\text{O}$; $\text{W}_2\text{O}_5 + \text{H}_2 \rightleftharpoons 2\text{WO}_2 + \text{H}_2\text{O}$ and $2\text{WO}_3 + \text{H}_2 \rightleftharpoons \text{W}_2\text{O}_5 + \text{H}_2\text{O}$ at a series of temperatures and have compared their results with the widely diverging results of Chaudron (A., 1920, ii, 379), of Wöhler and Prager (A., 1917, ii, 455), and of Wöhler and Balz (A., 1921, ii, 633). In the case of the equilibrium between tungsten and the dioxide, it is found that equilibrium is set up at 685° in the presence of 74% of hydrogen, at 830° in the presence of 65% of hydrogen, and at 920° with 58% of hydrogen. These values are all somewhat higher than those found by the authors named above. In the case of the equilibrium between the blue oxide (W_2O_5) and the dioxide, equilibrium is set up at 830° in the presence of 43% of hydrogen and at 700° with 55% of hydrogen. The value found at 830° is identical with that of Chaudron but higher, as is also the value at 700°, than the other results. In the third case, blue oxide-tungsten trioxide, the results are widely

divergent, and it seems impossible to give the so-called blue oxide a definite composition. The blue compounds obtained in the present work vary in composition from $\text{WO}_{2.95}$ to $\text{WO}_{2.2}$, so that no trustworthy figures for this equilibrium can be quoted. J. F. S.

The Acid-Base Equilibrium in Simple Two-phase Systems.

CECIL D. MURRAY (*J. Biol. Chem.*, 1923, **56**, 569—591).—By combining the distribution law with the law of mass action, equations have been developed which relate the distribution of a weak acid in a two-phase system with the P_H of the aqueous phase. The effect of the second (non-aqueous) phase on the buffer value of the weak acid is also considered. Various possible applications of the equations are discussed. E. S.

Ternary System Sucrose-Citric Acid-Water. Theory of Edible Ices from the Point of View of the Phase Rule.

ROBERT KREMANN and HERMANN EITEL (*Rec. trav. chim.*, 1923, **42**, 539—546).—The authors have constructed freezing-point diagrams for the binary systems, water-sucrose and water-citric acid and for the ternary system water-sucrose-citric acid. It is shown that the eutectic between citric acid hydrate and ice lies at -11.4° to -11.6° and contains 46.5% of citric acid. The eutectic between sucrose and water cannot be obtained directly from the freezing curve, but from the intersection of the freezing curve and the solubility curve the eutectic is shown to lie at -14.5° and to contain 62.5% of sucrose. The solubility of sucrose has been determined at various temperatures and the following values expressed in g./100g. of solution are recorded: 0° , 64.2; 5° , 64.9; 10° , 65.6; 15° , 66.3; 20° , 67.1; 25° , 67.9, and 30° , 68.7. The freezing-point curves of the ternary system have been determined for four concentrations of citric acid and the spatial model has been constructed. J. F. S.

The Velocity Constant of a Unimolecular Reaction.

JAMES RICE (*Phil. Mag.*, 1923, [vi], **46**, 312—320).—From a statistical investigation of interactions between molecules represented by a mechanical model in which two bodies are bound by a quasi-elastic force, the author derives an expression for the velocity constant κ of a unimolecular reaction in the form $\kappa = kT e^{-\mu\phi(c)} / \int_0^c \int_{-\infty}^{\infty} e^{-\epsilon} dq dp$, where the double integral in the denominator is proportional to the number of undissociated molecules, the number of these included in the phase extension q, p to $q+dq, p+dp$ being represented by $A e^{-\epsilon} dq dp$, where A is a constant. The energy associated with the mechanism referred to is given by $\epsilon = p^2/4a + \phi(q)$, where a is in general a function of q . c is the critical distance of separation of the components, beyond which the potential energy associated with the molecular model either decreases or remains constant. k and T have their customary significance. It is shown that by suitable modification of the expression derived for κ , in any one of several ways suggested by quantum considerations, formulæ approximating to that derived empirically by Dushman (A., 1921, ii, 315) for the velocity constant of a unimolecular reaction, in the form $\kappa = \nu e^{-h\nu/kT}$ may be obtained. Thus, assigning to the molecular model the

properties of a harmonic oscillator, the expression $\kappa = 2\nu e^{-h\nu/kT}$ is derived. A more general expression in the form $\kappa = (2n/n-1)\nu' e^{-h\nu'/kT}$, where $\nu' = (n-1)\nu$, is also derived.

J. S. G. T.

The Velocity of a Unimolecular Reaction. A. McKEOWN (*Phil. Mag.*, 1923, [iv], 46, 321—327).—Applying Einstein's conception of the mechanism of energy exchanges between molecules and radiation (*Physikal. Z.*, 1917, 18, 121) and employing Christiansen's postulation of the existence of "stationary states" (this vol., ii, 62) regarded respectively as the normal, n , and the activated, m , which are such that $\epsilon_m - \epsilon_n = h\nu$, the symbols having the customary significance, the author deduces an expression for the velocity k_1 of a unimolecular chemical change in the form $k_1 = p_m/p_n \cdot \nu e^{-h\nu/kT}$, where p_n and p_m denote the respective *a priori* probabilities of the states n and m . The expression agrees formally with Dushman's empirical relation $k_1 = \nu e^{-h\nu/kT}$ (A., 1921, ii, 315).

J. S. G. T.

Velocity of a Unimolecular Chemical Reaction. W. C. McC. LEWIS (*Phil. Mag.*, 1923, [vi], 46, 327—329).—In a previous paper (A., 1920, ii, 100), the author deduced an expression for the velocity of a unimolecular change which involved a refractive index term, and afforded a value of the velocity only one ten-millionth of that actually observed. The discrepancy is removed in the present communication by assuming that the oscillator involved is capable of drawing on the radiation present in a volume which is great compared with the magnitude attributed to the oscillator itself. Along these lines, it is shown that the velocity, κ , of an unimolecular change is given by $\kappa = 8e^{-h\nu/kT} d\nu$, where the symbols have the customary significance, and where $d\nu$ represents the width of the band or range of frequencies in the neighbourhood of ν which the molecule is capable of absorbing. Assuming, in agreement with the results of Ribaud (*Compt. rend.*, 1920, 171, 1134), that $d\nu = 0.17\nu$, the author obtains $\kappa = 8 \times 0.17 \nu e^{-h\nu/kT}$, in close agreement with Dushman's empirical formula $\kappa = \nu e^{-h\nu/kT}$ for the velocity of a unimolecular change (A., 1920, ii, 315).

J. S. G. T.

Temperature of Ignition of Electrolytic Gas. H. VON WARTENBERG and H. KANNENBERG (*Z. physikal. Chem.*, 1923, 105, 205—210).—The ignition temperature of electrolytic gas (hydrogen and oxygen) has been determined under conditions which eliminate the possibility of a catalytic action of the walls of the apparatus, by bringing together the separately heated gases. The fall of temperature of the gases due to radiation was evaluated in two ways and the ignition temperature at 1 atm. pressure found to be 642°, or 52° lower than the value found by Dixon (T., 1899, 75, 600). The temperature of ignition of carbon disulphide vapour in oxygen is found to be 236°, a value identical with Dixon's value.

J. F. S.

The Propagation of the Explosive Wave. P. LAFFITTE (*Compt. rend.*, 1923, 177, 178—180).—A study of the propagation of waves of combustion and explosion in spherical vessels containing a mixture of carbon disulphide (1 vol.) and oxygen (2 vols.) (cf. this vol., ii, 472). Ignition of the mixture was effected in two ways:

(1) By means of an electric spark at the end of a narrow tube projecting into the centre of the vessel. In this case, the explosive wave sent down the tube became a wave of combustion in the main vessel. (2) By means of mercury fulminate, detonated in the centre of the vessel. In this case, an explosive wave was set up instantaneously, with a velocity of 1800 metres per second.

E. E. T.

The Simultaneous Combustion of Hydrogen and Carbon Monoxide. R. T. HASLAM (*Ind. Eng. Chem.*, 1923, 15, 679—681).—In the combustion of coal any hydrocarbons are consumed first and the combustible gases remaining are hydrogen and carbon monoxide. In a series of gas analyses of samples taken at various points along a 12·2 m. flue into which the products of combustion of a coal fire burning with excess of air passed, the conditions are suitable for a determination of the relative velocity of combustion of those two gases. These velocities are— $d\text{CO}/dt = k_1(\text{CO})^m(\text{O}_2)^n$ and $d/dt \cdot (\text{H}_2) = k_2(\text{H}_2)^r(\text{O}_2)^s$.

If it is assumed that $n=s$ and $m=r=1$, the relative velocity constant $k_1/k_2[\log(\text{CO})_1 - \log(\text{CO})_2]/[\log(\text{H}_2)_1 - \log(\text{H}_2)_2]$.

The experimental data obtained as above give concordant figures for the quantity k_1/k_2 on these assumptions as regards the values of m, n, r, s , but not on other assumed values. It is therefore deduced that these assumptions are correct, *i.e.*, that both reactions are termolecular, $2\text{CO} + \text{O}_2 = 2\text{CO}_2$ and $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$, and that the relative rate of combustion $k_1(\text{CO})/k_2(\text{H}_2) = 0\cdot35$ (approx.). These conclusions, which are contrary to those of various other investigators, are limited to the case of combustion of a gas mixture under the conditions above described.

C. I.

The Relative Influences of Water Vapour and Hydrogen upon the Explosion of Carbon Monoxide-Air Mixtures at High Pressures. WILLIAM A. BONE, DUDLEY M. NEWITT, and DONALD T. A. TOWNEND (*T.*, 1923, 123, 2008—2021).

Velocity of the Action of the Halogens, Oxygen and Nitrogen, on Metals, Determined by the Colours of the Surface Films. G. TAMMANN (*Rec. trav. chim.*, 1923, 42, 547—551).—The velocity with which gases react with finely polished metal surfaces may be followed by observation of the colours of the metal surfaces. It is necessary to ascertain the thickness of the air layer which will produce the same colour, and this air thickness is proportional to the thickness of the film. Thus air thicknesses of $140\ \mu\mu$, corresponding with straw-yellow, to $1000\ \mu\mu$ corresponding with the fourth order red, can be observed which in the case of the action of iodine on silver correspond with from forty-three to three hundred and thirteen molecules of silver iodide. The rate at which the film thickens in the case of the action of the halogens on silver, copper, and lead follows the law $y^2 = 2pt$, where y is the thickness of the layer, t the time, and p a constant. In the case of silver iodide, the value of p is really constant between 15° and 145° ; at the latter temperature it increases to three times its original value

and then becomes constant again to 185° . This jump in the value occurs at the transition point of silver iodide. In the case of the action of nitrogen or oxygen on iron and cerium, the rate at which the film increases in thickness is given by $y = [\log_e(t+a) - \log_e a]/b$ at constant temperature, where y is the thickness, t the time, b the fraction by which the concentration of the gas is reduced in the length, dy , of the film, and a is a constant. The authors have calculated the time necessary for the formation of a visible film when oxygen acts on dry metals at 15° . The following values are recorded: lead, ninety years; zinc, 31×10^2 years; cadmium, 19×10^5 years; copper, 6×10^8 years; tin, 36×10^8 years; iron, 25×10^{17} years, and nickel 475×10^{17} years (cf. A., 1920, ii, 248; 1922, ii, 852).
J. F. S.

Hydrolysis of Potassium Hydrosulphide in Aqueous Solution. JARL A. WASASTJERNA (*Soc. Sci. Fennica Com. Phys.-Mat.*, 1923, 1, No. 39, 1—15).—The rate of hydrolysis of ethyl acetate at 25° by solutions of potassium hydrosulphide of various concentrations has been determined with the object of ascertaining the degree of hydrolysis of potassium hydrosulphide. Two new methods of analysing the reacting system at any given moment are described and have been used in the present work. The hydrolytic constant is found to be 10.5×10^{-8} , and from this value the first dissociation constant of hydrogen sulphide is found to be 7.8×10^{-8} . Combining the present value of the dissociation constant for 25° with that found by Walker and Cormack for 18° (T., 1900, 77, 5), the heat of dissociation of hydrogen sulphide is found to be -7700 cal., whilst the value calculated from thermochemical data is -6500 cal. Potassium hydrosulphide, by its presence, reduces the velocity of hydrolysis of ethyl acetate. This effect is about three-quarters of that produced by a corresponding amount of potassium chloride. With very large concentrations of potassium hydrosulphide, the degree of hydrolysis falls very much below the value calculated.
J. F. S.

Hydrolysis of Potassium Monosulphide. JARL A. WASASTJERNA (*Soc. Sci. Fennica Com. Phys.-Mat.*, 1923, 1, No. 40, 1—24).—The velocity of hydrolysis of ethyl acetate by solutions of potassium monosulphide has been determined at 25° with the object of determining the degree of hydrolysis of this salt. The course of the saponification was followed by measuring the change of either the refractive index or the electrical conductivity with time, and corrections were introduced for the neutral salt action of the sulphide. The hydrolytic constant is found to be 15 at 0° and a $0.833N$ -solution of potassium sulphide is shown to be hydrolysed to the extent of 95%. The second dissociation constant of hydrogen sulphide has been calculated from the results and the value 6×10^{-17} found. From the temperature coefficient of the hydrolytic constant the heat of dissociation of the HS' -ion has been calculated. The result of this calculation, which is somewhat uncertain, is $HS' \rightarrow H^+ + S'' - 18,000$ cal.
J. F. S.

Saponification of Fats. Influence of the Adsorption of the Emulsifier at the Boundary of Fat and Water Phase on the Saponification Velocity in Boiling Emulsions. J. P. TREUB (*Rec. trav. chim.*, 1923, **42**, 556—567).—A theoretical paper in which it is shown that in the saponification of fats with dilute mineral acids and stearo-naphthalene sulphonic acid as emulsifier (Twitchell's process) the increase of the surface of contact between the fat and the aqueous solution alone cannot explain the influence of the emulsifier on the velocity of reaction. An equation is deduced showing that the emulsifier increases the concentration of the hydrogen-ions at the interface also, and consequently the saponification velocity per unit area of surface of contact. By the increase of the surface of contact and the increase of the hydrogen-ion concentration at this surface, the influence of the Twitchell emulsifier is explained. From the equation deduced, it appears that the emulsifier repels the mineral acid from the boundary of fat and water. Addition of mineral acid cannot therefore increase proportionally the saponification velocity, a deduction in complete accord with fact. Analogous considerations on the saponification with lye show that the abnormal decrease of the saponification velocity near the end of the reaction is due to the repulsion of the hydroxyl-ions from the surface of contact by the adsorbed soap. It appears therefore that the emulsifiers used in saponification in acid media increase both surface of contact between fat and water phase and saponification velocity per unit area of this surface; in saponification in alkaline media, however, the soap formed increases the surface of contact but decreases the saponification velocity per unit area.

J. F. S.

Speed of Reaction in Concentrated Solution and the Mechanism of the Inversion of Sucrose. II. GEORGE SCATCHARD (*J. Amer. Chem. Soc.*, 1923, **45**, 1581—1592; cf. A., 1922, i, 230).—A theoretical paper in which a kinetic interpretation of activity is given which justifies the expression of velocity of reaction in terms of activities and demands that the velocity so expressed be defined as mols. transformed in 1 mol. of all components. This interpretation offers a possible explanation of the effect of salts on the velocity of reaction. The expression of Brönsted (A., 1922, ii, 699) must be modified for concentrated solutions. An analysis of experimental work shows that it is of little value for determining the relation of the velocity of reaction to the viscosity. The kinetic theory, however, demands that the velocity of reaction should be independent of the viscosity. These conclusions lead to the formula for the inversion of sucrose previously put forward (*loc. cit.*) when the concentration of electrolyte is unchanged. The experimental measurements cannot serve as a criterion for choice between the various hypotheses of the mechanism of the reaction, for the difference in agreement between the various formulæ is too small. Any interpretation of the experiments depends on the assumption that the liquid junction potential with saturated potassium chloride is independent of the sucrose concentration.

Interpreted by the formula previously put forward (*loc. cit.*), the velocity of inversion catalysed by hydrochloric acid adds confirmation to the statement that six molecules of water react with each molecule of sucrose. The agreement is not quite so good as with sulphuric acid. J. F. S.

Influence of the Speed of Stirring on the Solution of Magnesium in Acids. M. CENTNERSZWER (*Rec. trav. chim.*, 1923, 42, 579—584).—The rate of solution of magnesium at 25° in *N*/8-hydrochloric acid has been determined under various conditions of stirring. A few experiments are also described on the rate of solution in *N*/8-sulphuric acid or *N*/4-hydrochloric acid when the magnesium is rotated. The experiments show that velocity constant increases proportionally with the rate of stirring the solution. The solution takes place more rapidly when the metal is rotated in the opposite direction to the solution. J. F. S.

The Geometrical Arrangement and Chemical Reactions of the Atom. H. J. PRINS (*Chem. Weekblad*, 1923, 20, 402—403).—A criticism of Hermans (this vol., i, 767). The present theories of valency and structure explain many otherwise unrelated and apparently contradictory phenomena, and should not too lightly be condemned. S. I. L.

The Model of the Neutral Helium Atom. A. SOMMERFELD (*J. Opt. Soc. Amer.*, 1923, 7, 509—515).—The model of the neutral helium atom originally proposed by Bohr (A., 1913, ii, 688, 943) and that proposed by Kemble (A., 1921, ii, 478) afford calculated values of the ionisation potential of helium which do not agree with the experimental value, 24·5 volts. Moreover, the models represent helium as being paramagnetic. The author discusses the quantum-relativistic dynamics of a model comprising two electrons moving in opposite senses in two coplanar Keplerian elliptic orbits about a common nucleus. The quantum numbers employed in the analysis refer, not to the single electrons, but to the system as a whole. This model conforms with the diamagnetic character of the neutral helium atom, and with the possibility of the existence of doubly-ionised helium atoms, as found by Millikan (*Physical Rev.*, 1921, 18, 456). Also, it affords a correct value of the ionisation potential. In general, it appears to be impossible that there should exist in the interior of every atom a system possessing angular momentum and magnetic moment, such as Bohr's model of the *K*-shell. J. S. G. T.

Electron Valency Theories and Stereochemistry. SAMUEL SUGDEN (T., 1923, 123, 1861—1865).

Note on the Theory of Free Rotation. THOMAS MARTIN LOWRY (T., 1923, 123, 1866—1867).

The Octet Theory of Induced Alternate Polarities; the Domains Occupied by Octet-stable and Octet-unstable Centres. RONALD FRASER and J. E. HUMPHRIES (*Phil. Mag.*, 1923, [iv], 46, 331—334).—The authors seek to vindicate their

interpretation of Lapworth's principle of induced alternate polarities, in which they postulate an electron transference between stable and unstable octets as the necessary accompaniment of the manifestation of such polarities, by considering the domains occupied by stable and unstable centres attached to the benzene nucleus in the case of various chlorobenzenes. In accordance with the view expressed, it is shown that, in every case, the introduction of an octet-stable chlorine centre causes an increase in the average volume of the chlorine atom, whilst an octet-unstable chlorine causes a decrease. Moreover, it is shown that the average volume of the chlorine atom in *m*-dichlorobenzene is about 3% greater than the largest value characterising the poly-substituted chlorobenzenes. J. S. G. T.

Chemical Constants of Diatomic Gases. J. R. PARTINGTON (*Phil. Mag.*, 1923, [iv], 46, 329—330).—In a recent paper (A., 1922, ii, 839), the author deduced the expression $\log_e m^{5/2} r^{29/2} \pi^{7/2} k^{7/2} / h^5$ for the chemical constant of a diatomic gas consisting of molecules composed of two like atoms. A similar expression, viz., $\log_e m^{5/2} r^{29/2} \pi^{7/2} k^{7/2} / h^5$ deduced by Sackur (A., 1913, ii, 128), is considered by the author to be in excess of the correct value by $\log_e 2$. J. S. G. T.

The Ammonium Chloride Problem. A. SMITS (*Rec. trav. chim.*, 1923, 42, 826—829).—A discussion of the effect of intensive drying of ammonium chloride. J. F. S.

A Pressure Regulator for the Quantitative Measurement of the Velocity of Filtration. WERNER RATH (*Kolloid Z.*, 1923, 33, 109—111).—A manostat is described by which the pressure may be kept at any desired pressure less than atmospheric during a filtration. J. F. S.

Apparatus for the Continuous Extraction of Solutions by Means of Solvents without the Application of Heat. M. JAVILLIER and L. DE SAINT-RAT (*Bull. Soc. chim.*, 1923, [iv], 33, 996—999).—Continuous extraction of an aqueous solution is obtained by withdrawing the heavier extracting solvent from below and causing it to fall in a stream of drops through the lighter layer to be extracted. In the case where the solvent used is lighter than the solution to be extracted, it is the latter which is circulated. [See *J.S.C.I.*, 1923, 42, 868A.] H. H.

Dschâbir and Geber. ERNST DARMSTAEDTER (*Chem. Ztg.*, 1923, 47, 621—622; cf. Holmyard, this vol., ii, 148; Partington, *ibid.*; Lippmann, this vol., ii, 314).—Geber and Dschâbir are considered to be two distinct individuals; the Arabic manuscripts of the latter are, in fact, believed to have no connexion with Geber or the "Summa perfectionis." Alchemical writings ascribed to Avicenna are stated to contain passages from the "Summa perfectionis." A. A. E.

Inorganic Chemistry.

The Hydration of Hydrogen-ions. J. BABOROVSKÝ (*Chem. Listy*, 1923, **17**, 170—171; cf. A., 1922, ii, 816).—The mass m_2 of the hydrogen gram-ion in aqueous solution is calculated from the equation $m_1 u_1 \eta_1 = m_2 u_2 \eta_2$, where m_1 is the mass of a gram-ion of hydrogen in gaseous hydrogen, u_1 and u_2 the velocities of hydrogen-ions in hydrogen and water, respectively, and η_1 and η_2 the viscosities of hydrogen and of water. The values so obtained for m_2 correspond with 0.66 molecule of water in one case and 0.83 molecule in another per hydrogen-ion, the correct value being probably 1 molecule.

R. T.

Relative Determination of the Atomic Weight of Chlorine in Bamle Apatite. MARGOT DORENFELDT (*J. Amer. Chem. Soc.*, 1923, **45**, 1577—1579).—The paper describes work undertaken to ascertain whether the chlorine contained in an old mineral, which has not been in contact with water, contains the two isotopes of chlorine in the same proportion as in ordinary chlorine obtained from sodium chloride. The method of work consisted in determining the specific gravity of saturated solutions of ordinary sodium chloride with that of solutions of sodium chloride prepared from Bamle apatite, using a pycnometer of the type previously adopted by Fajans and Lambert (A., 1917, ii, 472) for a similar purpose. The specific gravity at 18° is found to be the same for both samples. The solubility of both specimens is found to be identical in the two cases, namely, 26.357%. Consequently, the author concludes that the chlorine isotopes in Bamle apatite occur in the same proportion as in ordinary sodium chloride.

J. F. S.

The Kinetics of Chlorate Formation. A. V. PAMFILOV and (MILE) O. S. FEDOROVA (*Bull. Inst. Polytech. Ivanovo-Voznesensk*, 1923, **7**, 79—84).—The electrolytic formation of sodium chlorate from the hypochlorite is greatly favoured by the addition of a dichromate or free chromic acid. The acceleration of the reaction is observed in strongly acid as well as feebly acid solution, and it is shown that although rather considerable quantities of dichromate have to be added, the latter functions as a true catalyst, the initial and final amounts remaining the same.

G. A. R. K.

Activation of Oxygen. W. P. JORISSEN (*Rec. trav. chim.*, 1923, **42**, 855—858).—The author directs attention to a case similar to the atmospheric oxidation of arsenite in the presence of sulphite. A mixture of benzaldehyde and acetic anhydride is oxidised quantitatively to a benzoyl acetyl peroxide by air or oxygen in the presence of sand, $2\text{Ph}\cdot\text{CHO} + \text{O}(\text{COMe})_2 + 2\text{O}_2 \rightarrow \text{H}_2\text{O} + 2\text{COPh}\cdot\text{O}_2\cdot\text{COMe}$. In this case, the quantity of oxygen taken up is twice as large as that taken up by benzaldehyde in its oxidation to benzoic acid and equal to that taken up in the oxidation of benzaldehyde in the presence of indigo.

J. F. S.

Production of Sulphuric and Hydrochloric Acids from Sulphurous Acid and Chlorine. BERNHARD NEUMANN and FRANZ WILCZEWSKI (*Z. angew. chem.*, 1923, **36**, 377—381).—Measured volumes of sulphur dioxide and chlorine are brought together in the presence of water or, preferably, of strong hydrochloric acid, which is maintained in the form of a spray. As the proportion of sulphuric acid produced increases, the density of the acid mixture rises until, at *d* 1.6, the hydrochloric acid has been almost completely eliminated. The sulphuric acid always contains a considerable proportion of dissolved sulphur dioxide, even if chlorine is added in excess, but either of these gases can be removed by blowing air through the acid. The reaction proceeds quantitatively if sufficient water is present, its velocity being very considerably increased by raising the temperature. The sulphuric acid formed is of 66—88% strength, and the hydrogen chloride is absorbed in the usual manner. Sulphur trioxide is not obtainable according to the equation $\text{SO}_2 + \text{Cl}_2 + \text{H}_2\text{O} = \text{SO}_3 + 2\text{HCl}$, the product being sulphuric acid. [Cf. *J.S.C.I.*, 1923, **42**, 827A.] W. T. K. B.

Sulphamide. WILHELM TRAUBE and EMIL REUBKE (*Ber.*, 1923, **56**, [B], 1656—1663).—Sulphamide absorbs 1.4 molecular proportions of dry ammonia at +20°, 3.0 molecular proportions at 0°, and 5.4 molecular proportions at -20°. The product so formed has an electrical conductivity about 150 times that of a 4*N*-aqueous solution of sulphamide. Furthermore, a 4*N*-aqueous solution of sulphamide-ammonia has a conductivity twenty-five times that of a 4*N*-solution of ammonia alone. It is therefore suggested that sulphamide can also exist in an *aci*-form, thus, $\text{SO}_2 < \begin{smallmatrix} \text{NH}_2 \\ \text{NH}_2 \end{smallmatrix} \rightleftharpoons$

$\text{NH}:\text{SO} < \begin{smallmatrix} \text{OH} \\ \text{NH}_2 \end{smallmatrix}$, just as in the case of carbamide. The *sodium*, *lithium*, *potassium*, *barium*, and *calcium* salts are described as colourless, non-hygroscopic crystals, whilst the *cupritetrammine* and *cupriethylenediamine* salts were obtained as blue, crystalline solids.

Benzylidenesulphamide, $\text{NH}_2 \cdot \text{SO}_2 \cdot \text{N}:\text{CHPh}$, was obtained by the elimination of water from benzaldehyde and sulphamide by means of anhydrous copper sulphate. It forms needles, m. p. 135°, soluble in methyl alcohol, ethyl alcohol, and benzene. *Monochloro-sulphamide*, prepared by the action of hypochlorous acid on sulphamide, melts at 66° with decomposition, and is easily soluble in water, alcohol, or chloroform. Details are given of an improved method of preparation of sulphamide from sulphuryl fluoride.

H. H.

Protective Colloids. X. Saponin as Protective Colloid.
III. Colloidal Selenium. A. GUTBIER and U. RHEIN (*Kolloid Z.*, 1923, **33**, 35—36; cf. *A.*, 1921, ii, 538).—Colloidal solutions of selenium may be prepared by the cautious addition of a 1 : 1000 solution of hydrazine hydrate to solutions of selenious acid containing saponin with continuous stirring. During the formation, there is a continuous loss of selenium as a red precipitate due to the coagulation of the colloid in the foam produced. The sols

prepared are of various colours, vermilion, bright red, yellow, dark red, and bluish-red, the last-named being very unstable. Solutions, after dialysis, may be preserved for long periods, but have the property of settling into two layers which, however, may be readily made homogeneous again by simply shaking. The sols may be concentrated by freezing and warming, to both of which they are relatively stable, but the solid colloids are not entirely reversible and in many cases are quite irreversible. J. F. S.

Fixation of Atmospheric Nitrogen by the Cyanide Process.

KIYOMATSU TERADA (*Rikwagaku Kenkyujo Ihô*, 1923, 2, 234—242).—A mixture of 100 parts of sodium carbonate, 100 parts of potassium carbonate, 220 parts of charcoal, and 220 parts of ferric oxide was used as the catalyst. The reaction takes place at 600°; the yield of the cyanide is about 80% at 700°, and above 85% at 750°; the velocity of the passing nitrogen is 4.5—5 litres per minute, and the reaction is almost complete in sixty minutes. The catalyst was contained in an iron tube, which was scarcely acted on owing to the low temperature of reaction. K. K.

Synthesis of Ammonia from its Elements in the Low Voltage Arc.

H. H. STORCH and A. R. OLSON (*J. Amer. Chem. Soc.*, 1923, 45, 1605—1615).—The factors controlling the rate of formation of ammonia from nitrogen and hydrogen in the low voltage arc have been investigated. It is shown that the earlier work of Andersen (A., 1922, ii, 562), in which a wave type curve was obtained for the rate of reaction as a function of the accelerating voltage, is to be explained by the preliminary experiments described in the present paper. The curve is found to be due to a superposition of the curve described below and a "fatigue" factor in the mechanism used for absorbing the ammonia gas. The variation of the rate of reaction, at constant tube current, with the accelerating voltage is such as to give abrupt increases in the rate of reaction at specific voltages which are about four volts apart. The formation of ammonia in quantities sufficient to be detected by Nessler's reagent does not occur unless an arc is present. The magnitude of the rate at any given voltage, and at constant tube current, depends primarily on the diameter of the hot filament used as the source of electrons. An increased percentage of nitrogen in the gaseous mixture favours a higher rate of reaction. J. F. S.

Catalytic Oxidation of Ammonia by Air in Contact with Pure Palladium.

E. DECARRIÈRE (*Compt. rend.*, 1923, 177, 186—188).—Using an apparatus already described (this vol., ii, 155), the author has investigated the oxidation of ammonia by the above method. It is found that the yield of oxides of nitrogen is a function of the temperature of the catalyst and of the percentage of ammonia originally present, and also depends on the physical state of the metal. E. E. T.

Catalysts for the Oxidation of Ammonia. I. KENKEI INABA (*Rikwagaku Kenkyujo Ihô*, 1923, 2, 222—233).—A mixture of iron and bismuth was used as a catalyst for the oxidation of ammonia,

air being used as the source of oxygen. When the ratio of the oxides of iron and bismuth was 67 : 33, the yield was 85%; the temperature of the catalyst being 750—800°, thickness of the layer of the catalyst 0.5 cm., the current of gas contained 8% of ammonia and the velocity of the gas about 1 litre per minute. By adding thorium oxide to the catalyst, the yield was increased. If the content of oxygen in the gas is increased to 40%, the yield became 95%. The catalysts were prepared from the nitrates; oxides prepared by other methods gave a smaller yield. K. K.

The Formation of Nitric Acid in the Manufacture of Liquid Carbon Dioxide. L. HACKSPILL and A. CONDER (*Compt. rend.*, 1923, 176, 1811—1813).—Under conditions which exclude the possibility of mechanical admixture, the potassium hydrogen carbonate which is formed as an intermediate product in the manufacture of carbon dioxide from coke contains a small quantity of potassium nitrite. This has its origin in the oxidation of the nitrogen content of the coke. The nitrous acid is partly liberated by the carbonic acid formed in the process and may be oxidised to nitric acid, which rapidly corrodes the plant in which the manufacture is carried out. H. J. E.

Crystal Structures of the Cubic Forms of Arsenious and Antimonious Oxides. RICHARD M. BOZORTH (*J. Amer. Chem. Soc.*, 1923, 45, 1621—1627).—The crystal structures of arsenious and antimonious oxides have been determined by means of Laue photographs and X-ray photographs. These crystals may be regarded as composed of As_4O_6 and Sb_4O_6 molecules having a diamond arrangement, each molecule corresponding with one carbon atom. The arrangements are derived from the space group O_h^1 . The sizes of the unit cubes containing eight molecules of As_4O_6 or Sb_4O_6 are 11.06 Å. for arsenious oxide and 11.14 Å. for antimonious oxide. The shortest distance between arsenic and oxygen atoms is 2.01 Å. and between antimony and oxygen atoms 2.22 Å. J. F. S.

Carbon. PELAYO POCH (*Anal. Fis. Quím.*, 1923, 21, 291—304).—Carbon was prepared by decomposition of carbon monoxide passed through a porcelain tube in a combustion furnace with ferrosiferrous oxide as catalyst, and also by the decomposition of cyanogen in an electric arc. X-Ray examination of the products obtained showed that the carbon from cyanogen was the more finely crystalline. Its heat of combustion was greater than that of carbon from carbon monoxide, but slightly less than that of Schering's "absorption carbon." The possibility of obtaining diamond from black carbon is discussed. G. W. R.

The Evaporation of Carbon. WERTENSTEIN and JEDRZEJEWSKI (*Compt. rend.*, 1923, 177, 316—319).—The blackening of carbon filament lamps has been attributed to evaporation and also to disintegration of the filament. By studying the evaporation of carbon filaments in a vacuum, applying formulæ used by Fajans

(A., 1920, ii, 469) and Langmuir (*Physikal. Z.*, 1913, **14**, 1273), it is shown that the above blackening is due to sublimation. The loss of carbon increases rapidly between 2,800° and 3,500° Abs., whereas if disintegration were the causal process no appreciable temperature coefficient would be observed. Also, the sublimate is distinctly crystalline. From the results obtained, the authors find the b. p. of carbon to be 5,100° Abs. (*i.e.*, a higher temperature than is reached in a carbon arc crater) and the atomic heat of sublimation, referred to the absolute zero, to be 216,000 cal. E. E. T.

Silicon Hydrides. XVI. The Higher Members of the Series. ALFRED STOCK, PAUL STIEBELER, and FRIEDRICH ZEIDLER (*Ber.*, 1923, **56**, [B], 1695—1705).—An investigation of the composition and properties of the less volatile silicon hydrides obtained by the action of acid on magnesium silicide. The liquid products were fractionally distilled in a vacuum and the fractions of the distillate collected at temperatures from -185° upwards. A yellow, amorphous, solid residue was obtained which, from its analysis and its behaviour towards bromine, appeared to be a polymeride of silicon monohydride, $[\text{SiH}]_x$. The following physical measurements were made. Silicopropane, Si_3H_8 , d_4^0 0.743, m. p. -117.4° , b. p. 53° ; silicobutane, Si_4H_{10} , d_4^0 0.825, m. p. about -90° , b. p. 109° . The higher members of the series are less stable to light and appear to decompose according to the scheme $\text{Si}_5\text{H}_{12} \rightarrow 2[\text{SiH}]_x + \text{Si}_2\text{H}_6 + \text{SiH}_4$. This unsaturated hydride apparently cannot be obtained in a volatile form of low molecular weight. Whether obtained by the auto-decomposition of the silicoparaffins, by the action of the silent electric discharge on these compounds, by the action of acids on silicides, or by the action of sodium amalgam on silicoparaffins and their chlorides, it always appears in the solid, yellow, associated form, its composition varying between $[\text{SiH}]_x$ and $[\text{SiH}_{1.6}]_x$. H. H.

The Crystal Structure of Quartz. L. W. MCKEEHAN (*Physical Rev.*, 1923, **21**, 503—508).—It has been confirmed by the powder method of X-ray crystal analysis that the space lattice of quartz is hexagonal. An atomic arrangement consistent with the observed intensities of the lines requires the molecules to be obtuse-angled isosceles triangles, having an angle at the silicon atom centre of $115^{\circ} 14'$, and a distance between the silicon and oxygen atom centres of 1.631×10^{-8} cm., lying in the basal planes of each of three interpenetrating hexagonal space lattices. A. A. E.

Les Gaz Rares des Gaz Naturels. PROFESSOR CHARLES MOUREU, President of the Société Chimique de France (*T.*, 1923, **123**, 1905—1947).—A lecture delivered before the Chemical Society on June 14th, 1923.

Equilibrium of Liquid and Gaseous Phases of Helium at Low Pressures. H. KAMERLINGH ONNES (*Rec. trav. chim.*, 1923, **42**, 535—538).—A discussion of the equilibrium between the liquid and gaseous phases of helium at very low pressures. It is shown that a maximum exists in the latent heat of vaporisation

of helium, as is predicted by the equation $L = Tdp/dT(v_g - v_l)$, but it is not so pronounced as calculations based on this equation indicate.
J. F. S.

Purification of Neon and a New Determination of the Critical Temperature of Neon. C. A. CROMMELIN (*Rec. trav. chim.*, 1923, **42**, 814—817).—A technique for the purification of neon is described which may be used for quantities up to 20 litres. The method consists in fractionation from a vessel originally at the temperature of boiling liquid hydrogen, after the removal of all gas which is not solidified at this temperature. With the pure material thus obtained, the author has redetermined the critical temperature and finds the value -228.71° on the Kelvin scale.

J. F. S.

Preparation of the Alkali Metals. M. BUON (*Bull. Soc. chim.*, 1923, [iv], **33**, 994—995).—Hackspill's method (A., 1911, ii, 602) is modified for students' use in that the vacuum is obtained by means of a water vacuum pump and drying tube. The reaction tube is heated at 350° until no more gas is evolved, when it is shut off from the pump and the temperature raised to 800° . The yield of metal is only slightly below that obtained by the original method.

H. H.

The Determination of the Degree of Hydration of Salts by a Radioactive Method. HENRY TERREY and VICTOR GEORGE JOLLY (*T.*, 1923, **123**, 1979—1982).

The Causticisation of Potassium Carbonate. P. P. BUDNIKOV and J. K. SYRKIN (*Bull. Inst. Polytech. Ivanovo-Voznesensk*, 1923, **7**, 97—101).—The formation of potassium hydroxide from solutions of the carbonate and solid calcium oxide was studied at 20° . It was found that the reaction proceeded practically to completion (91 to 98%) if the initial concentration did not exceed $2N$; in more concentrated solutions there was a loss, due to the formation of the solid compound $K_2CO_3 \cdot CaCO_3$ (Barre, A., 1912, ii, 254); this loss is not observed if baryta or strontia is used instead of lime (Bodländer, A., 1905, ii, 634), the carbonates of these metals being unable to form such double salts. A curve is constructed to express the conditions governing the equilibrium of the reaction.

G. A. R. K.

Catalytic Decomposition of Sodium Hypochlorite by Cobalt Peroxide. OWEN RHYS HOWELL (*Proc. Roy. Soc.*, 1923, [A], **104**, 134—152).—The rate of decomposition of sodium hypochlorite by cobalt peroxide has been investigated at 25° and 50° under various conditions. It is shown that the rate of decomposition is directly proportional to the quantity of cobalt peroxide present. The rate of decomposition is accelerated by the presence of sodium salts; in the case of sodium chloride it is directly proportional to the square root of the concentration of sodium-ions present. This is explained by assuming the mechanism of the reaction to consist in the linking of hypochlorite-ions to the positive oxygen,

and sodium-ions to the negative oxygen of the peroxide, with subsequent immediate decomposition of the quadrivalent oxygen compound. In the presence of a fixed amount of hypochlorite, the rate is then proportional to the degree of adsorption of the sodium-ions. The rate is retarded by alkali, and the retardation is proportional to the adsorption of hydroxyl-ions. This is explained by the fact that hydroxyl-ions are attracted by the positive oxygen of the peroxide, yielding an inactive compound to the exclusion of hypochlorite-ions. The rate of the reaction has been measured at 25° and 50°, and the average temperature coefficient over this range is 2.37 and the Arrhenius activation coefficient $E=16,574$. The catalyst is not affected by any of the catalyst poisons, hydrogen sulphide, potassium cyanide, mercuric chloride, arsenious oxide.

J. F. S.

The Allotropic Transformation of Ammonium Nitrate at 32°. P. MONDAIN MONVAL (*Compt. rend.*, 1923, **177**, 175—178; cf. Millican, Joseph, and Lowry, T., 1922, **121**, 959).—The solubility of ammonium nitrate has been determined carefully for the temperature range 26.7—39.2° (eleven readings), the transition-point being found to be 31.8° (240 g. of ammonium nitrate in 100 g. of water). The ratio of the tangents to the two halves of the curve (ds/ds') was found to be 1.17, which (cf. Le Chatelier, *Compt. rend.*, 1900, **130**, 1606) should be equal to the ratio of the latent heats of solution for the two forms of the salt. The actual figure obtained for the second ratio (for method, cf. Mondain Monval, this vol., ii, 131) was 1.158 (L/L'), determinations being made at 28° and 36°.

E. E. T.

Ammonium Dichromate. E. MOLES and F. GONZÁLEZ (*Anal. Fis. Quím.*, 1923, **21**, 204—212).—Data are given for the density, solubility, and heat of solution of ammonium dichromate. Tranquil decomposition takes place at about 225°, the oxidation of the ammonium to nitrogen being the most complete where the reaction takes place most rapidly. The black residue thereby obtained is shown to be chromium peroxide.

G. W. R.

The Hydration of the Lithium-ion. J. BABOROVSKÝ and J. VELÍŠEK (*Chem. Listy*, 1923, **17**, 171—172; cf. A., 1921, ii, 573; 1922, ii, 816; this vol., ii, 288, 532).—Certain numerical data given in a preceding paper (A., 1922, ii, 816) are corrected. The degree of hydration of the kations of a solution of hydrochloric acid is found to be "four times less" than that of lithium kations, and cannot be accurately determined by gravimetric methods. An interferometer must be used.

R. T.

Lithium-Ammonium. F. BENOIT (*Bull. Soc. chim.*, 1923, [iv], **33**, 908—917).—From a study of the isotherms obtained by the method of Biltz and Hüttig (A., 1921, ii, 201), it is shown that the lithium-ammonium poorest in ammonia is Li_4NH_3 . This compound easily decomposes into lithamide, LiNH_2 , hydrogen, and ammonia, and it is possibly this fact which led earlier investigators to describe compounds denoted by the erroneous

formulae Li_2NH_3 and Li_3NH_3 . The analysis of the compound corresponds with the tetrammine formula, whilst molecular weight determinations point to the double formula $\text{Li}_2\cdot 8\text{NH}_3$. The heat of formation is given by the equation $2\text{Li}(\text{solid}) + 8\text{NH}_3(\text{gas}) = \text{Li}_2\cdot 8\text{NH}_3(\text{liquid}) + 8\cdot 67 \text{ Cal.}$ H. H.

Dispersoid Synthesis of Silver and Mercury by the Formaldehyde Method. P. P. VON WEIMARN (*Kolloid Z.*, 1923, **33**, 81—82).—Colloidal silver sols of great stability may be prepared by identically the same method as has been used for gold (see this vol., ii, 645). Mercury hydrosols are prepared by pouring 10 c.c. of a 0.04—0.075% solution of mercurous nitrate into 100 c.c. of a solution containing 90 c.c. of 0.2*N*-potassium hydroxide or potassium cyanide and 10 c.c. of 35% formaldehyde solution. Reduction takes place in either hot or cold solutions but is never complete, some mercurous oxide being formed. The mercury sol is yellow in colour and highly dispersed, but its colour changes rapidly to brown. The stability cannot be increased by boiling, for the mercury passes into the molecular disperse condition very rapidly. J. F. S.

General Colloid Chemistry. VII. Analysis and Constitution of Colloidal Silver. I. PAUL NEUREITER and Wo. PAULI (*Kolloid Z.*, 1923, **33**, 67—73; cf. this vol., ii, 329).—Measurements of the electrical conductivity of silver sols, prepared by the reduction of an ammoniacal solution of silver chloride by dilute hydrazine hydrate solution, have been carried out with the dialysed sol. The minimum precipitating values of potassium nitrate, silver nitrate, sulphuric acid, barium nitrate, and mercuric chloride have been found for the dialysed sol, and analyses of the coagulum and the filtrate made. The results indicate that unprotected colloidal silver has the composition and constitution represented by $[x\text{Ag}\cdot y\text{AgCl}\cdot \text{AgCl}'_2]\text{Ag}\cdot (\text{NH}_3)_2$. J. F. S.

Double Decomposition in the Absence of Solvents. I. The System Silver Nitrate—Mercuric Iodide. A. G. BERGMAN (*J. Russ. Phys. Chem. Soc.*, 1921, **53**, 181—191).—A fusion diagram is constructed for the system silver nitrate—mercuric iodide. Two compounds, $2\text{AgNO}_3\cdot \text{HgI}_2$, yellowish-green crystals, m. p. 107° , and $\text{AgNO}_3\cdot \text{HgI}_2$, m. p. 117 — 118° , are found to occur. The latter compound is dimorphous, its colour changing at 52° from canary-yellow to orange-yellow. It is interesting that no double decomposition occurs, as in the case of silver nitrate and potassium halides (Kablukov, A., 1907, ii, 865). This is probably due to the greater stability of the compounds in this case, and possibly also to the exothermic nature of the reaction which would be involved. R. T.

Symmetry of Calcium Thiosulphate Hexahydrate. W. T. ASTBURY (*Nature*, 1923, **112**, 53—54).—By the use of Bragg's ionisation spectrometer, it has been shown that the unit cell of calcium thiosulphate hexahydrate contains two molecules. The substance is therefore considered to be a member of the pinacoidal

class, rather than the unique example of the triclinic asymmetric class.
A. A. E.

Studies on the Dolomite System. II. ALLAN ERNEST MITCHELL (T., 1923, 123, 1887—1904).

System $\text{BaS}_2\text{O}_6\text{--Na}_2\text{S}_2\text{O}_6\text{--H}_2\text{O}$. W. C. DE BAAT (*Rec. trav. chim.*, 1923, 42, 643—646).—The system sodium dithionate-barium dithionate-water has been investigated by means of solubility determinations at 30° , 20.1° , and 12° , and the results have been combined in an equilibrium diagram. It is shown that neither double salts nor mixed crystals are formed.
J. F. S.

System Lead-Antimony. R. S. DEAN (*J. Amer. Chem. Soc.*, 1923, 45, 1683—1688).—Investigation by means of differential heating curves and microscopic examination shows that antimony is soluble in solid lead up to between 2% and 3% of antimony at the eutectic temperature. The alloys containing up to 13% of antimony show a higher eutectic temperature on heating than on cooling. This is explained by hysteresis. A tentative equilibrium diagram has been constructed which assumes the existence of a compound, Pb_4Sb , containing 12.6% of antimony, which forms a eutectic with its solid solution in lead at 10% of antimony. The data are insufficient to fix these points accurately. The compound forms very slowly, and when the mixture is cooled it is not formed from the liquid, but from the solid eutectic between antimony and the solid solution. As a result of the reluctance of this compound to form, the system as it cools behaves as an antimony solid solution eutectic and hence freezes at 247° . When this is heated, the compound forms and the melting point is the eutectic point between the compound and the solid solution at 258° .
J. F. S.

Thallic Sulphates and Thallic Selenates. JULIUS MEYER (*Rec. trav. chim.*, 1921, 42, 614—619).—The solubility of thallic oxide, the basic sulphate, $\text{Tl}(\text{OH})\text{SO}_4 \cdot 2\text{H}_2\text{O}$, and the acid sulphate, $\text{HTl}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, has been determined in sulphuric acid of various concentrations from 10% to 90% at various temperatures and the stability diagram constructed. It is shown that no other thallic sulphate exists under the above-named conditions and that the other thallic sulphates described in the literature are mixtures the formation of which is due to the slowness of the change from one salt to another. The transition point of the two sulphates mentioned above lies at about 40° . The corresponding selenates have also been investigated, and are found to be very similar to the sulphates; the main point of difference between them is that the transition point lies at 45° .
J. F. S.

Separation of Isotopes. Application of Systematic Fractionation to Mercury in a High Speed Evaporation-Diffusion Apparatus. ROBERT S. MULLIKEN (*J. Amer. Chem. Soc.*, 1923, 45, 1592—1604; cf. this vol., ii, 31).—An apparatus is described for the rapid partial separation of mercury into its isotopes by a combined process of distillation and molecular diffusion at low

pressure, the latter process being the major factor in the separation. The diffusion membrane in each unit consists of a tube of filter-paper a metre long, this material being selected primarily because of its thinness. The operation of the apparatus is carried on as a systematic fractionation, in which six units are used independently. Preliminary operation of the apparatus has given a separation of 0.102 unit of atomic weight between extreme fractions of 22 c.c. A separation of 0.3 unit with 50 c.c. fractions should be obtainable in a year of steady work. The method by which the new value, 0.0063, for the separation coefficient of mercury was obtained is described in connexion with the preliminary studies on the design of the apparatus. Systematic fractionation requires the maintenance of a permanent stock of intermediate fractions, of some minimum size, Q_0 , in order to extend the range of a separation. A thorough study of the course of systematic fractionation has yielded valuable results which are applicable to all methods of separation by diffusion or in an analogous manner. The simple and systematic method of fractionation in which a cut of two is made in each individual operation is probably the most rapid for practical operation. The time required for the production of any fraction after the necessary preliminary or intermediate fractions have been produced is given by the formula $t = C(\Delta M)^2 Q_0 / DE^2 B^2$, where E is the efficiency, B the separation coefficient, D the rate of production of the light fraction, and C a constant. This serves to establish a criterion for the value (V) of any fraction, which may be defined as $V = (\Delta M)^2 Q$. This criterion is applied to the calculation of loss of value by mixing and other causes. The time required for the production of any extreme fraction, taking into account the total time used in building up the intermediates, is given by $t = C'(\Delta M)^3 Q_0 / DE^3 B^3$. A consideration of this equation shows the difficulty of obtaining large values of ΔM , especially if B is low. It also shows the relative importance of Q_0 , D , and E , and this relation, somewhat modified by other practical considerations, was used in the design, and is also used in the operation of the present apparatus. The optimum speed of operation is shown to be that for which $E^{3.5} D$ or $E^4 D$ is a maximum. The equation above can also be used as a basis for a criterion of value for extreme fractions, namely, $V' = (\Delta M)^3 Q$. The approximate proportionality of the time required for a given separation to the cube of the degree of separation shows that whilst considerable separations can be effected by systematic fractionation, nothing approaching complete separation can be expected by methods of the diffusion type, unless in the most favourable cases and by factory scale operation. It is, further, the opinion of the author that there seems to be little prospect that any other method or methods yet proposed will prove greatly superior to those of evaporation and molecular diffusion, although the centrifugal method may prove useful, especially for elements of higher atomic weight. For any particular element, the most favourable method depends greatly on the nature of the substance.

J. F. S.

Surface Tension of Mercury in the Presence of Oxygen. T. BATUECAS (*Anal. Fis. Quím.*, 1923, **21**, 259—264; cf. Palacios and Lasala, this vol., ii, 166).—The surface tension of freshly distilled mercury decreases in air or in oxygen containing traces of ozone. This is attributed to condensation on the surface and not to chemical reaction between ozone and mercury. G. W. R.

The Replacement of the Metals of the Second Odd Group of the Periodic System from their Salt Solutions by Means of Hydrogen at High Temperatures and Pressures. W. IPATIEV and A. STARYNKEVITSCH (*Ber.*, 1923, **56**, [B], 1663—1667).—A study of the conditions under which hydrogen will react with aqueous solutions of the salts of mercury, zinc, cadmium, and magnesium. Hydrogen at 100 atm. for thirteen hours at 160° reduces a solution of mercurous nitrate to metallic mercury and a salt which may have the formula $2\text{Hg}_2\text{O}, \text{N}_2\text{O}_5$. When heated at 225°, reduction to metallic mercury is complete. Mercuric nitrate is similarly reduced to the mercurous salt at 170—180°, and to metallic mercury at 240—250°. Cadmium nitrate at 110 atm. and 180° is not attacked, but at 135 atm. and 220° it yields a hitherto unknown salt of the composition $\text{Cd}(\text{NO}_3)_2, 7\text{CdO}$. At 270° and 220 atmospheres, the nitrate is further reduced to crystalline, metallic cadmium. Cadmium sulphate at 250 atm. and 260—290° is reduced to the yellow, crystalline sulphide and traces of metallic cadmium. Zinc nitrate is similarly reduced to the oxide and the metal, whilst the sulphate under corresponding conditions yields the sulphide and the metal. Magnesium nitrate was reduced to the hydroxide, but not to the metal, whilst the sulphate gave, first, the sulphide and, later, the hydroxide. It is noteworthy that the solid products of these reactions were almost invariably deposited in a crystalline form.

The reduction of carbonates to formates under similar conditions was also studied. Potassium hydrogen carbonate was reduced to the formate in 11% yield by heating for four hours with hydrogen under 380 atm. at 350°. H. H.

The Precipitation of Metals by Hydrogen Sulphide. G. MCPHAIL SMITH (*Science*, 1923, **57**, 447—449; cf. Neuhausen, this vol., ii, 396).—On treatment of an aqueous solution of mercuric perchlorate (prepared by dissolving mercuric oxide in excess of perchloric acid, evaporating to small volume, and crystallising) with a solution of hydrogen sulphide, precipitation does not at first occur, but there is obtained a brown, opalescent solution which gives a white precipitate with hydrochloric, nitric, or sulphuric acid. The solution, which evidently contains a complex salt, on keeping deposits white crystals of the compound $\text{Hg}(\text{ClO}_4)_2, 2\text{HgS}$. A. A. E.

Phototropic Compounds of Mercury. M. L. DEY (*Nature*, 1923, **112**, 240; cf. Venkataramaiah and Rao, this vol., i, 764).—Phototropy is exhibited to a greater or less extent by complex salts of the formula HgS, HgX_2 or $2\text{HgS}, \text{HgX}_2$, where X is a halogen or univalent acid radicle, including thiocyanate. A. A. E.

Positive Ray Analysis of Copper. A. J. DEMPSTER (*Nature*, 1923, **112**, 7; cf. Aston, this vol., ii, 596).—By the use of a molybdenum furnace, three isotopes of copper have been observed separated by two units in atomic weight, and having relative intensities 1.4:1:1. Failing direct comparison, a consideration of the chemical atomic weight of copper indicates the masses of the isotopes to be 62, 64, and 66, respectively. The existence of two isotopes of molybdenum, giving a mean atomic weight of 85.51, was confirmed. A. A. E.

The Melting-point and Equilibrium Diagram of the Copper-Tin Alloys. O. BAUER and O. VOLLENBRUCK (*Z. Metallk.*, 1923, **15**, 119—125, 191—195).—Copper retains a maximum of 13.9% of tin in solid solution, but tin can retain only traces of copper. The compound Cu_3Sn exists in two modifications; the α -form is stable up to 676° , above which the β -form is the stable modification and melts unchanged at 720° . The existence of the compound Cu_4Sn has been definitely proved, and a new compound, Cu_6Sn_5 , has been found in and isolated from alloys containing more than 60% of tin. It is stable below the eutectic point at 225° in all alloys containing more than 61% of tin. [Cf. *J.S.C.I.*, 1923, **42**, 227A.] A. P. R.

Binary Systems of Salts with Components Capable of Sublimation. ERNST JÄNECKE (*Rec. trav. chim.*, 1923, **42**, 740—744).—A discussion of binary systems of two salts, one of which may be sublimed. The systems described are: cuprous chloride—mercurous chloride, in which the eutectic lies at 330° with 65% of mercurous chloride; silver chloride—mercurous chloride, which has a eutectic at 250° with 55% of mercurous chloride; silver chloride—ammonium chloride, which has a eutectic at 245° with 80% of ammonium chloride; mercurous chloride—ammonium chloride, in which the mass is completely melted at a composition between 17 and 25% of mercurous chloride, and in which the eutectic lies at 135° with 79% of mercurous chloride; mercuric chloride—ammonium chloride, which forms two compounds, $\text{HgCl}_2 \cdot \text{NH}_4\text{Cl}$ and $\text{HgCl}_2 \cdot 4\text{NH}_4\text{Cl}$. The first compound has m. p. 204° and b. p. 350° , and forms clear, lustrous crystals with a weak double refraction. The second compound, m. p. 244° , decomposes when heated into ammonium chloride and a liquid containing 70% of mercuric chloride. J. F. S.

Formation of Sulphide, Selenide, and Telluride of Copper. FELICE GARELLI (*Rec. trav. chim.*, 1923, **42**, 818—820).—A discussion of the formation of sulphide, selenide, and telluride of copper when the respective non-metals, wrapped with copper wire, are placed in a solution of a copper salt. With cold solutions, cupric derivatives are formed, but with boiling solutions, the cuprous compounds are formed. J. F. S.

The Crystal Structure of Various Heusler Alloys, by the Use of X-Rays. J. F. T. YOUNG (*Phil. Mag.*, 1923, [vi], **46**, 291—305).—By the method of X-ray analysis, the author has

determined that aluminium and copper crystallise in a face-centred cubic system of lattice constant 4.05 Å. and 3.60 Å., respectively. In the case of two Heusler alloys of definite composition, the magnetic properties of which were studied by McLennan (*Physical Rev.*, 1907), it is shown that these occur in two crystal forms, *viz.*, a face-centred cubic crystal of constant 3.70 Å., and a combination of this with a body-centred cubic crystal of lattice constant 2.98 Å. It is tentatively suggested that the alloys are solid solutions of manganese-aluminium alloy in copper, and the author considers that the magnetic effects exhibited by the alloys are ultimately associated with the valency electrons, and not with the molecule or atom or any complex group of these. J. S. G. T.

The Ternary System: Aluminium-Zinc-Tin. E. CREPAZ (*Giorn. Chim. Ind. Appl.*, 1923, 5, 115—285).—The experiments performed confirm the equilibrium diagram for zinc-tin alloys as obtained by Lorenz and Plumbridge (*A.*, 1913, ii, 1056). It was found that the relative variation of the potential of the cell $\text{Sn}_x\text{Zn}_{(1-x)}|\text{N}|\text{ZnSO}_4|\text{E}|\text{N}$ with mercurous chloride is equal to that of the cell investigated by Herschkowitsch, $\text{Zn}|\text{N}|\text{SO}_4|\text{Sn}_x\text{Zn}_{(1-x)}|$.

The equilibrium diagram given by Gwyer for aluminium-tin alloys was also confirmed. The regular variation of the hardness diagram shows the improbability of the existence of solid compounds or solutions.

The superficial treatment has a strong influence on the potential of aluminium. The cell $\text{Al}|\text{N}|\text{10KAl}(\text{SO}_4)_2|\text{E}|\text{N}$ with mercurous chloride gives a maximum value of 1.1 volts.

It was found that the potential of aluminium-zinc alloys is independent of concentration, higher than that of aluminium, and practically constant in the whole interval of concentration. For the cell $\text{Al}_x\text{Sn}_{(1-x)}|\text{N}|\text{10KAl}(\text{SO}_4)_2|\text{E}|\text{N}$ with mercurous chloride 1.4 volts was found to be a mean constant value.

Hanson and Gayler's equilibrium diagram was confirmed, however, with formation of a solid solution instead of the compound Al_2Zn_3 .

The study of the ternary alloy aluminium-zinc-tin together with the micrographic investigation thereof, shows that the eutectoid is practically independent of aluminium, and may be identified with the eutectoid of the binary alloy zinc-tin. The decomposition of the solid solution, β , is favoured by the presence of tin.

The mechanical properties of quenched alloys containing β vary with time. Their hardness seems to reach a definite value after four days. E. M. V.

Equilibrium Studies in the Quaternary System Aluminium-Magnesium-Silicon-Zinc. W. SANDER and K. L. MEISSNER (*Z. Metallk.*, 1923, 15, 180—183).—The equilibrium diagrams of the four tertiary systems are briefly considered, and from these the quaternary diagram, in which each of these four systems is reproduced on a side of a regular tetrahedron, is built up. No tertiary or quaternary compounds are formed, although five binary compounds, Al_3Mg_4 , Al_3Mg_2 , AlZn , MgZn_2 and Mg_2Si , are

known; consequently the whole system may be divided into seven separate quaternary systems. [Cf. *J.S.C.I.*, 1923, **42**, 892A.]

A. R. P.

[Method for] The Sublimation of Aluminium Chloride.

EINAR BILLMANN (*Bull. Soc. chim.*, 1923, [iv], **33**, 995—996).—Freshly sublimed aluminium chloride is very necessary for Friedel and Crafts' reactions, and may be obtained in about 40 g. quantities by the following method. The lower part of a test-tube ($1\frac{1}{2}$ inches \times 7 inches) is surrounded with a jacket of wire gauze and is supported in an inclined position. The upper portion is cooled by means of a stream of water and a cotton wick. By the application of heat, the chloride may be made to sublime from the lower to the upper part of the tube.

H. H.

Separation of Gallium from Commercial Aluminium.

R. LLORD Y GAMBOA (*Anal. Fis. Quím.*, 1923, **21**, 280—284).—The presence of gallium has been verified spectroscopically in samples of bauxite and aluminium. A method is described for the separation of gallium. [See, further, *J.S.C.I.*, 1923, **42**, 780A.]

G. W. R.

Permanganates. III. E. MOLES and M. CRESPI (*Anal. Fis. Quím.*, 1923, **21**, 305—315; cf. this vol., ii, 161, 565).—A description of the preparation and properties of the permanganates of silver, copper, glucinum, magnesium, zinc, and cadmium. Those which decompose at high temperatures give a residue stable up to 450°, consisting of the manganite and a solid solution of the manganate and manganese peroxide. Those decomposing at lower temperatures yield below 450° all the oxygen corresponding with the decomposition of the manganate and manganese peroxide. The temperature of decomposition of the permanganates is shown to be a periodic function of the atomic number of the metals.

G. W. R.

Oxides of Iron. JOHN B. FERGUSON (*J. Washington Acad. Sci.*, 1923, **13**, 275—281).—The system hydrogen-water vapour-iron-ferrous oxide has been investigated. It is shown that the iron phase does not contain appreciable quantities of oxygen. The transition temperature of the ferrous oxide phase appears to be lowered by solution of the magnetic oxide in it. The quadruple point lies below 577°. A value, which is slightly less than 0.54, and certainly less than 0.57, has been obtained for the equilibrium constant, $K = \text{H}_2\text{O}/\text{H}_2$, at 750° by the stream method. This agrees with the value obtained by interpolation from the results of Chaudron (*A.*, 1914, ii, 721; 1921, ii, 178, 584), and furnishes a confirmation of the latter.

J. F. S.

Iron and the Lower Oxides of Iron. JOHN BRIGHT FERGUSON (*Canad. Chem. and Met.*, 1923, **7**, 175—176).—No change takes place if pure iron is heated in a mixture of hydrogen and water vapour at temperatures above 750°, and slightly oxidised specimens of iron were completely reduced after this treatment, thus showing that iron forms no oxide lower than ferrous oxide. Ferrous oxide appears to be stable above 526°; below that temperature it decom-

poses into iron and ferrosferric oxide, thus, $4\text{FeO} \rightleftharpoons \text{Fe} + \text{Fe}_3\text{O}_4$, provided the temperature is not too low. The reaction is strictly reversible, the mixture being quantitatively reconverted into ferrous oxide above 607° , although the reaction starts at 577° . Admixture of ferric oxide with ferrous oxide lowers the transition temperature. Oxidation of iron at 750° begins to take place with a gas mixture having a ratio of water vapour to hydrogen of slightly less than 0.54.

A. R. P.

Preparation of Easily Filtrable Iron Hydroxide by Precipitation with Thiosulphate and Iodate. FRIEDRICH L. HAHN and MARIA HERTRICH (*Ber.*, 1923, 56, [B], 1729—1732).—A method of precipitation of bi- or ter-valent iron is described which is simple, rapid, and cheap; it gives a heavy, powdery precipitate, easily washed and filtered, which contains no basic salt even when moist, and gives the theoretical quantity of iron oxide on ignition. The reactions involved are: $2\text{Fe}^{+++} + 2\text{S}_2\text{O}_3^{--} = 2\text{Fe}^{++} + \text{S}_4\text{O}_6^{--}$, $2\text{Fe}^{++} + 6\text{H}_2\text{O} + \text{IO}_3' + 4\text{S}_2\text{O}_3^{--} = 2\text{Fe}(\text{OH})_3 + \text{I}' + 2\text{S}_4\text{O}_6^{--}$. A ferric salt is neutralised and then warmed with thiosulphate solution until practically colourless. It is then warmed with twice the theoretical quantity of thiosulphate and a slight excess of iodate calculated on the second of the above equations. Ammonium chloride should be added before the iodate. The volume of solution from which precipitation occurs should be about 400 c.c. for every 0.2 g. Fe_2O_3 . It is sufficient to warm the solutions on the water-bath, but the precipitate should be ignited at the blow-pipe. A ferrous salt is naturally not reduced, but is precipitated straightaway from a neutral or slightly acid solution.

H. H.

Iron and Copper Oxides. RUDOLF RUER and MINORU NAKAMOTO (*Rec. trav. chim.*, 1923, 42, 675—682).—The region of stability and the pressure of oxygen in equilibrium with ferric oxide and cupric oxide have been investigated. In the case of ferric oxide, it is shown that heating this substance in a current of pure dry nitrogen causes no loss of weight at temperatures up to 1125° ; at 1200° , the oxide loses 3.28% of its weight, and above this temperature oxygen is lost continuously up to 1550° , when the substance melts. A repetition of the experiment shows that oxygen is lost very slowly at 1150° , and this is the lowest temperature at which a loss of oxygen occurs. The loss of oxygen at 1150° continues until the compound Fe_3O_4 is formed, which contains about 2% of ferric oxide dissolved in it. At 1550° , the solid is the magnetic oxide containing 4% of ferrous oxide in solid solution. Further experiments, in which ferric oxide was heated in air and oxygen, respectively, are described, which show that at 1470° ferric oxide loses oxygen when heated in this gas at 1 atm. pressure, but takes up the amount lost at 1440° . From this it follows that the dissociation pressure of ferric oxide is 1 atm. at 1455° . The dissociation pressure at 1150° is scarcely measurable, and at 1383° it is 0.20 atm. Similar experiments with cupric oxide show that at 775° this substance loses oxygen in a stream of nitrogen and passes into cuprous oxide; the rate of loss is much more rapid at 800° ,

but at both temperatures the change to cuprous oxide may be completed without the formation of any intermediate compound. Cuprous oxide is quite stable in a current of nitrogen at temperatures up to 1222° , when it melts. Cupric oxide has a dissociation pressure of 1 atm. at 1105° , and at 1109° the mixture of cuprous and cupric oxides melts. The dissociation pressure at 1031° is 0.20 atm. J. F. S.

Solubility. VIII. The Solubility of Cobaltammines. FRITZ EPHRAIM (*Ber.*, 1923, **56**, [B], 1530—1542).—The theory is developed that solubility depends on solvate formation between solute and solvent. Aqueous solutions are considered, and it is maintained that there are three factors influencing the possibility of solvate formation: (a) relative size of anion and cation, disparity in size favouring solubility; (b) the heat of hydration of the ions, inequality again favouring solubility; (c) the effect of steric hindrance. The solubilities of many cobaltamine salts are given and several regularities are pointed out. The polar character of the mechanism of solvate formation is supported by the fact that, whilst salts with trivalent kations, e.g., $[\text{Co}(\text{NH}_3)_6]^{+++}$, bivalent kations, e.g., $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{++}$, and univalent kations, e.g., $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]^+$, are soluble, neutral molecules of the type $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$ are practically insoluble. The last are also non-electrolytes. The following new compounds are mentioned. *Hexamminecobaltifluosilicate*; *mono-aquo-pentamminecobaltiperchlorate*, the *naphthalene- β -sulphonate*, *picrate*, and *iodide*; *diaquatetramminecobaltinitrate*, the *picrate* and *naphthalene- β -sulphonate*; *chloropentamminecobaltiperchlorate*, *picrate*, *naphthalene- β -sulphonate*, *thiosulphate*, and *oxalate*; *bromopentamminecobaltii-iodide*, the *perchlorate*, *chlorate*, *thiosulphate*, *picrate*, and *naphthalene- β -sulphonate*; *iodopentamminecobaltichlorate*; *nitropentamminecobaltii-iodide*, the *perchlorate*, *picrate*, and *naphthalene- β -sulphonate*; *nitratopentamminecobaltii-iodide*, the *chlorate*, *perchlorate*, *fluosilicate*, *picrate*, and *naphthalene- β -sulphonate*; *cis-dinitrotetramminecobaltibromide*, the *chlorate*, *perchlorate*, *fluosilicate*, and *picrate*; *trans-dinitrotetramminecobaltichlorate*, the *perchlorate*, *fluosilicate*, *oxalate*, and *picrate*. H. H.

Crystal Structure of Natural and Synthetic Oxides of Uranium, Thorium, and Cerium. V. M. GOLDSCHMIDT and L. THOMASSEN (*Videnskapsselskapets Skrifter. Mat. Naturv. Klasse*, 1923, 5—48; from *Chem. Zentr.*, 1923, i, 1149—1150).—Pitchblende, bröggerite, cleveite, thorianite, and the oxides of uranium, thorium, and cerium were examined by the Debye-Scherrer and Laue methods. The dioxides (uranous oxide, cerium dioxide, and thorium dioxide) are isomorphous. The metallic atoms are arranged in a regular face-centred lattice, and the oxygen atoms probably in a lattice of the calcium fluoride type. The edges are, for uranous oxide, 5.47 \AA , for thorium dioxide, 5.61 \AA , and for cerium dioxide, 5.41 \AA . The structure of uranoso-uranic oxide (U_3O_8) is irregular. Uranic oxide was only obtained in an amorphous form. The minerals all show crystal structure, the edges being for thorianite, 5.57 \AA ;

for bröggerite, 5.47 \AA ., and for cleveite, 5.47 \AA .. They correspond with isomorphous mixtures of the three oxides and also of lead peroxide. The crystalline substance in thorianite and bröggerite has a uniform arrangement with a distortion of the single points as if the crystal were composed of sub-parallel planes. Cleveite yields uranosouranic oxide on ignition. Bröggerite, after ignition, shows the uranous oxide structure. The crystal substance in pitchblende is present in a finely divided state (10^{-4} to 10^{-7} cm.). The uranium atoms form face-centred cubes with edges $5.42\text{--}5.45 \text{ \AA}$.. It is supposed that, as the ground lattice of these minerals is uranous oxide, the excess of oxygen corresponding with uranic oxide is present in solid solution. This case is analogous to the occurrence of yttrium fluoride in calcium fluoride. Bröggerite in which uranium is partly transformed to lead retains the original lattice arrangement. G. W. R.

Should the Element of the Atomic Number 72 be called Celtium or Hafnium? G. URBAIN (*Chemistry and Industry*, 1923, 42, 764—769).—The author reviews briefly the literature dealing with the element of atomic number 72, and advances a claim to its discovery prior to the work of Coster and von Hevesy. A bibliography of the subject is given. J. S. G. T.

Hafnium and Celtium. HAROLD S. KING (*Nature*, 1923, 112, 9).—Priority is claimed for the statement that the chemical properties of celtium, as described by Urbain, do not agree with theoretical considerations of atomic structure. A. A. E.

The Discovery of Hafnium and the Present Position of our Knowledge of this Element. GEORG VON HEVESY (*Ber.*, 1923, 56, [B], 1503—1516).—A summary of the work leading up to the discovery of hafnium and an account of its physical and chemical properties as far as at present known. H. H.

Dispersoid Synthesis of Gold. I. P. P. VON WEIMARN (*Kolloid. Z.*, 1923, 33, 74—81).—Making use of ordinary distilled water and commercial reagents, bright red gold sols are prepared by adding 10 c.c. of a 0.1% solution of chloroauric acid ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$) to 500 c.c. of water and, with vigorous stirring, 10 c.c. of a solution containing 12 g. of potassium hydroxide and 100 c.c. of 35% formaldehyde solution per litre. The reduction is instantaneous, but the sol produced is not very stable; usually after forty-eight hours it has completely coagulated. If, however, the reaction is carried out at the boiling point and the sol boiled gently for some time, it is found that the stability increases with the time during which it has been boiled. Thus after five minutes' boiling the sol coagulates in forty-eight hours, after sixty minutes' boiling it is stable for several months. Similar sols of similar properties may also be obtained by substituting an approximately 0.2N-solution of potassium carbonate for the potassium hydroxide. J. F. S.

Mineralogical Chemistry.

Fumaroles of the Katmai Region, Alaska. E. T. ALLEN and E. G. ZIES (*Contrib. Tech. Papers, National Geogr. Soc., Washington*, 1923, *Katmai Ser.*, No. 2, 75—155).—An illustrated account is given of the fumaroles in the "Valley of Ten Thousand Smokes," and the methods of recording the temperatures (50° to 650°) and collecting the gases are described. Steam forms 98.65 to 99.85 vol. % of the gases, the remainder being hydrogen chloride, carbon dioxide, hydrogen sulphide, nitrogen, hydrogen fluoride, and sometimes methane, with minor quantities of oxygen, carbon monoxide, argon, and ammonia. The water is probably of surface origin, and the nitrogen and argon are from the atmosphere. Incrustations include ammonium chloride, sulphur, iron salts, and rarely arsenic sulphide. L. J. S.

Transparent Preparations of Coal for Microscopical Investigations. J. LOMAX and J. R. LOMAX (*Lancs. Cheshire Coal Res. Assoc. Bull.*, 1923, No. 14).—A discussion of various methods for the preparation of transparent sections of coal and a detailed description of one found very satisfactory in practice. T. S. W.

Vauxite and Paravauxite, Two New Minerals from Bolivia. SAMUEL G. GORDON (*Proc. Acad. Nat. Sci. Philadelphia*, 1923, 75, 261—270).—These occur on wavellite in brecciated tin-veins in rhyolite at Llallagua, Oruro. Vauxite occurs as radiating aggregates of sky-blue, triclinic crystals with $a : b : c = 1.1510 : 1 : 1.2624$, $\alpha = 99^{\circ} 32'$, $\beta = 102^{\circ} 14'$, $\gamma = 110^{\circ} 14'$; $d\ 2.375$, $H\ 3\frac{1}{2}$; refractive indices $\alpha\ 1.551$, $\beta\ 1.555$, $\gamma\ 1.562$, optically positive. Paravauxite forms colourless, triclinic crystals of prismatic habit with good $b\ (010)$ cleavage; $a : b : c = 0.5058 : 1 : 0.6882$, $\alpha = 97^{\circ} 42'$, $\beta = 110^{\circ} 22'$, $\gamma = 100^{\circ} 56'$; $d\ 2.291$, $H\ 3$; refractive indices $\alpha\ 1.554$, $\beta\ 1.558$, $\gamma\ 1.573$, optically positive. Analyses by J. E. WHITFIELD gave I for vauxite and II for paravauxite.

	FeO.	MnO.	Al ₂ O ₃ .	P ₂ O ₅ .	H ₂ O at 104°.	H ₂ O above 104°.	Total.
I.	19.34	0.18	14.89	31.33	3.68	30.24	99.60
II.	15.47	—	17.89	29.80	16.40	20.34	99.90

The minerals are readily soluble in hydrochloric acid. The water content of the paravauxite varies considerably with the humidity of the atmosphere. Formulæ :

Vauxite : $4\text{FeO}, 2\text{Al}_2\text{O}_3, 3\text{P}_2\text{O}_5, 24\text{H}_2\text{O} + 3\text{H}_2\text{O}$.

Paravauxite : $5\text{FeO}, 4\text{Al}_2\text{O}_3, 5\text{P}_2\text{O}_5, 26\text{H}_2\text{O} + 21\text{H}_2\text{O}$.

L. J. S.

Electronic Structures of the Spinel. MAURICE L. HUGGINS (*Physical Rev.*, 1923, 21, 509—516).—In the cases of crystals of the formulæ ZnAl_2O_4 , ZnCr_2O_4 , ZnFe_2O_4 , MgAl_2O_4 , MgCr_2O_4 , MnAl_2O_4 , MnCr_2O_4 , CdCr_2O_4 , and FeFe_2O_4 , the distances between adjacent atomic centres have been calculated from the densities, and the

positions of the oxygen centres determined. The densities of the compounds MgFe_2O_4 and MnFe_2O_4 are calculated to be 4.47 and 4.90 g./cm.³, respectively. When the oxygen radius (the distance from the atomic centre to the valency electron-pair) is assumed to be 0.65 Å., atomic radii may be computed as follows: Zn^{+2} , 1.31 Å.; Fe^{+2} , 1.27—1.30; Mg^{+2} , 1.29; Mn^{+2} , 1.39; Cd^{+2} , 1.51; Fe^{+3} , 1.38; Al^{+3} , 1.26; Cr^{+3} , 1.35. It is considered that the empirical formula $\text{R}''\text{R}'''_2\text{O}_4$ is the only one which correctly represents the structure of the spinels in the crystalline state. A partial explanation of the cause of ferromagnetism may possibly be found in the suggestion that it arises from a concentration of electron triplets in the same end of each atomic kernel. A. A. E.

The Chemical Formula of Uraninite. ALFRED SCHOEP (*Bull. Soc. chim. Belg.*, 1923, 32, 274—281).—The author has analysed specimens of Katanga pitchblende, estimating total uranium as U_3O_8 and UO_2 in presence of UO_3 by Hillebrand's method of heating the mineral in a sealed tube with dilute sulphuric acid in an atmosphere of carbon dioxide, and volumetric estimation of the dioxide with potassium permanganate. The results lead to the conclusion that the purified mineral (*i.e.*, uraninite) has the formula $(\text{UO}_2)_3(\text{UO}_3)_2$ (cf. Blomstrand, A., 1884, 1102). This is discussed in comparison with results obtained by other workers for pitchblende from Katanga and other sources, and also for thorianite, and reasons are given for regarding the UO_3 as an oxidation product of the UO_2 of which the original mineral consisted. Thus the author maintains that the formula of uraninite is UO_2 as that of thorianite is ThO_2 , the two minerals being isomorphous and analogous in chemical composition. The percentage of the dioxide is greater in fresh specimens of the mineral; some consist of ThO_2UO_3 in which all the uranium compound has undergone oxidation. Thorianite contains various proportions of UO_2 and isomorphous mixtures of the two dioxides may be prepared artificially. H. J. E.

Bavalite from Bas-Vallon, Brittany. J. ORCEL (*Compt. rend.*, 1923, 177, 271—273).—Bavalite is an oolitic iron-ore consisting of a mixture of chlorite and magnetite: the name is restricted to the chloritic constituent. The pure sample analysed has $d\ 3.20$; it is finely scaly, and is optically negative with small axial angle. Analysis gave:

SiO_2 .	TiO_2 .	Al_2O_3 .	Fe_2O_3 .	FeO .	MnO .	MgO .	CaO .	Alkalis.	H_2O .	Total.
21.71	0.08	21.35	0.82	43.01	0.05	2.33	0.16	0.35	10.21	100.07

This corresponds with $2\text{SiO}_2\text{Al}_2\text{O}_3\cdot 3\text{FeO}\cdot 3\text{H}_2\text{O}$, or a ferrous salt of the acid $\text{Al}_2\text{Si}_2\text{O}(\text{OH})_{12}$. Of the water 0.11% is lost at 107° , 9.03% at 485° , and 1.07% at 735° . The composition is near that of chamosite.

L. J. S.

Hodgkinsonite, Datolite, and Calciiothomsonite from Franklin, New Jersey. SAMUEL G. GORDON (*Proc. Acad. Nat. Sci. Philadelphia*, 1923, 75, 271—274).—Crystallographic descrip-

tions are given of hodgekinsonite and datolite. The calciothomsonite is colourless and radiating with $d\ 2.405$, and refractive indices for yellow mercury light $\alpha=1.530$, $\beta=1.532$, $\gamma=1.542$. Analysis by J. E. WHITEFIELD shows the mineral to be thomsonite with $\text{CaO} : \text{Na}_2\text{O} = 5 : 1$.

SiO_2 .	Al_2O_3 .	CaO .	MgO .	Na_2O .	K_2O .	H_2O at 100°.	$\text{H}_2\text{O} > 100^\circ$.	Total.
36.44	30.34	15.94	trace	3.50	0.18	0.26	13.26	99.92

L. J. S.

Analytical Chemistry.

X-Ray Spectroscopy as a Means of Qualitative and Quantitative Chemical Analysis. D. COSTER (*Chem. News*, 1923, 127, 65—70).—A useful summary of present knowledge.

Screw Modification of the Mohr Pinch Clamp. WILLIAM M. CRAIG (*J. Amer. Chem. Soc.*, 1923, 45, 1723).—A modification of the Mohr pinch clamp is described which allows a dropwise delivery from a burette. The modification consists in removing one of the finger plates from the ordinary pinch clamp and soldering it through a hole to a piece of brass plate 3 mm. thick, 10 mm. wide, and 20 mm. long. This plate lies in such a position that its length is above the straight arms of the clamp. A hole is bored through the brass plate, tapped, and fitted with a suitable screw, which is left in such a position that it prevents the clamp being opened more than enough to allow the liquid to pass more rapidly than dropwise when the clamp is opened. The screw may be adjusted to allow any desired rate of flow from the burette.

J. F. S.

The Electrometric Titration of Acids and Bases with the Antimony Indicator Electrode. ALFRED UHL and WILHELM KESTRANEK (*Monatsh.*, 1923, 44, 29—34).—The hydrogen and mercury-mercuric oxide electrodes possess certain disadvantages in electrometric titrations, the copper electrode is not satisfactory, and a silver-silver oxide electrode is useful only in absence of chloride-ions. A suitable metal for the electrode must be insoluble in dilute acids, must respond accurately to hydroxyl-ion concentration, and its oxide must possess a very small solubility-product. A metal giving salts which are hydrolytically dissociated to a high degree by water, and giving an amphoteric hydroxide, should provide an excellent electrode. Antimony satisfies these requirements.

Good results were obtained initially, using an antimony electrode in presence of antimony oxide, but it was afterwards found that antimony, after being cast, contains sufficient oxide for the purpose of providing an efficient electrode. Decinormal solutions of sodium hydroxide were titrated satisfactorily against similar solutions of hydrochloric acid (at 15°, at 50°, and also in presence of large

quantities of ammonium nitrate) and acetic acid (in presence or absence of potassium chloride). Tartaric acid gave only slightly less good results. Constant potential (after each addition of titrating liquid) was attained within thirty seconds, but it is not necessary to wait for this constancy, owing to the sensitiveness of the electrode.

A simple apparatus in which the side tube of a calomel electrode is replaced by an H-tube, the latter being in contact with the solution to be titrated, is described.

E. E. T.

Limits of Hydrogen-ion Concentration as Determined by Electrometric Titrations in Water Solutions of Carbon Dioxide, Calcium Sulphate, and Calcium Carbonate. J. W. SHIPLEY and IVAN R. MCHAFFIE (*J. Soc. Chem. Ind.*, 1923, **42**, 311—319T).—A method for performing an electrometric titration with carbon dioxide gas is described. The range of hydrogen-ion concentration for mixtures of calcium carbonate and carbon dioxide (up to a partial pressure of 1 atm.) in aqueous solution has been determined experimentally by means of the hydrogen electrode. The range of hydrogen-ion concentration in solutions containing calcium carbonate, calcium sulphate, and carbon dioxide has been determined experimentally. A strong buffer solution is produced at a hydrogen-ion concentration of 7.77×10^{-6} or p_H 5.11, when water is saturated with carbon dioxide in the presence of solid calcium carbonate and sulphate. No end-point for calcium hydrogen carbonate was obtained in the electrometric titration of calcium hydroxide with carbon dioxide or in the titration of calcium carbonate with sulphuric acid. The equilibrium of the system calcium carbonate—calcium sulphate—carbon dioxide determines the hydrogen-ion concentration in ground waters found in contact with calcareous soils containing gypsum. The importance of this equilibrium to the corrosion of iron pipes laid in the earth is discussed.

J. F. S.

Polarimetric Estimation of Acidic and Basic Groups of Various Compounds. II. J. GROOT (*Biochem. Z.*, 1923, **139**, 188—198).—The fall of rotation of dextrose under the influence of alkali follows the unimolecular law. For normalities of potassium hydroxide between 0 and 0.237*N*, it is found that the velocity constant is proportional to the concentration of alkali. The velocity constant was then determined in the presence of phloroglucinol and alkali, and from this the alkali inactivated by the phloroglucinol could be calculated. Phloroglucinol behaves as a dibasic acid.

H. K.

Detection of Chlorine and Bromine in the Presence of Closely Related Ions. M. DIMITROFF (*Z. anal. Chem.*, 1923, **62**, 451—452).—Chlorine-ions can be detected in the presence of bromine-, iodine-, cyanogen-, and thiocyanogen-ions by treating the solution with potassium permanganate and driving the liberated halogens by means of a stream of air through 3—4 c.c. of water containing 0.025 g. of potassium bromide. This solution is then evaporated to 1 to 2 c.c. and 6 c.c. of 2% sodium bromate solution

and 6 c.c. of 5*N*-sulphuric acid are added. Air is passed through the liquid to expel the free bromine, and 25 c.c. of water and a few drops of 3% silver nitrate solution are added; a white turbidity shows the presence of chlorine if more than 0.025 mg. of chloride was present in the original solution.

Bromine-ions are detected by treating the original solution as described above and expelling the liberated halogens by means of air into 4—5 c.c. of water containing 0.025 g. of potassium iodide. This solution is boiled whilst passing a stream of air through it, cooled, treated with a few drops of chlorine water, and shaken with a little chloroform or carbon disulphide. A brown upper layer proves bromides to be present in the original solution. A. R. P.

Detection of Chlorate and Bromate in Mixtures of Halogenates, Qualitative Investigation of Such Mixtures, and Application of the Process in Testing Chlorates and Iodates for the Presence of Bromate. M. DIMITROFF (*Z. anal. Chem.*, 1923, 62, 453—455).—Zinc and sulphuric acid reduce chlorates in the cold quantitatively to chlorides; with bromates and iodates the free halogen is liberated and subsequently reduced by the nascent hydrogen. In hot solutions, the second reaction does not take place, as the iodine and bromine distil off. To test for chlorate in the presence of the other compounds, therefore, 5 c.c. of the solution are boiled with 50 c.c. of 2*N*-sulphuric acid and two or three pieces of granulated zinc until all free halogen is expelled. If the resulting solution gives a white turbidity with silver nitrate chlorates were originally present. To detect bromates in a mixture of halogenates, 5 c.c. of the solution are treated with 5 c.c. of 1:1-sulphuric acid and 1 c.c. of chloroform. A 0.5% alcoholic iodine solution is then dropped in slowly with constant shaking; in the presence of bromate, the original rose-red colour of the chloroform turns brown. A. R. P.

Use of Bromate in Volumetric Analysis. III. Estimation of Bromate in the Presence of Ferric Iron. G. FREDERICK SMITH (*J. Amer. Chem. Soc.*, 1923, 45, 1666—1675; cf. this vol., ii, 504, 573).—The estimation of bromates in the presence of ferric iron has been investigated, and three methods are put forward for this estimation. The methods have been tested and their application has been demonstrated. They are: (i) Iodometric method. Phosphoric acid solutions containing sodium pyrophosphate, in which the dissociation of the resulting iron complex to give ferric-ions is less than in the presence of either reagent alone, are analysed for their content of bromate by the addition of potassium iodide in excess and titration of the liberated iodine after two to three minutes with sodium thiosulphate. The time rate of reduction of bromate by potassium iodide with various concentrations of phosphoric acid has been determined and the necessary variation in the concentration of phosphoric acid and sodium pyrophosphate with increasing amounts of ferric iron has been evaluated. (ii) Oxalate-permanganate method. The bromate is reduced by excess of sodium oxalate in boiling sulphuric acid

solution in the presence of mercuric perchlorate and the excess of oxalate determined by titration with potassium permanganate. It is shown that this reaction furnishes the basis of an improved method for iodometric standardisation, using sodium oxalate as the primary standard. (iii) Ferrous sulphate-permanganate method. This involves the same procedure as in the last method, except that ferrous sulphate is substituted for sodium oxalate and the titration is effected in a cold instead of in a hot solution. J. F. S.

Chronometric Estimation of Iodine in Soluble Iodides.

EM. RIEGLER (*Bul. Soc. Chim. România*, 1923, **5**, 3—5).—Ten c.c. of the iodide solution are placed in a test-tube and 5 drops of 2% sodium nitrite solution, 5 drops of starch solution, and 5 drops of dilute sulphuric acid are added successively; the contents of the tube are mixed, 1 c.c. of a 2% ethyl acetoacetate solution is added and the time required for the absorption of the liberated iodine is noted by means of a stop-watch. The iodide solution should contain between 0.2 and 1.0 mg. of iodine per 10 c.c.; within these limits, the rate of absorption of the iodine is directly proportional to the quantity of iodine, that is, 0.2 mg. is absorbed in ten seconds and 1.0 mg. in fifty seconds. W. P. S.

Winkler's Titration of Iodides. I. M. KOLTHOFF (*Pharm. Weekblad*, 1923, **60**, 841—845).—Winkler's method is not accurate in presence of bromides, but this difficulty may be overcome by using bleaching powder solution in place of chlorine water for the oxidation, the effect on bromides being dependent on the acidity of the solution. The correct hydrogen-ion concentration is obtained by the addition of succinic acid. Accurate results can be obtained in presence of large excess of bromide. If iron only is present besides iodide, phosphoric acid may be used for the estimation. Organic matter interferes. S. I. L.

Detection of Iodates in the Presence of Chlorates, Bromates, Dichromates, Nitrates, and Similar Salts. M. DIMITROFF (*Z. anal. Chem.*, 1923, **62**, 452—453).—Five c.c. of the solution are shaken with 2 to 3 drops of starch solution, 5 drops of dilute sulphuric acid, and 1 drop of a 0.5% solution of sodium thiosulphate. A deep blue iodine-starch colour proves the presence of iodate. The test may also be applied by mixing the first two reagents, then adding 1 to 2 c.c. of the thiosulphate solution so as to give two layers. A blue ring is then obtained at the interface in the presence of as little as 0.05 mg. of an iodate. A. R. P.

Estimation of Sulphur and some of its Compounds. J. M. TAYLOR (*J. Soc. Chem. Ind.*, 1923, **42**, 294—297r).—The estimation of sulphates by precipitation as barium sulphate is most trustworthy when the sulphate solution and barium chloride solution are added slowly and simultaneously to boiling water acidified with hydrochloric acid. Precipitation from strongly acid solution also yields a pure form of barium sulphate. Methods are described for the analysis of native sulphur, sulphur chloride, chlorosulphonic acid, and thionyl chloride. W. P. S.

Errors in the Estimation of Hydrogen Sulphide. FRED H. HEATH and FRANK A. LEE (*J. Amer. Chem. Soc.*, 1923, 45, 1643—1647).—The methods of estimating hydrogen sulphide in natural waters have been investigated, and it is shown that the presence of small quantities of salts such as nitrites, nitrates, and alkali salts generally introduce large errors into the iodometric estimation of hydrogen sulphide. It is therefore suggested that this method of estimating hydrogen sulphide in natural water be abandoned and that the colorimetric method of Mecklenburg and Rosenkränzer in which methylene-blue is formed be substituted (A., 1914, ii, 380). The need of a qualitative as well as a quantitative method is further shown by the fact that some samples of water gave no reaction by this latter method, but positive results were obtained by the iodometric method. J. F. S.

Detection of Sulphates in the Presence of Ferric Salts. FRIEDRICH L. HAHN (*Ber.*, 1923, 56, [B], 1733).—It is shown that the delicacy of the barium reaction for sulphates is much impaired in the presence of ferric salts, but that reduction of the latter by means of hydrazine or hydroxylamine enables the detection of the sulphate-ion to be made with certainty. Without reduction, it is impossible to detect less than 0.1% SO_3 in 0.4—0.8 g. Fe_2O_3 , but with preliminary reduction, as little as 0.02% may be detected. Neither aluminium nor chromium salts affect noticeably the delicacy of the test for sulphates. H. H.

Estimation of Persulphuric Acids. R. WOLFFENSTEIN and V. MAKOW (*Ber.*, 1923, 56, [B], 1768—1771).—A method for the estimation of hydrogen peroxide, Caro's acid, and persulphuric acid in a mixture of all three is described. The total active oxygen is determined by the addition of a known amount of a ferrous salt and back titration of the excess with potassium permanganate. The hydrogen peroxide is estimated by direct titration with permanganate. The difficulty arises in the attempt to differentiate between Caro's acid, $\text{HO}\cdot\text{SO}_2\cdot\text{O}\cdot\text{OH}$, and persulphuric acid, $\text{HO}\cdot\text{SO}_2\cdot\text{O}\cdot\text{O}\cdot\text{SO}_2\cdot\text{OH}$. The former liberates iodine instantaneously from potassium iodide, whilst the latter requires a considerable time. In practice, however, it is found that the hydrolytic change of persulphuric acid into Caro's acid during the titration of the latter is sufficient, unless precautions are taken, to impair the accuracy of the results. In order to arrest this hydrolysis, the solution must be kept cool and as acid as possible.

The above method estimates persulphuric acid only by difference. A direct method for the estimation of all three peroxide components is as follows. The hydrogen peroxide is first titrated with permanganate. Then sodium acetate is added to the solution until it contains free acetic acid, and the Caro's acid is estimated by titration with sodium sulphite, using iodine as indicator. Finally, the persulphuric acid is estimated by warming with a ferrous salt and titrating the excess of the latter with permanganate. The results may be checked by an estimation of the total active oxygen.

H. H.

Analysis of Hydrogen for Traces of Nitrogen. R. L. DODGE (*J. Amer. Chem. Soc.*, 1923, **45**, 1688—1691).—A modification of the usual method for the estimation of hydrogen by combustion over copper oxide has been devised and applied to the analysis of hydrogen for traces of nitrogen. The method consists in drying the hydrogen and admitting it to a system evacuated to 0.01 mm. of mercury. As the gas enters the system it passes along a column of copper oxide 34 cm. long heated to a maximum temperature of 400°. The water formed is condensed in a graduated glass tube which is immersed in ice, and the unburnt gas circulated back through the copper oxide tube. After the whole of the hydrogen is burnt, the residual gas is pumped into a water-jacketed burette and measured. The method is accurate to 0.005%. J. F. S.

Behaviour of Nitro-derivatives of Aromatic Hydrocarbons in Kjeldahl's Process. B. M. MARGOSCHES and W. KRISTEN (*Z. ges. Schiess. Sprengstoffw.*, 1923, **18**, 73—76).—The results of the treatment of a number of nitro-derivatives of aromatic hydrocarbons by various modifications of Kjeldahl's process are given in a series of tables. In no case was the theoretical percentage of nitrogen obtained, owing to the volatilisation of the nitro-compound during the digestion. Tests were carried out with 20 c.c. of sulphuric acid alone, and with the addition of 10 g. of potassium sulphate, 0.5 g. of copper sulphate, 0.5 g. of mercuric oxide and also with the simultaneous addition of copper sulphate and mercuric oxide. The reduction of the period of digestion necessary by the addition of copper sulphate or mercuric oxide is very marked. H. C. R.

Influence of the Method of Precipitation of Proteins on the Results of the Estimation of Total Non-protein Nitrogen in Blood, Plasma, and Corpuscles. P. CRISTOL and S. NIKOLITCH (*Bull. Soc. Chim. biol.*, 1923, **5**, 469—486).—Detailed results are presented of a large number of estimations of the non-protein nitrogen in blood plasma and corpuscles, using metaphosphoric acid, tungstic acid, or trichloroacetic acid as protein precipitant. The acidity of the filtrate appears to exert considerable influence on the result. Highest values for non-protein nitrogen are obtained with filtrates of low acidity, whichever precipitant is used. With filtrates of high acidity, the results obtained with the different precipitants diverge considerably. E. S.

Micro-Kjeldahl Methods in the Tanning and Gelatin Industries. O. GERNGROSS and W. E. SCHAEFER (*Z. angew. Chem.*, 1923, **36**, 391—394).—An improved micro-Kjeldahl apparatus based on that of Bang is described and illustrated, together with a micro-burette capable of being read to 0.001 c.c. In leather or bone meal analyses, 0.5—1.0 g. of the sample is taken for the preliminary digestion, the contents of the flask diluted to 250 c.c., and 1 c.c. of this solution taken for distillation in the micro-apparatus. When dealing with dilute albuminous solutions such as are met with in the gelatin industry, 1 c.c. of the carefully homogenised solution may be taken directly for the digestion with 2 c.c. of concentrated

sulphuric acid and 3 drops of 10% copper sulphate. The digestion is in such cases complete in thirty to forty minutes. The precautions necessary in the distillation and titration are fully described. The titration may be carried out iodometrically after adding potassium iodide and potassium iodate, or by using a 1% alcoholic solution of *p*-nitrophenol as indicator, which is sensitive to 0.01 c.c. of *N*/80-sodium hydroxide, but cannot be used by artificial light.

H. C. R.

Method for the Estimation of Ammonia in Urine. MALTE LJUNGDAHL (*Compt. rend. Soc. Biol.*, 1922, **87**, 1414—1416; from *Chem. Zentr.*, 1923, ii, 556).—By rapid distillation with steam, the whole of the ammonia in (1 c.c. of) urine may be obtained in three to four minutes. Continuation of the distillation to ten minutes results in an increase of 0.05—0.09 mg. of ammonia obtained. The results obtained agree with those by the Folin method. The ammonia is collected in 2 c.c. of 0.1*N*-sulphuric acid and titrated with 0.1*N*-sodium hydroxide, using methyl-red as indicator. G. W. R.

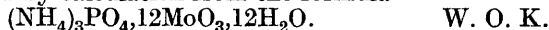
Formation of Glucoheptonitrile in Urines containing Sugar and Cyanides as Cause of Error in the Estimation of Ammonia. Value of Schaffer's Sodium Carbonate Method. W. MESTREZAT and (MLLE) M. JANET (*Bull. Soc. Chim. biol.*, 1923, **5**, 464—468).—In the estimation of ammonia in urine by Schloesing's bell method (cf. A., 1922, ii, 453), high results are obtained if large quantities of sugar are present in the urine. This is due to hydrolysis of the nitrile formed by interaction of the hexose and the mercuric cyanide used as antiseptic. Good results may, however, be obtained with such urines if sodium carbonate is used in place of milk of lime according to the technique of Schaffer. E. S.

The Estimation of Ammonia and Urea in Urine and other Fluids. SAMUEL LEVY-SIMPSON and DENIS CHARLES CARROLL (*Biochem. J.*, 1923, **17**, 391—402).—The method is based on the fact that when a mixture of urea and ammonia is distilled with steam and alcohol, only ammonia comes over during a certain stage of the distillation. Using 5 to 10 c.c. of the liquid and 90 c.c. of alcohol, it is found that all the ammonia distilled before frothing commenced. Details of the conditions under which accurate results can be obtained by this method are given. The method, which is claimed to be accurate, has the advantage of being rapid. An ammonia determination requires seven minutes, whilst a complete determination of ammonia and urea can be made with one apparatus in thirty minutes. S. S. Z.

Decomposition of Carbamide and other Nitrogenous Compounds during the Distillation of Urine with Steam. MALTE LJUNGDAHL (*Compt. rend. Soc. Biol.*, 1922, **87**, 1411—1413; from *Chem. Zentr.*, 1923, ii, 556).—In the estimation of ammonia in urine by distillation with steam, if a rapid current is employed the whole of the ammonia comes over within four minutes, whilst a longer time is required for the decomposition of carbamide and glycine.

G. W. R.

A Micro-method for Estimating the Total Phosphoric Acid in Blood and Fæces. WERNER GROTE (*Z. physiol. Chem.*, 1923, **128**, 254—256).—The phosphoric acid content of blood and of fæces may be estimated by destroying the organic matter with nitric acid and sulphuric acid, precipitating the phosphoric acid with ammonium molybdate, and estimating the ammonium in the filtrate as in Kjeldahl's method. It is found that each c.c. of *N*/70·2-hydrochloric acid used up by the ammonia distilled over corresponds with 0·00021 g. of P_2O_5 instead of with 0·000337 g., the value obtained by calculation from the formula



Estimation of the Carbon Content of Solutions. JOSEPH NEEDHAM (*Biochem. J.*, 1923, **17**, 431—434).—The solution is burned in a silica boat placed in a quartz combustion tube. The carbon dioxide is caught in a receptacle containing baryta, from which solution it is liberated by the addition of tartaric acid and is estimated in a Haldane gas measuring apparatus. S. S. Z.

The Estimation of Carbon Monoxide in Vitiated Air. F. S. SINNATT and L. SLATER (*Lancs. Cheshire Coal Res. Assoc. Bull.*, 1923, No. 13).—A modification of the apparatus of Winmill (*T.*, 1914, **105**, 1996) and Graham (*A.*, 1919, ii, 117) is described, and its applications and those of the methods of Graham (*loc. cit.*) and Sinnatt and Cramer (*A.*, 1914, ii, 383) are discussed in detail.

T. S. W.

Bicarbonate Equilibrium. J. W. SHIPLEY and IVAN R. MCHAFFIE (*J. Soc. Chem. Ind.*, 1923, **42**, 319—326T).—From data obtained in the electrometric titration of calcium hydroxide by carbon dioxide (see this vol., ii, 649), the condition of calcium hydrogen carbonate has been investigated. It is shown that the degree of hydrolysis of calcium carbonate in water at 20° is 10%. The solubility product of calcium hydroxide at 20° as calculated from the electrometric titration was found to be $0\cdot64 \times 10^{-5}$. Electrometric titrations of sodium carbonate and calcium carbonate in very dilute solutions were carried out in a closed electrode vessel, using hydrochloric acid as the titrating acid. A new constant, $H^+ \times CO_3'' = 5 \times 10^{-13}$, was found to hold for carbonate equilibria. The primary constant, $k_1 = H^+ \times HCO_3' / H_2CO_3$, decreases with dilution, and the secondary constant, $k_2 = H^+ \times CO_3'' / HCO_3''$, increases on dilution, but the product, $H^+ \times CO_3''$, remains constant. The proportion, *n*, of the total carbon dioxide in solution existing as molecular carbonic acid, H_2CO_3 , has been calculated and a curve constructed showing the variation of this proportion with dilution. This variation is directly proportional to the dilution. J. F. S.

Colorimetric Estimation of Small Quantities of Metals in Foodstuffs and the Preliminary Destruction of the Organic Matter. K. K. JÄRVINEN (*Z. Unters. Nahr. Genussm.*, 1923, **45**, 183—190).—Details of a method for the destruction of the organic matter in foodstuffs, preparatory to the colorimetric estimation of small quantities of metals are given. The organic

matter is oxidised with strong nitric acid (*d* 1.40) in a Kjeldahl digestion flask. Sulphuric acid is added after a preliminary oxidation with nitric acid alone. Oxides of nitrogen are afterwards removed by dilution with water and boiling and sulphites by the addition of sodium thiosulphate and burning off the sulphur precipitated. Ten g. of organic dry matter can be completely destroyed in one to three hours and the method is suitable for use in estimating all metals except mercury, which is volatilised during the destruction of the organic matter. Details of colorimetric methods of estimating a few mg. of the following metals in 100 g. of foodstuffs are given: tin and lead in the presence of one another, copper and zinc in the presence of one another, aluminium, nickel, arsenic (in carpets, etc.), and antimony. The methods depend on the colour developed by passing hydrogen sulphide or adding sodium sulphide to the solution containing the metal after the removal of all organic matter and oxidising and reducing substances, and comparing it with the colour of a standard solution of the same metal treated under exactly similar conditions. The deposition of finely divided sulphur is prevented by the addition of 50% alcohol. Very accurate results were obtained in this way.

H. C. R.

Microscopic Characterisation of the Picrates and Tartrates of Potassium and Sodium. ED. JUSTIN-MUELLER (*J. Pharm. Chim.*, 1923, [vii], 28, 15—17).—The picrates of potassium and sodium, although similar macroscopically, are easily distinguishable microscopically, sodium picrate forming slender, yellow needles and potassium picrate long, yellow prisms. With tartaric acid, potassium salts give a precipitate visible to the naked eye only at a certain concentration, whilst with sodium salts the tartrate formed is never visible microscopically. The salt formed may, however, be identified by microscopic examination of the sediment after standing or centrifuging. Potassium tartrate forms abundant lozenges, sodium tartrate octagonal plates and clinorhombic prisms. Sketches of the crystals are given.

W. T. K. B.

The Kramer-Tisdall Method for the Estimation of Calcium in Small Amounts of Serum. FREDERICK F. TISDALL (*J. Biol. Chem.*, 1923, 56, 439—441; cf. A., 1921, ii, 595).—Removal of the supernatant fluid from the calcium oxalate precipitate by decantation is simpler than using a siphon as originally described. E. S.

Analysis of Calcium Phosphate. ROKURO NAKASEKO (*Mem. Coll. Sci. Kyoto*, 1923, 6, 157—164).—A method for the simultaneous estimation of calcium and phosphoric acid in calcium phosphate is described. The calcium is precipitated as oxalate from an acetic acid solution, and the phosphoric acid in the filtrate from the calcium oxalate is precipitated as ammonium manganese phosphate, after the excess of oxalic acid has been destroyed by the addition of the requisite quantity of potassium permanganate. Secondary and tertiary phosphates in a mixture may be estimated by titration with *N*/10-acid, using methyl-orange as indicator. The titration of primary calcium phosphate, after it has been rendered neutral

towards methyl-orange with standard alkali solution, using phenolphthalein as indicator, yields untrustworthy results. W. P. S.

Estimation of Barium as Oxalate. BARBU N. ANGELESCU (*Bull. Soc. Chim. România*, 1923, **5**, 12—15).—A solution containing from 0.20 to 0.25 g. of the barium salt is mixed with three times its volume of alcohol, and ammonium oxalate solution is added. The mixture is heated on a water-bath for fifteen minutes and, after a further sixty minutes, the precipitated barium oxalate is collected on a filter, washed with 75% alcohol, dried at 70°, and weighed; 0.002 g. is added to the weight found as an allowance for the solubility of the barium oxalate. W. P. S.

Detection and Estimation of Mercury in Gauze Dressings. ET. BARRAL (*J. Pharm. Chim.*, 1923, [vii], **28**, 49—51).—In order to effect complete solution of the mercury the gauze is heated with eight to ten times its weight of dilute aqua regia containing 10% of strong hydrochloric acid and 2% of strong nitric acid. The warm liquid is filtered and evaporated nearly to dryness. Evaporation must be carried out at room temperature (or a maximum of 40—45°) to avoid loss of mercuric chloride by volatilisation. The slightly moist residue is tested with (a) stannous chloride, (b) diphenylcarbazide in benzene solution (after neutralising with a little sodium hydrogen carbonate), (c) potassium iodide, sodium carbonate, and ammonia, and (d) hydrogen sulphide. The above method of extraction may also be employed for the estimation of the mercury present in the gauze, but an accuracy greater than 5% is not obtainable. W. T. K. B.

Colorimetric Methods with the Aid of Wilhelm Ostwald's Colour Standards. F. V. VON HAHN (*Z. angew. Chem.*, 1923, **36**, 366—369).—By the application of the Ostwald colour standards, colorimetric analysis is simplified and the necessity for preparing and keeping a number of standard colour solutions obviated. A known thickness of the coloured solution, contained in a cell, is illuminated from below by normal white light of the same intensity as that falling on the colour scale, and the two are viewed simultaneously through a tube into which a suitable colour filter can be inserted. By varying the filter and comparing with the standard colour scale, the colour of the solution is analysed into its components and so characterised. Details and tables for the colorimetric estimation of copper (as cuprammonium or potassium copper ferrocyanide), manganese (as permanganic acid), and lead (as colloidal lead sulphide) are given, and a "colorigram," with a triangular system of co-ordinates, drawn. The light used may with advantage be polarised, especially when artificial light is employed. W. T. K. B.

Detection and Separation of Indium. ISABURO WADA and SUNAO ATO (*J. Chem. Soc. Japan*, 1923, **44**, 1—36).—When the residue obtained by evaporation of an aqueous solution of indium nitrate is heated at 120° during one hour, the element does not form any dehydrated compound insoluble in nitric acid,

thus differing from the metals of the tungsten and columbium group. Indium cannot be separated from other elements by distillation of the bromide from its hydrobromic acid solution, or by precipitation of its chloride. In neutral solution, indium is completely precipitated by hydrogen sulphide, even when it is present alone. When mixed with the elements of the hydrogen sulphide group, indium is largely precipitated by hydrogen sulphide if the concentration of the acid in the solution is less than $0.3N$, but to a very slight extent only if the concentration is $0.6N$. In $0.6N$ -acid solution the elements of the hydrogen sulphide group are nearly completely precipitated by sufficient excess of hydrogen sulphide, only a small quantity, with practically all the indium, remaining in the filtrate. From this filtrate on dilution with an equal volume of water all the elements of the hydrogen sulphide group are completely precipitated with a very small quantity of indium. The indium present in the precipitate is separated together with bismuth from the other metals. Platinum, iridium, rhodium, ruthenium, etc., are not completely precipitated under the same conditions, but are precipitated on heating the solution (acidity $1N$), after saturation with hydrogen sulphide, in a pressure bottle in boiling water for one hour. The bismuth can be almost completely separated from indium by hydrolysis, the small quantity remaining in solution being precipitated as sulphide from $0.6N$ -acid solution. Indium behaves like titanium and zirconium with ammonia and ammonium sulphide, sodium hydroxide, peroxide, or carbonate or treatment with ether. It can be separated from the two elements by means of tartaric acid, ammonia, and ammonium sulphide.

K. K.

Treatment of Permanganate Solutions for Volumetric Analysis. G. BRUHNS (*Chem. Ztg.*, 1923, **47**, 613—615; cf. A., 1906, ii, 577).—A discussion of the preparation and use of standard solutions of potassium permanganate for volumetric analysis, with reference to their stability.

A. A. E.

Titration of Solutions of Permanganate and Sodium Arsenite. WILLIAM T. HALL and CARL E. CARLSON (*J. Amer. Chem. Soc.*, 1923, **45**, 1615—1620).—The estimation of manganese in steel by the method of oxidation to permanganate and titration with sodium arsenite solution has been investigated. It is shown that under the conditions which usually prevail in the analysis of steel, the electrometric titration of permanganate with sodium arsenite solution causes the manganese to be reduced from a valency of seven to an average valency of 3.3 when the bismuthate method is used. This result is in agreement with the results of Rose (A., 1919, ii, 36) and Geloso (A., 1921, ii, 115). The reaction may be expressed $6\text{MnO}_4' + 11\text{H}_2\text{AsO}_3' + 15\text{H}^+ \rightarrow 2\text{Mn}^{++++} + 4\text{Mn}^{+++} + 11\text{HAsO}_4'' + 13\text{H}_2\text{O}$. The reduced condition corresponds with an oxide, Mn_3O_5 , but it is improbable that such an oxide actually exists. The colour of the solution indicates the presence of tervalent manganese and the fact that manganese dioxide often separates on keeping shows that the quadrivalent manganese readily assumes the condition of colloidal dioxide and finally forms the gel. Probably this reaction takes place

thus : $2\text{Mn}^{++++} + 4\text{Mn}^{+++} + 8\text{H}_2\text{O} \rightarrow 2\text{Mn}^{++} + 4\text{MnO}_2 + 16\text{H}^+$. The fact that halide causes a more complete reduction of the manganese is in accord with the usual behaviour of hydrogen halide in permanganate titrations. It prevents the formation of colloidal dioxide and keeps the manganese in a more reactive condition. The electro-metric titrations show that when arsenite is titrated with permanganate in 2.5*N*-sulphuric acid solution the manganese is reduced to an average valency of 2.5, $4\text{MnO}_4' + 9\text{HAsO}_3'' + 14\text{H}^+ \rightarrow 2\text{Mn}^{++} + 2\text{Mn}^{+++} + 9\text{HAsO}_4'' + 7\text{H}_2\text{O}$. Whenever the reaction between permanganate and arsenite is used in practice to determine either manganese or arsenic, it is important to direct attention to such details as temperature, acid concentration, and presence of halide or manganous salt, and to standardise the solutions under exactly the same conditions as prevail in the analysis. J. F. S.

Alleged Influence of Silicic Acid Hydrosol on the Volumetric Estimation of Iron in Hydrochloric Acid Solution. L. BRANDT (*Z. anal. Chem.*, 1923, **62**, 417—450).—The alleged action of silicic acid hydrosol in inhibiting the oxidation of hydrochloric acid by permanganate in titrations of iron has been completely investigated anew (cf. Schwarz and Rolfes, A., 1919, ii, 170; Schwarz, A., 1919, ii, 480; 1920, ii, 389; Brandt, A., 1919, ii, 373, 428; 1920, ii, 269). It has now been found that commercial water-glass contains oxidisable impurities which tend to give erratic results, but the addition of a pure silicic acid sol made from silicon tetrachloride has no inhibiting action on the liberation of small amounts of free chlorine in side reactions. It is definitely proved that the addition of silicic acid sol has no influence on the results obtained in titrating ferrous chloride with permanganate either in the presence or absence of manganese sulphate. A. R. P.

Gravimetric and Volumetric Methods for the Estimation of Tin in Alloys. ANTONÍN JÍLEK (*Chem. Listy*, 1923, **17**, 24—27; cf. this vol., ii, 186, 436).—The stannic oxide obtained in the analysis by Czerwek's method of tin alloys does not adsorb copper or lead salts, but can adsorb considerable quantities of antimony, particularly if potassium is present in solution. Thus the addition of potassium antimonyl tartrate to the solution from which the stannophosphate is precipitated gives results which may be as much as 17.5% high. This error can be diminished by thorough washing of the stannophosphate with a solution of the same composition as that recommended by Czerwek for the solution of bearing metal, instead of dilute nitric acid, which he used. With the modified method, results obtained are 1% high for alloys containing above 60% of tin, accurate for alloys containing about 14% of tin, and low for those containing less tin than this. R. T.

New Characteristic Microchemical Reaction for the Detection of Antimony and Tin. ANDREI P. ORODOCSU and (MILE) MARCELLE RESSY (*Bull. Soc. chim.*, 1923, [iv], **33**, 991—994).—A drop of the solution under investigation is placed on a microscope

slide side by side with a drop of a solution of sodium chloride containing 17 g. per litre. The drops are made to coalesce and are allowed to crystallise. The presence of tin is indicated by the appearance of six-pointed stars of the composition $2\text{SnCl}_2, 3\text{NaCl}$. Antimony appears as four-pointed stars of the composition $\text{SbCl}_5, \text{NaCl}$. The forms are quite characteristic and distinctive, and are given by no other common metal. H. H.

The Electrolytic Estimation of Antimony. A. LASSIEUR (*Compt. rend.*, 1923, 177, 263—265).—Hitherto all estimations of antimony by the electrolytic method have given incorrect values (cf. Henz, A., 1904, ii, 150). The error may be avoided by using a platinum electrode on which mercury has been electrolytically deposited. The difference of electrode potentials should be of the order of 1.3 volts, and the deposit then obtained is of good adherence and may be dried at 100° for weighing. The author suggests that the excessive values obtained when antimony is deposited directly on the platinum are due to the hydrogenating properties of the latter element. H. J. E.

Hexamethylenetetramine as a Reagent in Microscopic Qualitative Chemical Analysis. HOWARD IRVING COLE (*Philippine J. Sci.*, 1923, 22, 631—637).—Solutions in hydrochloric acid of salts of antimony, bismuth, cadmium, gold, iridium, mercury, palladium, platinum, tin, and silver (in nitric acid solution) give characteristic crystalline precipitates with hexamethylenetetramine, whilst solutions of salts of antimony, bismuth, cadmium, palladium, platinum, and tin also give characteristic precipitates, usually at greater dilutions, if potassium iodide is added as well as hexamethylenetetramine. Crystalline compounds not sufficiently characteristic for identifying the metals are also formed in the presence of calcium, iron, magnesium, manganese, and titanium. Hydrochloric acid, nitric acid, and sulphuric acid alone give crystalline precipitates with hexamethylenetetramine and potassium iodide, but the crystals are easily distinguished from those formed in the presence of any of the above metals. The procedure recommended for applying the test is to add a fragment of solid hexamethylenetetramine to a drop, 2—4 mm. in diameter, of the solution to be tested, and then to examine the solution under a low-power microscope, a fragment of potassium iodide being added subsequently if necessary. A description is given of the shape, colour, and effect on polarised light of the characteristic crystalline compounds, and photographs of most of them are reproduced. The test is most sensitive with antimony and bismuth, the addition of potassium iodide enabling these metals to be identified at dilutions of 1 : 15,000 and 1 : 100,000, respectively. L. A. C.

Titration of Very Small Amounts of Gold. W. B. POLLARD (*Bull. Inst. Mining Met.*, 1923, 223).—For the estimation of quantities of gold up to 5 mg., the metal is dissolved in 2 c.c. of aqua regia, the liquid being carefully boiled, the flask meanwhile being rotated, until only one or two drops remain. In order to avoid

deposition of gold after dilution, nitrous acid must be removed by the addition of 2 c.c. of 1% paraldehyde solution, the fumes blown out of the flask, and the liquid allowed to remain for two minutes. Twenty-five c.c. of water are then added, together with 1 c.c. of a 0.1% solution of *o*-tolidine in 10% hydrochloric acid, and a small quantity of a dilute solution of silver nitrate as catalyst. The liquid is then titrated with 0.01*N*-*p*-methylaminophenol sulphate in 2% hydrochloric acid, the mixture finally being gently heated. Titration may be repeated on the same sample after evaporation to dryness, treatment with aqua regia, and repetition of the process. In the presence of iron, ammonium fluoride must be added; large quantities of copper cause somewhat high results. With the *o*-tolidine reagent, it is possible to detect gold by the development of a yellow or brown colour at a dilution of 1 in 2×10^7 .

CHEMICAL ABSTRACTS.

Estimation of the Easily Dehydrated Alcohols in Essential Oils. L. S. GLICHITCH (*Compt. rend.*, 1923, 177, 268—270).—The estimation of such alcohols as linalool and terpineol by acetylation with subsequent estimation of the ester formed is inaccurate owing to the incompleteness of the first stage by reason of the dehydration of a portion of the alcohol. Dilution of the reaction mixture with an inert solvent (Boulez, A., 1907, ii, 306; Schimmel & Co., A., 1907, ii, 782) diminishes but does not eliminate the error. By treatment of the alcohols with a mixture of acetic anhydride and formic acid at the ordinary temperature the alcohols are converted into formates (cf. Béhal, A., 1899, i, 734; 1900, i, 580) and these may be employed to obtain correct values by saponification in the usual way. Comparative results obtained by the normal method of acetylation, acetylation in presence of xylene, and by the above method are given.

H. J. E.

Reaction of α - and β -Naphthol with Sodium. HERMANN KUNZ-KRAUSE (*Chem. Ztg.*, 1923, 47, 646).—0.01—0.1 G. of the naphthol is dissolved in a few c.c. of absolute alcohol and thin pieces of sodium are dropped in as long as they will dissolve, the tube being cooled in water. In the case of α -naphthol, only a pale bluish-green colour is produced with a faint fluorescence, but with β -naphthol a deep royal blue colour appears, with a bluish-violet fluorescence. Further additions of sodium change the colour to olive-green, brown, and orange, in that order. The fluorescence remains throughout these colour changes. This test is recommended as superior to the ammonia test in aqueous solution for distinguishing between α - and β -naphthol.

H. C. R.

Rapid Reduction Method for the Estimation of Sugar in Blood. G. DENIGÈS (*Compt. rend. Soc. Biol.*, 1922, 87, 1283—1285; from *Chem. Zentr.*, 1923, ii, 607—608).—The use of trichloroacetic acid for the removal of proteins from blood prior to estimation of sugar with Fehling's solution is inapplicable. A solution containing 29 g. of sodium chloride in 71 g. of water containing 10% of trichloroacetic acid is recommended for this purpose.

After adding this solution to an equal volume of blood or serum the mixture is shaken and placed for three minutes on a boiling water-bath. After clarifying by centrifuging and making up to the original volume, one-tenth by volume of sodium hydroxide solution is added. The mixture is added to 1 c.c. of boiling Fehling's solution (Bonnans), containing ferrous cyanide and the boiling continued. For the completion, if necessary, of the reduction of the Fehling's solution, a solution of dextrose containing 0.36 g. in 10 c.c. of water is used. The reaction is not affected by the precipitate of calcium phosphate obtained on neutralisation.

G. W. R.

Inositol. I. A Method of Estimation. JOSEPH NEEDHAM (*Biochem. J.*, 1923, **17**, 422—429).—The tissues are extracted with dilute aqueous acetone, and from this the inositol is precipitated with a saturated basic lead acetate solution. The precipitate is then decomposed with hydrogen sulphide, filtered, and the inositol in the filtrate is further precipitated with alcohol and is estimated by determining the carbon in it, utilising the author's micro-method (cf. this vol., ii, 655). Inositol of ox muscle is identical with that produced by the hydrolysis of phytin.

S. S. Z.

Comparative Experiments on the Different Methods of Estimating Maltose formed by the Fission of Starch. K. JOSEPHSON (*Ber.*, 1923, **56**, [B], 1758—1761).—The results obtained by Bertrand's method in following the course of the fission of starch by amylase are uniformly trustworthy; the process does not appear to be inferior to the hypoiodite method of Willstätter and Schudel (*A.*, 1918, ii, 337). The main advantage of the latter procedure lies in the possibility of estimating aldehydic in the presence of ketonic sugars, if other substances which react with iodine are absent.

In the estimation of maltose in pure aqueous solution, the data obtained by Bertrand's process are uniformly somewhat higher than those obtained by the hypoiodite method. In general, slightly high results are obtained in estimating sugars by Bertrand's solutions which have been preserved during some months. In the estimation of maltose formed by the action of malt amylase on starch, the results obtained by the hypoiodite process are uniformly slightly lower than those by the Bertrand method; it appears possible that a slight, systematic error is inherent to the former procedure.

H. W.

Comparison of Methods of Estimating Starch. K. ALPERS and H. ZIEGENSPECK (*Z. Unters. Nahr. Genussm.*, 1923, **45**, 163—174).—Twelve different methods of estimating starch in flours and brans were tested and the results obtained are given in a table. All the methods suffered from certain disadvantages, some being troublesome and some giving inaccurate results. Mayrhofer's gravimetric method (*A.*, 1897, ii, 525) gives accurate results only with pure starches and fails in the case of foodstuffs like flour containing bran or substances yielding pentosans. This method

can, however, be employed in the case of sausage meats containing pure starch, but care must be taken that errors do not arise from the incomplete solution of the starch in the aqueous alkali. A method based on the estimation of the dextrose produced after treating the sample with alcoholic potassium hydroxide is also only applicable to pure starches. This method is preferable to that of Mayrhofer for estimations of starch in sausage meats. The results of estimations of starch in flours and brans by both these methods are much increased by the pieces of husk in the samples. The polarisation methods of Lintner and Belschner and of Evers are recommended on account of their simplicity. It is occasionally difficult to obtain a sufficiently clear solution for the polarimeter in Lehmann and Schowalter's polarisation method. The possible error of polarisation methods is assessed at more than 3%. When estimating starch in sausage meats, the possible decomposition of the starch by ferments and bacteria must not be overlooked.

H. C. R.

Estimation of Lactic Acid in Blood. J. J. R. MACLEOD [with M. E. ARMOUR] (*J. Lab. Clin. Med.*, 1923, 7, 635—642).—A modification of Fürth and Charnass's method (A., 1910, ii, 807). Proteins are precipitated from 25—50 c.c. of blood mixed with 100 c.c. of 2% hydrochloric acid by the addition of 5% mercuric chloride solution; dilution is followed by filtration and removal of the mercury as sulphide. An aliquot portion is nearly neutralised and evaporated below 40°, and then extracted with ether mixed with sodium hydroxide solution in a Dunbar apparatus, after addition of ammonium sulphate and phosphoric acid. After removal of the ether below 50°, the alkaline sodium lactate is distilled with 0.5% sulphuric acid in presence of potassium permanganate into a standard solution of potassium hydrogen sulphite, which is then titrated against iodine solution. Each 1 c.c. of 0.1*N*-iodine solution corresponds with 0.05 c.c. of 0.1*N*-lactic acid.

CHEMICAL ABSTRACTS.

Some Causes of Error in the Estimation of β -Hydroxybutyric Acid. CH. O. GUILLAUMIN (*Bull. Soc. Chim. biol.*, 1923, 5, 426—431).—The most practical method for the estimation of β -hydroxybutyric acid is that of Van Slyke (A., 1918, ii, 86). The blank estimation should not be carried out, since the value so obtained is usually due to the oxidation of some of the β -hydroxybutyric acid under the influence of the mercuric reagent. E. S.

A Modified Test for Phthalates, with Particular Reference to the Detection of Ethyl Phthalate. R. E. ANDREW (*Ind. Eng. Chem.*, 1923, 15, 838).—Ethyl phthalate is used as a denaturant for alcohol for certain purposes. The resorcinol test as generally given is not trustworthy, since a satisfactory blank cannot be obtained. In carrying out the test, it is necessary to avoid heating after adding acid to the resorcinol mixture. Ten c.c. of the solution to be tested are evaporated with 5 drops of a 10% solution of sodium hydroxide on a steam-bath, 0.5 c.c. of a 5%

solution of resorcinol is added, and the liquid again evaporated to dryness. It is removed from the bath and 6 drops of concentrated sulphuric acid are at once added and mixed thoroughly. When cool, 10 c.c. of water are added and it is transferred to a test-tube with 10 c.c. of wash water; 5 c.c. of 10% sodium hydroxide solution are added, when a green fluorescence will show the presence of phthalate.

E. H. R.

Precipitation of Tannic Acid by Gelatin. ARTHUR W. THOMAS and ALEXANDER FRIEDEN (*Ind. Eng. Chem.*, 1923, **15**, 839—841).—Gelatin is completely precipitated by gallotannic acid when the ratio of tannin to gelatin is not less than 2 : 1 and the gelatin-tannin precipitate is not soluble in excess of tannic acid. The optimum hydrogen-ion concentration for gallotannic acid is p_H 4.4—4.6, but there is a definite hydrogen-ion concentration for each sort of vegetable tannin for optimal precipitation. If the solution is not adjusted to near this value, the precipitate may fail to form. The presence of a neutral electrolyte broadens the range of hydrogen-ion concentration for precipitation, but does not increase the sensitiveness of the reaction at the optimum hydrogen-ion concentration. Under the best conditions, tannin can be detected at dilutions as high as 1 : 100,000—200,000, depending on the source of the tannin. The ageing of gelatin solutions has no effect on the sensitiveness in testing for tannin, provided bacterial action is prevented.

H. C. R.

Identification of Cacao Butters by Curves of Miscibility. MARANGE (*Compt. rend.*, 1923, **177**, 191—194).—Extending the work of Louise (A., 1911, ii, 548, etc.), the author studies the miscibility curves for mixtures, with aniline and alcohol, of various pure and adulterated cacao butters, and shows that these curves afford a ready indication as to the purity of the sample examined. E. E. T.

Schiff's Rosaniline-Sulphurous Acid Reaction for Aldehydes. KARL JOSEPHSON (*Ber.*, 1923, **56**, [B], 1771—1775).—Schiff's reaction can be applied to aldehydes only under definite conditions with regard to the acidity of the solution; the development of a not too weak violet coloration is regarded as a fairly definite proof of the presence of the aldehydic group.

A red coloration is caused by a number of organic substances, which in all probability do not contain the aldehydic groups. The tint is identical with that of rosaniline solutions. The effect is attributed to the withdrawal of a portion of the sulphurous acid from combination with rosaniline (to form salt-like compounds with the proteins), whereby rosaniline is liberated. A red coloration is also developed when Schiff's solution is treated with phosphate buffer solutions of P_H 4.5—7.8, the maximum intensity being observed at P_H 5.9—6.1.

H. W.

The Titration of Sodium Formaldehydesulphoxylate. BERNARD SALKIN (*Ind. Eng. Chem.*, 1923, **15**, 848—849).—Contrary to what has been stated (cf. Heyl and Greer, A., 1922, ii, 288), sodium formaldehydesulphoxylate can be titrated with

ammoniacal copper sulphate or with iodine with concordant results. The method of analysis now described involves three titrations, one with copper sulphate and two with iodine, from the results of which may be calculated the sodium formaldehydesulphoxylate, hyposulphite and hydrogen sulphite-formaldehyde present. In the first titration, the solution of the sample (15 g. in 100 c.c.) is run into a standard solution of copper sulphate (125 g. of crystals per litre) made strongly ammoniacal, at 55° (1 mol. of $\text{CuSO}_4 \equiv 0.5$ mol. of hyposulphite or 0.5 mol. of sulphoxylate). For the second titration, 25 c.c. of a solution of the sample (6 g. per litre) are titrated with 0.1*N*-iodine solution, 2 c.c. excess of the iodine solution are added, and after five minutes titrated back with thiosulphate solution. In this case, 1 mol. of iodine $\equiv 1/6$ mol. of hyposulphite or 1/4 mol. of sulphoxylate. These two titrations taken together give both hyposulphite and sulphoxylate. In the third titration 50 c.c. excess of 0.1*N*-iodine solution over that used in the second titration are added to 25 c.c. of the sample solution, followed by sodium hydroxide solution to give a yellow colour. After ten minutes, the solution is acidified and titrated back with thiosulphate. From the number of c.c. of iodine consumed, one and a half times the number of c.c. used in the second titration are subtracted. The difference is the equivalent of the sodium hydrogen sulphite-formaldehyde present. All the titrations must be made in absence of air.

E. H. R.

Estimation of Aldehydes and Ketones in Essential Oils.

C. T. BENNETT and F. C. L. BATEMAN (*Perf. and Essent. Oils Rec.*, 1923, 14, 268).—A critical examination of the two methods generally adopted for the estimation of aldehydes and ketones in essential oils, namely the "bisulphite" method and the "neutral sulphite" method.

E. M. V.

Some Observations on the Detection of Acetone in Urine.

B. A. VAN KETEL (*Pharm. Weekblad*, 1923, 50, 833—836).—The methods of Legal and le Nobel are not very sensitive, but the modification of Rotheva gives much better results. The ammonia used must be free from acetone; ammonia often contains traces of acetone, which may be due to its preparation from plant residues or from turf. Acetoacetic acid, which may be present in the urine of persons suffering from diabetes, readily forms acetone, and may thus invalidate the test, but β -hydroxybutyric acid does not give a positive result with the ordinary methods.

S. I. L.

Estimation of Acetone and of Ethyl Alcohol in Mixtures of the Two. J. H. BUSHILL (*J. Soc. Chem. Ind.*, 1923, 42, 216—218*T*).—The acetone is estimated iodometrically by the method described by Rakshit (A., 1916, ii, 544); the quantity of alcohol present is calculated from the specific gravity of the mixture after allowance has been made for the acetone. Tables are given, showing the specific gravity of solutions containing small quantities of acetone and alcohol.

W. P. S.

Volumetric Estimation of Acetone. AL. IONESCU, (MILE) ELISE SPIRESCU, and D. POPESCU (*Bul. Soc. Chim. România*, 1923, **5**, 15—21).—Ten c.c. of acetone solution (about 0.5%), 10 c.c. of 50% sulphuric acid, 10 c.c. of mercuric sulphate solution (50 g. of mercuric oxide dissolved in 200 g. of sulphuric acid and diluted to 1 litre), and 100 c.c. of water are boiled together in a reflux apparatus for twenty minutes. The precipitate is then collected on a filter, washed with 200 c.c. of water, transferred to a flask and dissolved by heating with 25 c.c. of a mixture of sulphuric acid and nitric acid (sulphuric acid, 2 parts, nitric acid, 1 part). The solution is treated with a few drops of permanganate solution to destroy nitrous compounds, diluted with 100 c.c. of water, 12 drops of 10% sodium nitroprusside solution are added, and the turbid mixture is titrated with *N*/10-sodium chloride solution, the disappearance of the turbidity denoting the end-point of the titration. Each c.c. of *N*/10-sodium chloride solution is equivalent to 0.0028 g. of acetone; this factor is found by actual experiment with pure acetone and is higher than the theoretical value (0.002348).

W. P. S.

Estimation of Tryptophan. GEORGE E. HOLM and GEO. R. GREENBANK (*J. Amer. Chem. Soc.*, 1923, **45**, 1788—1792).—Some of the difficulties and errors in the various methods previously used are indicated. The effect of temperature and time on the reaction of tryptophan with *p*-dimethylaminobenzaldehyde in 20% hydrochloric acid has been studied. In this concentration of acid, the reaction requires greater time than is generally supposed. Thus at 37° about eight days are necessary. At higher temperatures, the time required for the development of the colour is less, but the colour is then less stable. Pure tryptophan in solution can be accurately estimated by this method (cf. May and Rose, this vol., i, 160). Experiments on casein, fibrin, and Witte's peptone show that the tryptophan content of proteins can also be accurately estimated by this method without previous hydrolysis of the protein, but apparently an enzyme-digested protein is more suitable. There is excellent agreement between the tryptophan content of fibrin as estimated by the colorimetric method (5.00%), and as found by the "humins" formation method (5.05%) of Gortner and Holm (*A.*, 1918, i, 84).

W. S. N.

Estimation of Urea by Urease. GEORGE MACFEAT WISHART (*Biochem. J.*, 1923, **17**, 403—405).—A method based on treating urea with soja bean meal in presence of sodium carbonate and blowing over the ammonia into standard acid. The method is accurate to less than 1%.

S. S. Z.

Estimation of Blood Urea. JEANETTE ALLEN BEHRE (*J. Biol. Chem.*, 1923, **56**, 395—404).—In the estimation of urea in whole blood, considerably higher (50%) results may be obtained when concentrated extracts of soja bean are used than when dilute extracts are employed. This is possibly due to the presence in the soja bean, in small concentration, of a second enzyme which produces

ammonia from some constituent of blood other than urea. This constituent is present mainly in the corpuscles; it does not diffuse through collodion. Blood filtrates, obtained by heat coagulation or by precipitation with tungstic acid, do not give increased values for urea with increased concentrations of extract. E. S.

Application of the Diazotisation of the Benzoyl'Group in the Toxicological Detection of Alkaloids. HENRI PECKER (*J. Pharm. Chim.*, 1923, [vii], **28**, 13—15).—Guerbet's method for the detection of alkaloids containing benzoyl groups (cf. A., 1920, ii, 517) is inapplicable in the presence of ptomaines, since the latter alone can give rise to the characteristic orange colour.

W. T. K. B.

Preparation and Comparison of Standards for the Estimation of Creatine and Creatinine. GRAHAM EDGAR (*J. Biol. Chem.*, 1923, **56**, 1—6).—Of the various substances which have been proposed as standards for the estimation of creatine and creatinine by Folin's colorimetric method (A., 1914, ii, 505), creatinine zinc chloride and creatinine picrate are considered to be the most suitable since they are readily obtained pure. Creatinine zinc chloride can be readily prepared by fusing commercial creatine with anhydrous zinc chloride. E. S.

Physiology and Pathology of the Bile'Secretion. I. Estimation of the Bile Acids in Human Duodenal Bile. F. ROSENTHAL and M. FREIHERR VON FALKENHAUSEN (*Arch. expt. Path. Pharm.*, 1923, **98**, 321—338).—The various methods for the estimation of the bile acids are reviewed and a new method, suitable for clinical use, is described in which the gasometric method of Foster and Hooper (A., 1919, ii, 376) is combined with a sulphur estimation of the alcohol-soluble fraction of the bile. When applied to human bile, the gasometric estimation gives the total glycine and taurine derived from the bile acids, whilst the sulphur estimation gives the amount of taurocholic acid present. The value for glycocholic acid is then obtained by calculation. E. S.

Means for Differentiating between Chondrin and Glutin. M. A. RAKUZIN (*Chem. Ztg.*, 1923, **47**, 602).—Chondrin gives a very opalescent solution which gives the xanthoproteic reaction, whereas gluten gives a clear transparent solution in concentrations up to 0.75% which is not coloured by nitric acid. A hot 10% gelatin solution containing chondrin is immediately gelatinised by the addition of a saturated solution of chrome alum. A 0.2% chondrin solution shows no appreciable difference on addition of barium chloride owing to the already strong opalescence; if, however, the solution is stirred with 10% of aluminium hydroxide and filtered, the filtrate gives an immediate precipitate with barium chloride of the barium salt of chondroitinsulphonic acid ($[\alpha]_D = +46.5^\circ$). A gelatin solution gives an immediate precipitate with barium chloride. A. R. P.

Preservative Principles of Hops. III. THOMAS KENNEDY WALKER (*J. Inst. Brewing*, 1923, **29**, 379—399; cf. this vol., i, 78).—Light petroleum does not appear to be a suitable solvent for the extraction of hops, as it is slow in its extractive action and, indeed, fails to extract the resins thoroughly in the cold, and is, moreover, liable to hasten the resinification of the β -acid. The author finds that extraction with methyl alcohol gives better results and a method is described for estimating the soft resins in hops by means of this solvent; the method gives higher results than those in common use. T. H. P.

Colorimetric Estimation of Hydrogen-ion Concentration in Soils. C. T. GIMMINGHAM (*J. Agric. Sci.*, 1923, **13**, 69—73).—A difficulty in the estimation of hydrogen-ion concentration in soil extracts has been due to their turbidity. The author has used the displacement method of Parker (A., 1922, i, 511), whereby it is possible to obtain comparatively clear liquid suitable for colorimetric hydrogen-ion estimations. Comparison of the results with those obtained electrometrically shows a fair agreement. In some cases, however, the hydrogen-ion concentration estimated colorimetrically on the first, clear, portion of the percolate showed a less satisfactory agreement with the electrometric figure than that determined on the later, more turbid, portions. G. W. R.

Estimation of Humus in Soils. V. AGAFONOFF (*Compt. rend.*, 1923, **117**, 404—406).—A comparison of three methods of estimating the humus content of soils: (1) The ignition method, taken as giving standard results, (2) Simon's method (this vol., ii, 506), and (3) the sulphuric-chromic acid oxidation method. It was found that the second method gives practically the same results as method (1), whilst being much less tedious. Method (3) gives low results, which falls in line with Simon's work, and indicates that whilst all the humus substances in some soils are oxidised under the given conditions, in other soils only a portion of the humus is oxidised. The chlorine index of a soil gives a rough indication of its humus content. E. E. T.

General and Physical Chemistry.

Open-spark Spectra and their Application in Chemical Analysis. C. AUER VON WELSBACH (*Ann. Physik*, 1923, [iv], 71, 7—11).—The author advocates the more general application of spectrum analysis, and more especially the use of open-spark spectra in chemical analysis. Attention is directed to the change occurring in the spectrum of a substance due to the presence of other substances. J. S. G. T.

Grouping of the Lines in the Secondary Spectrum of Hydrogen. K. BASU (*Phil. Mag.*, 1923, [vi], 46, 417—420).—Objections to the application of the quantum relation $h\nu=W$ to the process of molecular dissociation underlying the emission of the secondary spectrum of hydrogen are briefly reviewed. Assuming that the lines in this spectrum originate in two hydrogen nuclei separated by a definite distance, with an electron revolving about them, an expression involving amongst other factors azimuthal and radial quantum numbers, and the intra-nuclear distance is derived for the frequencies of the emitted lines. Assuming the intra-nuclear distance to be 10^{-8} cm. the author shows that the calculated frequencies fall into five classes, and that within each class there is very close agreement between the calculated and observed values of the frequencies. J. S. G. T.

The Band-spectrum of Iodine. R. MECKE (*Ann. Physik*, 1923, [iv], 71, 104—134).—Particulars are given of measurements of 130 lines constituting the heads of bands in the absorption band-spectrum of iodine. These are classified into ten series and it is shown that the frequencies of respective lines in the various series can be represented by a formula of the Deslandres type expanded as far as n^3 , namely, $\nu(n_1; n_2)=18320.97-213.76n_1+0.596n_1^2+0.0021n_1^3-80.66n_2-1.012n_2^2+0.0033n_2^3$, the values of n_1 ranging from 0 to 9, and of n_2 from -33 to +24. Particulars of wavelengths and frequencies are given for the constituent lines in the bands $\lambda\lambda$ 6781.89, 6877.36, 6837.32, and 6934.16 Å. The components may be represented by a Deslandres type of formula, thus: $\nu=\nu(n_1; n_2)-bm^2$, where the value of $2b$ deduced from measurements of one group of 50 lines is 0.0161, and from another is 0.0176, the value increasing with increase of the value of the parameter m . No evidence was obtained of the existence of P and R series of lines in the various bands. The relation of the resonance spectrum of iodine to its absorption spectrum is discussed. J. S. G. T.

The Effect of Metallic Surfaces on the Spectra of Mercury, Cadmium, Helium, and Oxygen. L. JANICKI and E. LAU (*Ann. Physik*, 1923, [iv], 7, 562—566).—Experiments carried out to ascertain the effect, if any, produced on the respective spectra of mercury, cadmium, helium, and oxygen excited in a discharge tube

by coating the constricted portion of the discharge tube with a semi-transparent layer of silver are described. In the case of the discharge in mercury vapour contained in such a tube, a mercury band-spectrum was strongly developed. In the case of the discharge in cadmium vapour, the band spectrum was more strongly developed in the silvered than in the unsilvered tube. A similar phenomenon was exhibited by the discharge in oxygen, the band spectrum being developed at a higher pressure in the silvered than in the unsilvered tube. Changes in the relative intensities of components of the line spectrum of mercury accompanied the development of the band spectrum in the vapour. No effect whatsoever was observed in the case of the discharge in helium. J. S. G. T.

Distribution of Intensity in, and Origin of the Band Spectrum of Nitrogen. H. KIRSCHBAUM (*Ann. Physik*, 1923, [iv], 71, 289—316).—Details are given of the variation with temperature of the intensities of lines in positive and negative groups of bands in the band spectrum of nitrogen, excited either in a canal-ray discharge or cathode ray discharge in the gas, the variation of temperature being effected either by external agency, or internally by electronic impacts at various gas pressures. The results indicate that the effects of high temperature in the positive column of the cathode discharge and of the impact of canal rays are the same, the respective intensities of the higher members of a band and the higher heads of bands in a group being in each case increased. It is concluded that either agency increases the amplitude of oscillation of the diatomic molecular systems originating the emission of the band spectrum. J. S. G. T.

The Band Spectrum of Carbon Monoxide. E. HULTHÉN (*Ann. Physik*, 1923, [iv], 71, 41—49).—It is shown that the wavelengths of the lines constituting the four bands $\lambda\lambda$ 5610, 5198, 4835, and 4393 Å. in the spectrum of carbon monoxide can be arranged in series, *P*, *Q*, and *R*, such that $R(m) - Q(m) = Q(m+1) - P(m+1)$, where the symbols have the customary significance. This relation is not quite so exactly satisfied by the band λ 4393 Å. as in the case of the other three bands. The relation $R(m) - Q(m) = 3.885m$ is found to hold for the bands $\lambda\lambda$ 5610, 5198, and 4835 Å., whilst for the remaining band, λ 4393 Å., the corresponding relation is $R(m) - Q(m) = 3.845m$. It is concluded that the three former bands originate in the same initial condition of the radiating molecule, whilst the bands $\lambda\lambda$ 4835 and 4393 Å. correspond with an identical final condition of the molecule. It is probable that the bands $\lambda\lambda$ 6622 and 6078 Å. belong to the system discussed. J. S. G. T.

Relation between the Spectra of Ionised Potassium and of Argon. P. ZEEMAN and H. W. J. DIK (*Ann. Physik*, 1923, [iv], 71, 199—203).—The electronic configurations of the ionised potassium atom and of argon resemble one another in that each comprises eighteen electrons, and differ only in that the nuclear charge in the case of the former is one unit greater than in the

latter case. The displacement law of Kossel and Sommerfeld (A., 1919, ii, 378) indicates that the spark spectrum of any element is related to the arc spectrum of the preceding element in the periodic table. Literature dealing with the characteristic arc and spark spectra of potassium and of argon is briefly reviewed. It is remarked that the spark spectrum of singly ionised potassium is most readily excited by means of an electrodeless ring-discharge in potassium vapour. Paulson (A., 1915, ii, 194) showed that for lines in the argon spectrum included between $\lambda\lambda$ 9233 and 3319 Å. the respective frequencies can be expressed in terms of constants B , C , and D connected by the relations $B=A+846.1$; $C=A+1649.3$; $D=A+2256.1$. The authors show that between the frequencies of lines included between $\lambda\lambda$ 6594 and 3063 Å. in the spark spectrum of potassium a similar and even simpler relation, expressed in the form $Q=P+847$; $R=P+1695$; $S=P+2542$, exists. The same numerical constant, approximately equal to 847, occurs in the expressions for A and Q , and the constant difference between succeeding members of the Q, R, S series is also equal to this constant. It is suggested that this constant has some simple physical significance.

J. S. G. T.

Series of Multiple Lines with Fourfold Rydberg Constant in the Spectrum of Potassium. KNUD AAGE NISSEN (*Astrophys. J.*, 1923, 57, 185—190).—Sixty-four lines between λ 1873 and λ 4608 have been arranged in one diffuse subordinate series, $(2p)-(md)$, and in sharp subordinate series, $(2p_x)-(ms')$, $(2p_y)-(ms'')$, $(2p_z)-(ms''')$, $(2p_x)-(ms')$, and $(2p_z)-(ms'')$. An average agreement within one unit is obtained between the observed values reduced to international vacuum wave-numbers and those computed by Ritz's formulæ. The results support Sommerfeld's suggestion that there is a relationship between the spark spectrum of an alkali and the arc spectrum of the inert gas with atomic number one less. (See also McLennan, A., 1921, ii, 667; Schillinger, *Sitzungsber. K. Akad. Wiss. Wien*, 1909, 118, II, A, 266; A., 1910, ii, 369; Nelthorpe, *Astrophys. J.*, 1919, 41, 16).

A. A. E.

The Spark Spectrum of Rubidium. H. REINHEIMER (*Ann. Physik*, 1923, [iv], 71, 162—177).—Particulars are given of 142 lines included between $\lambda\lambda$ 3320 and 7320 Å. in the spark spectrum of rubidium excited in a discharge tube containing helium at about 3 mm. pressure, and of 12 lines in the arc spectrum of the metal. The displacement law of Sommerfeld and Kossel (A., 1919, ii, 378) indicates that if the spark spectrum of rubidium is attributable to the singly ionised atom of the metal, this spectrum should be analogous in structure to the arc spectrum of krypton. A direct comparison of these two spectra is at present impossible, but the comparison may be effected by way of the neon spectrum which is known to contain 10 p -terms. In this manner it has been found possible to classify 103 lines in the spark spectrum of rubidium into series containing a large number of p -terms. This result is held to confirm qualitatively the validity of the displacement law.

J. S. G. T.

The Arc Spectrum of Lead. WALTER GROTRIAN (*Naturwiss.*, 1923, **11**, 255—256; from *Chem. Zentr.*, 1923, i, 1413—1414).—The absorption spectrum of lead at 700—800° shows a first line at 2823 Å., which is held to be due to the term corresponding with the normal lead atom. At 1100° lines occur at 3639, 3683, 4057, 2614, 2613, and 2577 Å. The line 2833 Å. is the fundamental line of a subsidiary series which occurs in emission as a transition from $2s$ to $2p_4$.
G. W. R.

Spectrum Analysis of the Rare Earths. J. M. EDER (*Ann. Physik*, 1923, [iv,] **71**, 12—18).—The main characteristics of the arc spectra of the rare elements yttrium, erbium, thulium, lutecium, neo-ytterbium, samarium, gadolinium, europium, "eurosamarium," terbium, "welsium," and holmium are discussed. The author considers the elemental character of thulium and terbium to be definitely established. That of samarium is not certain.

J. S. G. T.

The Spark Spectra of Aluminium. I and II. F. PASCHEN (*Ann. Physik*, 1923, [iv], **71**, 142—161; 537—561).—I. Particulars are given of the modes of excitation of the spectra of Al^I , Al^{II} , and Al^{III} . Various lines in the spark spectrum of doubly-ionised aluminium, Al^{III} , are classified into series and the spectrum is compared with those of Na^I , Mg^{II} , and H, the comparison confirming Bohr's conclusions relating to the electronic characteristics of these elements. In particular, it is pointed out that the ordinary spark spectrum of aluminium contains, in addition to a series of lines of the Fowler type, a series of lines analogous to those in the arc spectrum of Na^I , with the difference that Rydberg's constant, N , in the series-formula for the latter is replaced by $9N$ in the series-formula for the lines of Al^{III} , in accordance with Bohr's theory.

II. The author tabulates the intensities, wave-lengths, frequencies, and combination formulæ of about 300 lines in the spark spectrum of singly-ionised aluminium, Al^{II} . Various series of triplets in the spectrum are classified, and formulæ giving the frequencies of the series $4f_i - mf'_i$, $4p_i - ms$, $mp_i - md_j$ deduced. Similarly, values of the respective wave-lengths, frequencies, and differences of frequencies of the systems of triplets in the spectrum of chlorine excited between aluminium electrodes in an atmosphere of helium containing very little chlorine are tabulated and discussed. The spark spectrum of Al^{II} is compared with those of Mg^I and hydrogen.

J. S. G. T.

Regularities of the Spectral Lines of Iron and the Atomic Magnetic Field. H. NAGAOKA and Y. SUGIURA (*Nature*, 1923, **112**, 359).—A preliminary account of regularities observed, particularly between λ 2400 and λ 3000 Å. The results appear to support the magneton theory. It is thought that the intricate nature of the spectral lines in ferromagnetic metals may ultimately be traced to the existence of an inner atomic field.

A. A. E.

Symmetrical Series of Lines in the Spectrum of Iron.

A. HAGENBACH and H. SCHUMACHER (*Ann. Physik*, 1923, [iv], **71**, 19—40).—In continuation of previous work (*Arch. de Genève*, 1919, **1**, 231) the authors have found two pairs of symmetrical double series of lines, the symmetry relating to the frequencies of the lines in the spectrum of iron. The one pair of double series occurs towards the red end of the spectrum, the other towards the violet end. The centre of symmetry is very approximately the same for the respective members of each pair, thus for lines in the respective groups 1, 2, 3, and 4, the centres of symmetry occur at $\lambda\lambda$ 5135.395 ± 0.151 , 5132.943 ± 0.174 , 3683.04 ± 0.14 , 3682.05 ± 0.12 Å. Formulæ involving three constants and a single variable parameter are deduced for the frequencies of the lines in the various groups. There are as follows: Group I, $\nu = 194727 \pm 11412m^4 / (m^2 - 1.3544m + 13.581)^2$, $m = 3, 4, 5 \dots$; Group II, $\nu = 194820 \pm 11743m^4 / (m^2 - 0.5038m + 5.7173)^2$, $m = 2, 3, 4 \dots$; Group III, $\nu = 271515 \pm 6735m^4 / (m^2 - 0.384m + 6.48)^2$, $m = 2, 3, 4 \dots$; Group IV, $\nu = 271588 \pm 6136m^4 / (m^2 - 1.20279m + 10.4354)^2$, $m = 2, 3, 4 \dots$. The effects of pressure and of a magnetic field (Zeeman effect) on the various groups of lines are briefly discussed. The symmetrical character of the wave-lengths of certain groups of lines discovered by Gehrcke in the spectrum of iron (A., 1921, ii, 612; *Physikal. Z.*, 1922, **23**, 432) is critically examined, and the author concludes that the data available are insufficient to decide whether such symmetry is best expressed in terms of wave-lengths or frequencies.

J. S. G. T.

Regularities in the Arc Spectrum of Vanadium. W. F. MEGGERS (*J. Washington Acad. Sci.*, 1923, **13**, 317—325).—Of the 2000 lines already measured in the arc spectrum of vanadium about 15% have been now assigned to multiplets, tables of sixteen of which are given. Vanadium as a representative of Group V of the periodic classification is thus shown to conform to the alternation law of Kossel and Sommerfeld, which is now verified for arc spectra across the entire table.

A. R. P.

Tesla-luminescence Spectra. III. Some Mono-substitution Products of Benzene. WILLIAM HAMILTON MCVICKER, JOSEPH KENNETH MARSH, and ALFRED WALTER STEWART (T., 1923, **123**, 2147—2163).

Absorption Spectra of Nitrosylsulphuric Acid and of the Complex Compounds of Copper Sulphate and Ferrous Sulphate with Nitric Oxide. H. I. SCHLESINGER and ALBERT SALATHE (*J. Amer. Chem. Soc.*, 1923, **45**, 1863—1878).—The absorption spectrum of nitrosylsulphuric acid dissolved in sulphuric acid of various concentrations has been obtained and examined. The spectra show that appreciable quantities of the former remain undecomposed when the sulphuric acid is diluted to 50% with water, and that in sulphuric acid of greater concentrations relatively large amounts of nitrosylsulphuric acid are present. This result disproves one of the fundamental assumptions made by Raschig in his development of the theory of the chamber process. Absorp-

tion spectra of the complexes formed by ferrous sulphate with nitric oxide in solutions of sulphuric acid of various concentrations have been photographed. The spectroscopic data confirm the view that there are two such complexes, both of the composition $\text{FeSO}_4\cdot\text{NO}$, and show that one of them is stable when the concentration of the sulphuric acid is greater than 65%, and the other when the concentration of acid is below 50%. Absorption spectra of $\text{CuSO}_4\cdot\text{NO}$ have also been obtained and the spectra of these complex salts have been compared with those of the so-called ferrous and cupric nitrosulphonates and have been found to be identical. A preliminary investigation of the absorption spectrum of "nitrosulphonic acid" has shown it to be very similar to that of the ferrous sulphate-nitric oxide complex existing in concentrated sulphuric acid solution. This result supports the view that possibly nitrosulphonic acid should be regarded as an unstable solution of a complex compound of sulphuric acid and nitric oxide. Examination of the spectra of solutions of nitric acid in concentrated sulphuric acid, both before and after the solutions have been heated, shows that nitric acid is not readily decomposed in such solutions into nitrosylsulphuric acid, at least if the solution is not very concentrated with respect to nitric acid. The character of the absorption spectrum of nitrosylsulphuric acid favours the view that this substance is present in solution largely as nitrososulphonic acid.

J. F. S.

The Spectrophotometric Method for the Investigation of Dyes in Textile Fabrics by Transmitted Light. N. USPENSKI and G. WORONKOV (*Z. Physik*, 1923, 17, 112—116).—The application of the König-Martens polarisation spectrophotometer to the determination of the absorption curves of various dyes contained in various dyed textile fabrics—cotton, wool, and silk—is briefly described.

J. S. G. T.

Phosphorescent Zinc Sulphide. A. A. GUNTZ (*Compt. rend.*, 1923, 177, 479—482).—A study of the phosphorescence of mixed crystals of zinc and cadmium sulphides. The phosphorescence of zinc sulphide changes in colour from greenish-blue to red with increasing quantities of cadmium sulphide. With a 12%, 20%, and 30% content of the latter substance, the phosphorescence is, respectively, lemon-yellow, orange, and red. The orange phosphorescence induced by the addition of traces of manganese to zinc sulphide is neither vigorous nor persistent, whereas cadmium sulphide produces no effect unless present in fairly large quantities, and does not diminish the vigour or the duration of phosphorescence, the colour change being a light-absorption effect and not due to phosphorogenic action on the part of cadmium sulphide (cf. A., 1922, ii, 502).

E. E. T.

Chemical Constitution and Rotatory Power. VI. Influence of the Chemical Function of the Substituent Groups. MARIO BETTI (*Gazzetta*, 1923, 53, i, 417—431).—The results previously obtained (A., 1907, ii, 661, 726; 1916, ii, 279; 1921, i, 107) are summarised.

T. H. P.

Partial and Consecutive Reactions in the Photosensitive System: Quinine Sulphate, Chromic and Sulphuric Acids.

GEORGE S. FORBES, JOHN C. WOODHOUSE, and REGINALD S. DEAN (*J. Amer. Chem. Soc.*, 1923, **45**, 1891—1895).—The photochemical oxidation of quinine sulphate by chromic acid in the presence of sulphuric acid in the light emitted by a quartz mercury lamp has been investigated. With two photochemically activated reactants the total reaction velocity should be the sum of four partial reactions with four different velocity constants. One involves two activated molecular species, another only unactivated species, and two others involve one activated and one unactivated species. It is shown from the present work that species known to be activated in some reactions may give no evidence of activation in others. The concentration of a photochemically unactivated reactant is shown to be without effect on the velocity of a photochemical reaction, provided that its concentration is not so small that its reaction with activated reactants does not become the slow stage of the total process.

J. F. S.

Long-range Particles from Radium-active Deposit.

GERHARD KIRSCH and HANS PETTERSSON (*Nature*, 1923, **112**, 394—395).—By enclosing dry radium emanation mixed with oxygen in thin-walled capillaries of potassium glass or silica lined with aluminium foil (thickness $12\ \mu$) pressing well against the glass, a strong and practically constant source of hydrogen nuclei is obtained. This method has been applied to scandium, vanadium, and cobalt (as oxides), arsenic, and indium (as chlorides); these elements do not give off long-range particles (>30 cm. of air) in greater number than $3 \times$ or $4 \times N \cdot 10^{-8}$, where N is the number of α -particles from radium-C discharged within the capillary.

By spreading substances over copper foil (which, after removal of occluded gases, showed a comparatively small number of hydrogen particles, probably "neutral" particles), fairly conclusive evidence was obtained that hydrogen nuclei are emitted from silicon, glucinum (oxide), magnesium (oxide), and lithium (carbonate), the approximate maximal ranges in air being, respectively, 12 cm., 18 cm., 13 cm., and 10 cm.

A. A. E.

The β -Ray Spectrum of Uranium- X_1 and its Significance.

LISE MEITNER (*Z. Physik*, 1923, **17**, 54—66).—The β -ray magnetic spectrum of uranium- X_1 has been found to consist of three sharp lines corresponding, respectively, with values of $H\rho$ equal to 1057, 1028, and 927, and a faint band the centre of which corresponds with a value of $H\rho$ equal to 1163, H denoting the strength of the magnetic field employed measured in Gauss units, and ρ the radius of curvature (in cm.) of the respective paths of the emitted β -rays in the field. The three sharp lines originate in the L , M , and N levels and the corresponding rays are ejected by the K_α characteristic radiation of the thorium isotope uranium- X_1 excited by the primary β -rays. Individual atoms are concerned throughout the whole process of disintegration. Apart from characteristic Röntgen radiation, no γ -rays are emitted by uranium- X_1 . The

results indicate that the primary β -rays are emitted from the atomic nucleus with a definite velocity, and are in agreement with the suggestion of Rosseland (*Z. Physik*, 1923, **14**, 173) that an excited atomic system can pass to the unexcited state by the emission of one of its constituent particles in the form of a corpuscular ray as an alternative to the emission of radiation.

J. S. G. T.

The γ -Rays of Uranium-X and their Relation to Uranium- X_1 and Uranium- X_2 . OTTO HAHN and LISE MEITNER (*Z. Physik*, 1923, **7**, 157—167).—In continuation of previous work (preceding abstract), the authors have determined the absorption, by various thicknesses of lead, of the γ -rays emitted by uranium-X, and the distribution of the respective groups of rays amongst the components uranium- X_1 and uranium- X_2 . The experimental method employed eliminated the effect of β -rays from the observations. Three classes of rays were distinguished in the radiation emitted from uranium-X, and these were characterised by the following respective values of the thickness of lead required to reduce their initial activities by one-half: 9.6, 3.0, and 0.36 mm. Taken in conjunction with the results of Richardson (*A.*, 1914, ii, 160) the results indicate that four types of γ -rays are emitted by a mixture of uranium- X_1 and uranium- X_2 . Of these, the nuclear hard γ -rays (9.6 mm., 3.0 mm.) are associated with uranium- X_2 entirely, whilst the remaining group of γ -rays observed (0.36 mm.) and that observed by Richardson (half-absorption value 0.29 mm. aluminium) are associated entirely with uranium- X_1 and constitute, respectively, the characteristic *K*- and *L*-Röntgen radiation, a conclusion which is in agreement with a deduction drawn by Meitner from previous work concerned with the analysis of the β -radiation emitted by uranium-X (*loc. cit.*).

J. S. G. T.

Electrochemistry of Gases. S. C. LIND (*Amer. Electrochem. Soc.* [advance copy], 1923, 61—69).—A theoretical paper in which as a result of kinetic studies of gas reactions under ionising conditions (α -radiation), the following new principles, which are supported by recent electronic evidence may be put forward. Gaseous ions tend to form additive products with neutral molecules, which complexes are the intermediate products of gaseous electrochemical reactions. As a deduction from the above, ions do not interact, nor do molecules or atoms otherwise activated interact. Their momentary concentrations are too low; they react only with neutral or unactivated molecules. A low momentary concentration of an activated substance is capable of explaining the action of negative catalysts or inhibitors. Active ions may be destroyed by reverse action either in a uni- or multi-component system, without any effective chemical action resulting. This reversal may be prevented by a suitable acceptor. Free electrons will play a primary part in producing chemical reaction only in gaseous systems containing at least one gas with affinity for electrons. Absence of such a gas will result in a reaction with a lower *M/N* ratio than when one is present. A secondary rôle is always played by electrons in restoring final electrical neutrality.

J. F. S.

Electricity in Flames. H. A. WILSON (*Amer. Electrochem. Soc.* [advance copy], 1923, 51—60).—A theoretical paper in which the present state of knowledge on the electrical properties of flames is reviewed. The electrical conductivity of salt vapours in flames, ionic mobilities in flames, the behaviour of flames in a magnetic field, the charge carried by the ions of salt vapours at high temperatures, the electrical conductivity of flames for rapidly alternating currents, and the thermodynamical theory of ionisation at high temperatures are considered. A bibliography of the subject is appended to the paper. J. F. S.

The Quinhydrone Electrode as a Comparison Electrode. STIG VEIBEL (T., 1923, 123, 2203—2207).

Oxidation-Reduction. W. MANSFIELD CLARK (*U.S. Pub. Health Rep.*, No. 823).—A theoretical treatment of oxidation, involving the measurement of oxidation potentials. J. F. S.

Heat Losses and Chemical Action in the High-voltage, High-frequency Discharge through Air. FARRINGTON DANIELS, PAUL KEENE, and P. D. V. MANNING (*Amer. Electrochem. Soc.*, 1923, 141—151. [Advance copy]).—Experiments with a high frequency corona discharge at about 100,000 volts indicate that of the energy supplied to the discharge chamber, about 2% only was converted into chemical energy. This chemical efficiency is of the same order as that afforded by arc and other types of corona discharges in air. Short exposures to the discharge gave higher chemical efficiencies than long ones. The ratio of ozone to nitric acid produced by the discharge varied from 2.4 to 16, according to the character of the discharge, an increase of nitric acid accompanying an increase of intensity of the pink streamers, whilst uniformity of the blue corona increased the proportion of ozone. J. S. G. T.

Source of Trouble in Electrometric Measurements of Hydrogen-ion Concentration. W. T. BOVIE and WALTER S. HUGHES (*J. Amer. Chem. Soc.*, 1923, 45, 1904—1905).—It is pointed out that inaccuracies in the measurement of hydrogen-ion concentration may arise, which are due to the diffusion of mercuric chloride from the calomel electrode. This substance poisons the hydrogen electrode, slightly at first, but more as time goes on until eventually no trustworthy measurements can be made even with freshly platinised electrodes. A method of avoiding this error is described which can be used with a quadrant electrometer, which consists in closing the mouth of the calomel electrode with a very thin-walled glass bulb which is inserted in the liquid and is sufficiently conducting when an electrometer is used but not when a galvanometer is employed. J. F. S.

A Comparison of the Heating-curve and Quenching Methods of Melting-point Determinations. GEORGE W. MOREY (*J. Washington Acad. Sci.*, 1923, 13, 326—329).—Comparison of the results obtained with sodium metasilicate shows that the melting

point determined by the heating-curve method is about 2° lower than that obtained by the quenching method, which is probably the more correct. The latter point lies on the sharply rising section of the heating curve just after the section that is flattened out. [Cf. *J.S.C.I.*, 1923, Oct.]

A. R. P.

The Calorific Value of Carbon Compounds. DIMITRI KONOVALOV (T., 1923, 123, 2184—2202).

The Density of Liquids below 0° . JEAN TIMMERMANS (*Bull. Soc. chim. Belg.*, 1923, 32, 299—306; cf. A., 1912, ii, 738).—The densities between 0° and the freezing points of ammonia, phosphorus trichloride, carbon disulphide, ethyl bromide, propionitrile, ethyl alcohol, and *n*-propyl alcohol are determined. It is shown that the scale of low temperatures adopted by the French is identical with that adopted in America, but is different from the German. The rule previously enunciated, $d_{\max}/d_{\text{crit}} = d_{\text{crit}}/d_{\text{theor}}$, is confirmed.

H. H.

Metallic Cementation. H. WEISS (*Ann. Chim.*, 1923, [ix], 19, 201—275).—The author has studied the interfacial penetration of copper with nine other metals under various conditions, and, although the results show considerable variation both with temperature and with the nature of the second metal, he was able to draw certain general conclusions as to the nature and mechanism of the action. [Cf. *J.S.C.I.*, 1923, 982A.]

H. J. E.

Equilibrium of the Ternary System Bismuth-Tin-Zinc. SHEIKH D. MUZAFFAR (T., 1923, 123, 2341—2352).

The Kinetics of the Reaction between Ferrous Phosphate and Sulphur Dioxide in Phosphoric Acid Solution. SYDNEY RAYMOND CARTER and JOHN ALFRED VALENTINE BUTLER (T., 1923, 123, 2370—2380).

Inversion of Sucrose by Saccharase. H. VON EULER and K. MYRBÄCK (*Z. physiol. Chem.*, 1923, 129, 100—105).—The inversion of sucrose by purified saccharase is approximately unimolecular (cf. Kuhn, this vol., i, 401), the reaction constant at optimum p_H showing only a very slight increase with time. Michaelis's constant, $k_M = [23.75 \log (R+L)/(D+L) + 32 \times 0.305 (R-D)/(R+D)]/t$, remains very constant both for purified saccharase and for crude yeast extract.

W. O. K.

Influence of Neutral Salts on the Temperature Coefficient of Reaction Velocity. F. O. RICE and WILLIAM LEMKIN (*J. Amer. Chem. Soc.*, 1923, 45, 1896—1900).—The velocity of the reaction between iodine and acetone in the presence of nitric, hydrochloric, hydriodic, perchloric, benzenesulphonic, trichloroacetic and naphthalene-2-sulphonic acids and also in the presence of normal salts of sodium, potassium, rubidium, lithium, and magnesium has been determined at 25° and 23° , and the temperature coefficient calculated for each case. It is shown that the temperature coefficient is the same for all strong acids, and it is unaffected

by the presence of salts of the acid. The reaction has a lower temperature coefficient when catalysed by weak acids. If the acids are arranged in descending order of their strengths, this is also the order of diminishing temperature coefficients. When the reaction is catalysed by sulphuric acid, the presence of one of its salts diminishes the temperature coefficient considerably. This is probably true for all weak acids. Small quantities of about 0.01*M* of salts of the alkali metals increase the velocity slightly. There is no indication of any diminution such as might be expected on the basis of the law of mass action.

J. F. S.

Line Spectra and Atomic Structure. NIELS BOHR (*Ann. Physik*, 1923, [iv], 71, 228—288).—The quantum theory of the origin of spectral series, developed by the author, and the relation of spectra to atomic structure are reviewed.

J. S. G. T.

An Explanation of the Theory of the Rotation of the Atomic Nucleus. III. HERBERT HENSTOCK (*Chem. News*, 1923, 127, 18—21).—The author's theory (cf. this vol., ii, 477) is applied to the consideration of the structure of the oxides of the elements of groups I to IV of the periodic system. A double bond between a bivalent metal and oxygen may be formed by the juxtaposition of the faces of the respective cubic octets, the two nuclei being orientated perpendicularly to one another. In certain cases, for instance carbon monoxide, it is necessary to assume distortion of the octet. If the uncombined carbon atom has a tetrahedral form, in carbon monoxide it may have a semi-cubic, semi-tetrahedral form. The absence of free lines of force in the combined carbon atom will then account for the stability of the compound. A distorted octet must be characteristic of those atoms which have few electrons in their outer layers.

E. H. R.

Structure of the Molecule. A. PEARSE JENKIN (*Nature*, 1923, 112, 326).—The suggestion that both dynamic and static electrons take part in the formation of the molecule is applied to the cases of water and tartaric acid.

A. A. E.

A Static Model of the Hydrogen Molecule. H. STANLEY ALLEN (*Proc. Roy. Soc. Edin.*, 1922—1923, 43, 180—196).—A model of the hydrogen molecule, based on the assumption of the existence of the "quantum force," $n^2h^2/4\pi^2mr^3$, postulated by Langmuir (*Physical Rev.*, 1921, 18, 104), varying inversely as the cube of the distance, and of which the sign depends on the signs of the electrical charges involved, is described. The model possesses many of the properties of the Bohr model of the hydrogen molecule, with the important difference that the electrons are at rest relatively to the hydrogen nuclei. Of the various possible electronic equilibrium configurations, the most stable is that in which the nuclei and electrons are situated at the corners of a square, the nuclei being at the extremities of one diagonal and the electrons at the ends of the other. The length of the diagonal is 0.871 Å. and the moment of inertia of the molecule 6.261×10^{-41} c.g.s. unit. The work necessary for the complete disintegration

of the molecule corresponds with a potential difference of 30.06 volts. In the case of the charged hydrogen molecule with only one electron, the distance between the nuclei is 1.239 Å., and the ionisation potential 17.34 volts. Calculated and experimental values of the ionisation potentials are in moderately good agreement. A possible configuration for the molecule of triatomic hydrogen (Thomson, "Rays of Positive Electricity," 1921, 196), in which nuclei and electrons are disposed at alternate corners of a regular hexagon, is suggested. It is pointed out that a static model of the hydrogen molecule accords with the diamagnetic character of the element and with evidence derived from band spectra.

J. S. G. T.

The Curves of the Periodic Law. W. M. THORNTON (*Phil. Mag.*, 1923, [vi], 46, 442—448).—The minor fluctuations exhibited by the graph associated with the presentation of the periodic law, in which the densities of the elements are plotted as ordinates against the respective values of the atomic weights as abscissæ, are discussed. It is shown that the main features of the curve can be represented by a fundamental wave-form in which the amplitude and period vary; it represents the periodic change in the configuration of the outer electrons in an atom under their own forces. Superposed on this fundamental, in order to reproduce the minor fluctuations, is, after the manner employed in harmonic analysis, a smaller wave-form of double the frequency of the fundamental, the amplitude and phase of this second wave-form being chosen by inspection. It is shown that the physical and chemical properties of the elements appear to depend as much on the minor periodicity as on the fundamental. This is exhibited by a series of curves in which ordinates represent the densities of the respective elements and abscissæ represent the projections of the major harmonic curve, referred to, on the vertical axis. Properties of the elements—density, radioactivity, stability, contraction, and expansion, ductility—are discussed in connexion with these curves.

J. S. G. T.

Nature of Chemical Valency. W. NERNST (*Z. angew. Chem.*, 1923, 36, 453—455).—The hydrogen atom is the only chemical substance of the structure of which we have up to the present obtained a satisfactory and definite picture, because only in this case, that of two electrically charged units of mass, are the quantum energy relationships understood. Pauli's conception of the hydrogen molecule (A., 1922, ii, 703) as two hydrogen nuclei which may be considered as relatively at rest, around which a free electron vibrates round the surface of an ellipsoid of rotation, is considered to be a conception of the nature of valency capable of extension to all chemical compounds, although, of course, our knowledge does not enable us to supply the details in other cases. The conception is extended to the case of the theoretically simplest crystalline structure—that of hydrogen atoms—and the resultant forces exerted by the vibrating electrons are shown to be equivalent to

six subsidiary valencies arranged in space at right angles to one another. These valencies would not, however, exercise a continuous but a pulsating force, causing the positive nuclei to undergo vibrations of very small amplitude with relation to one another, even at the absolute zero of temperature. The same conception can be applied to the molecules in potassium chloride vapour, the molecule being held together by a free electron belonging to the potassium atom, travelling in an ellipsoidal path round the potassium and chlorine atoms. The distinction between polar and non-polar valency is considered to be determined by the behaviour of the free electron when the compound is decomposed. In the case of polar or dualistic compounds, the electron passes on decomposition to the other atom of the former compound and ionisation is the result. Ordinary crystals are cases of non-polar valency, the binding electrons remaining with their original partners on dissolution of partnership. Whether ionisation occurs or not will depend on the structure of the constellation of electrons associated with the atoms in question. These considerations apply only to matter in the neighbourhood of absolute zero of temperature. At higher temperatures, the matter is complicated by the superposition of heat vibrations on the simple vibrations here considered. The conception is also applicable to the conductivity of electricity through metals.

H. C. R.

Studies of Electrovalency. II. Co-ordinated Hydrogen.

THOMAS MARTIN LOWRY and HENRY BURGESS (T., 1923, **123**, 2111—2124).

The Relationship of the Tautomeric Hydrogen Theory to the Theory of Induced Alternate Polarities. FRED ALLSOP and JAMES KENNER (T., 1923, **123**, 2296—2315).

Chelate Co-ordination. J. D. MAIN SMITH (*Chemistry and Industry*, 1923, **42**, 847—850).—A criticism of Lowry's views (this vol., ii, 555) that two types of co-ordination exist, centric and cyclic; these two terms are not mutually exclusive, for all cyclic groups have centric atoms at their reacting ends. There is no need to modify the term "chelate group" until it has been proved that fundamentally different types of co-ordination exist. Lowry's criticism merely directs attention afresh to the fact, insisted on by Werner, that differences in stability in co-ordination compounds are due to differences in intensity, but not in type, of co-ordination. Against Lowry's view that ethylenediamine should not be regarded as a chelate group, evidence is quoted to show that it is, on the contrary, a chelate group of maximum activity. Morgan's idea of a chelate group is defined precisely as "a linked system of atoms which, in combination with another atom, completes a cyclic system." The resolution of the ferrous $\alpha\alpha$ -dipyridyl complex is quoted as evidence against Lowry's statement that ring formation does not directly promote co-ordination, and the fact that $\alpha\alpha$ -diquinolyl does not form co-ordinated ferrous compounds

contradicts Lowry's general conclusion that the maximum of stability should be reached in a six-atom ring containing three pairs of conjugated atoms. The fact that no compounds, stable or unstable, are found in the case of $\alpha\alpha$ -diquinolyl is proof that conjugation external to the chelate group is not even a minor factor in co-ordination. All co-ordination compounds are held to be of the same ("centric") type. F. A. M.

Electron Theory of Chemistry. Changes in Chemical Properties produced by the Substitution of One Element by Another, with Applications to Benzene Substitutions. (SIR) J. J. THOMSON (*Phil. Mag.*, 1923, [vi], 46, 497—514).—The author investigates the nature of the change in and around the molecule, and the effect produced on the chemical properties of the molecule, by the substitution of a univalent atom or radicle for an atom of hydrogen whereby the number of electrons in the molecule is increased. It is shown that the electrical effect of such substitution may be represented by the introduction of an electric doublet at the hydrogen atom. The sign of the doublet depends on the nature of the radicle. In the case of radicles of type I, including Cl, Br, I, OH, NH_2 , CH_3 , each containing 7 electrons forming an uncompleted octet, the positive end of the doublet will be directed towards the molecule with which the hydrogen is combined and its negative end away from it. In the case of the substitution of hydrogen by radicles of type II, including $\text{O}:\text{N}:\text{O}$, $\text{OH}:\text{C}:\text{O}$, $\text{H}:\text{C}:\text{O}$, and CN, each containing one electron in excess of the number required to form complete octets, the doublet will be directed in the opposite direction to that characterising type I. The magnitude of the electrostatic moment introduced by the respective substitutions indicates that, in agreement with experimental results, the specific inductive capacities of water, and methyl, ethyl, and propyl alcohols, referred to the same number of molecules in the liquid state, should be approximately equal. Immediate deductions from the natures of the electric field produced by the two types of substitutions referred to include the following. Where one carbon atom in a carbon compound has been halogenated, it is more likely to be still further halogenated than a carbon atom associated with hydrogen atoms none of which have been replaced by halogen atoms. The same rule applies to the process of oxidation of an organic compound. The substitution of hydrogen by atoms and radicles of type I, *e.g.*, the substitution of two hydrogen atoms in methyl alcohol to form formic acid, should increase the acidity of the compound. This is further illustrated by the relative acidities of mono-, di-, and tri-chloro-acetic acids, where, however, a further factor involving the period of existence of the acid in one or other of two phases is probably concerned. In the case of carbon atoms connected, as in ethylene, by a double bond, the substitution of a hydrogen atom by an atom of chlorine, etc., results in polarisation of the double bond. It follows that additive compounds would be more freely formed with a compound such as $\text{CH}_2:\text{CHCl}$ than with one like $\text{CH}_2:\text{CH}_2$.

In the case of a series of carbon atoms occupying positions designated in succession, starting from one end of the chain, by the numbers 1, 2, 3, 4, 5 . . . , when the substituent atom or radicle is of type I, the active carbons are those which are 1, 3, 5 . . . places from the atom where substitution took place, whilst when the substituent is of type II, the active carbon atoms are 2, 4, 6 . . . places away from the substituent. This is illustrated by the case of substitution of hydrogen in benzene. Substituents which direct a second substituent into the ortho- and para-positions include Cl, Br, I, OH, NH_2 , and CH_3 (type I), whilst NO_2 , CO, OH, CN, HSO_3 (type II), as substituents, direct a second substituent into the meta-positions. The high values of the respective specific inductive capacities of benzonitrile, nitrobenzene, and phenylacetonitrile are in accord with deductions from the theory. In the case of di-substituted benzenes, if both substituents belong to the same type, the specific inductive capacity will be least for the para- and greatest for the ortho-substitution, the value for the meta-substitution being unchanged. If the two substituents belong to different types, the specific inductive capacity will be greatest for the para- and least for the ortho-substitution. The author suggests that determinations of specific inductive capacities of di-substituted bodies might thus be employed in determining whether the second substituent enters into the ortho-, meta-, or para-position.

J. S. G. T.

The Geber Question. J. RUSKA (*Chem. Ztg.*, 1923, 47, 717—718).—Observations by an orientalist contributing to the study of works ascribed to Geber (cf. Darmstaedter, this vol., ii, 628).

A. A. E.

The Works of Geber. J. R. PARTINGTON (*Chemistry and Industry*, 1923, 42, 790—791).—Polemical against Lippmann (this vol., ii, 314; see also Partington, this vol., ii, 148, and Darmstaedter, this vol., ii, 628).

A. A. E.

Concerning Geber. CH. M. VAN DEVENTER (*Chem. Weekblad*, 1923, 20, 514—515).—In view of the work of Holmyard and of Partington (this vol., ii, 148) the author withdraws his view that Geber wished to pass as an older and more famous Dschâbir, but suggests the former name may have been a pseudonym of a writer of the early fourteenth century.

S. I. L.

Extraction Apparatus for Large Amounts of Liquids. HARTWIG FRANZEN (*Z. physiol. Chem.*, 1923, 129, 307—308).—An electrically driven and electrically heated apparatus, which can be run continuously for months, and may have a capacity of more than 25 litres, is described with the aid of a diagram.

W. O. K.

Inorganic Chemistry.

Chemical Action and the Disappearance of Gas in the Electrical Discharge Tube. F. H. NEWMAN (*Amer. Electrochem. Soc.* [advance copy], 1923, 43—49).—Hydrogen and nitrogen are absorbed in the presence of different elements, deposited on the walls of the cathode of a discharge tube, when the discharge is passing. The elements which exhibit this effect most strongly are phosphorus, sulphur, iodine, sodium, potassium, and the alloys of sodium and potassium. The rate of disappearance of the gas is greatest with phosphorus, sulphur, and iodine, and the final pressure attained is a minimum with phosphorus and sulphur. There is a similar absorption of these two gases when they are ionised by α -rays from polonium. The disappearance of the gas is due to the production of chemical compounds (nitrides and hydrides). The formation in this manner of nitrides of sodium, potassium, magnesium, and tin, and the hydrides of sodium, potassium, and sulphur have been proved by chemical analysis of the products. The gas under the ionising effect becomes modified, assuming an active condition which consists probably of triatomic molecules.

J. F. S.

The Photochemical Decomposition of Chlorine Monoxide. EDMUND JOHN BOWEN (*T.*, 1923, 123, 2328—2330).

Reaction between Bromine and Ammonium Salts and its Effect on the Precipitation of Manganese Dioxide. STEPHEN G. SIMPSON (*J. Amer. Chem. Soc.*, 1923, 45, 1883—1890).—The effect of the presence of ammonium salts on the precipitation of manganese dioxide by bromine water following a basic acetate separation has been investigated, by determining the amounts of bromine used up in reactions with solutions of (a) ammonium sulphate, (b) manganous sulphate, (c) mixtures of the two, under varying degrees of initial acidity and in the presence of varying amounts of alkali acetate. The results show that each of the reactions is progressively retarded by an increase in the initial concentration of acid, and progressively accelerated by an increase in the concentration of acetate present, and the effect is greater in the case of the manganese salt than in the corresponding case of the ammonium salt. In the absence of acid, ammonium-ion and manganous-ion are quantitatively oxidised by bromine water, but the amount of free bromine used up is slightly in excess of the amount theoretically necessary. The results can be explained by considering the mass-action effect of the hydrogen-ion and of the acetate-ion on the equilibrium reaction between bromine and water, and assuming that the hypobromous acid formed oxidises the ammonium-ion and the manganous-ion more readily than does bromine and under existing conditions also decomposes slightly into oxygen and bromine. When ammonium and manganous salts

are present together in neutral solution in the presence of acetate, the ammonium-ion is more readily oxidised by bromine water, and by its formation of hydrogen-ions retards the precipitation of manganese dioxide. J. F. S.

Thunderstorms and Ozone. WILLIAM C. REYNOLDS (*Nature*, 1923, 112, 397).—Analyses of atmospheric air showed that there was no appreciable increase of the nitrogen peroxide content of the air during or after a thunderstorm, whilst the quantity of ozone was increased by two to seven times. A. A. E.

The Ternary System, Sulphur-Selenium-Tellurium. L. LOSANA (*Gazzetta*, 1923, 53, i, 396—410).—The author summarises and supplements previous results obtained with the three binary systems included in the ternary system sulphur-selenium-tellurium, and gives the results of his own thermal, dilatometric, and micrographic investigations of the ternary system.

In the case of sulphur-selenium, Ringer (A., 1902, ii, 651) has shown that there is complete miscibility in the liquid, and partial solution in the solid, state, and that the compound Se_2S possibly exists within certain limits of temperature. For selenium-tellurium Pellini and Vio (A., 1906, ii, 663) found formation of mixed crystals, with no miscibility gap, throughout the whole extent of the system, so that the two component elements are isomorphous.

For sulphur-tellurium some disparity exists between the results of different investigators. The author's thermal measurements confirm the value, 1.9%, of tellurium given by Pellini (A., 1909, ii, 726, 805) to the limit of complete miscibility, and show that the minimum on the liquid curve is about 6% of tellurium, with which the maximum eutectic arrest corresponds. With more than 97.6% of tellurium there is no trace of arrest and the end of the solidification is perceptible with moderate clearness; Chikashigé's statement that mixed crystals are formed with 98—100% of tellurium (A., 1911, ii, 978) is thus confirmed. In its middle portion the curve agrees generally with the results of Chikashigé and, especially, of Pellini.

The ternary system exhibits formation of neither compounds nor ternary eutectics, but contains two zones of complete miscibility in which there exist mixed crystals of selenium and tellurium in sulphur and mixed crystals of sulphur and tellurium in selenium. The formation of mixed sulphur-tellurium crystals is favoured by the presence of selenium, which causes solid solutions with high proportions of tellurium to be formed; many of such solid solutions exhibit, however, the phenomenon of more or less rapid de-mixing. The first transformation point of sulphur is depressed considerably by selenium and tellurium separately and to a still greater extent by the two elements together. T. H. P.

Production of Nitrogen Oxides and Ozone by High Voltage Electric Discharges. KARL B. MCEACHRON (*Amer. Electrochem. Soc.* [advance copy], 1923, 71—86).—The production of nitric oxide and ozone in tubes of various designs under various

pressures and electrical conditions has been investigated. It is shown that the previous electrical history of the gas has a marked effect on the character of the discharge and the products formed. Traces of the products of previous experiments, made in small tubes of the Siemens type, modify the character of the discharge and decrease the absorbable products. Increase of current flowing in the discharge increases the yield of both ozone and nitric acid up to a certain maximum, beyond which further increase in current decreases the yields. With increase of pressure, the yields of ozone increase until a pressure near to that of the atmosphere is reached. At higher pressures, the yields in general decrease. With decreasing pressures, within the limits investigated, the yield of nitric acid increases with tubes in which sparking occurs, and decreases in tubes, like the rod tubes, in which sparking does not occur. Increase in the rate of air flow will in general increase the yields of nitric acid up to a certain maximum, the critical air flow rate being dependent on the tube used. Increased air rates give increased yields of ozone which tend to become constant at higher rates. Sparks passing through air cause a pressure increase much too rapid to be a heat effect. With an enclosed volume of air, a pressure decrease occurs at the instant the power is disconnected, which is the pressure change due to ionisation noted by Farwell. A tube of the rod type, if properly cooled, gives yields of ozone of sufficient magnitude, so that the tube becomes of importance as a commercial ozoniser. In air, the corona discharge favours the production of ozone, whilst sparks tend to produce oxides of nitrogen. Some exceptions may be found to this, as in Siemens tubes, where the yield of nitrogen pentoxide was at times quite large, and yet the discharge consisted of a fine glow only. A combination of sparks and corona produces the higher oxides which are desirable from the absorption point of view.

J. F. S.

The Slow Oxidation of Phosphorus. ELIZABETH GILCHRIST (*Proc. Roy. Soc. Edin.*, 1922—1923, **43**, 197—215).—Visible glow is emitted from phosphorus during oxidation only when the action occurs at a certain minimum rate, and is probably attributable to the oxidation of phosphorus trioxide, which must occur at a considerably slower rate than the oxidation of phosphorus to phosphorus trioxide preceding this action. The glow occurs chiefly in the gas phase, and may be steady, fluctuating, or intermittent. The rate of the reaction increases with rise of temperature, and at partial pressures of oxygen of about one atmosphere the rate is diminished with increase of oxygen pressure and may be slowed below the glowing point. The presence of ozone in oxygen greatly increases the glow, but the glow is not under ordinary conditions attributable to ozone produced in the reaction. A trace of moisture seems necessary to start the reaction, but as the pressure of water vapour increases, the rate attains a maximum value and thereafter falls. Gases and vapours capable of developing negatively-charged carbon molecules, *e.g.*, ethylene, acetylene, or ethane, are negative catalysts towards the reaction, whilst others,

including ammonia and methyl alcohol, are promoters of the reaction.
J. S. G. T.

The Reaction between Phosphorous Acid and Iodine.
ALEX DUNCAN MITCHELL (T., 1923, 123, 2241—2254).

Action of Potassium Carbonate on Lead Glass. H. DROOP RICHMOND (*Analyst*, 1923, 48, 260—262).—When stored in lead glass bottles, potassium carbonate may become contaminated with considerable quantities of lead and arsenic derived from the glass. This action of the salt on the glass is relatively rapid if moisture is admitted to the bottle owing to a defective stopper. W. P. S.

Correction to the Freezing-point Diagram of Lead-Sodium Alloys. G. CALINGAERT and W. J. BOESCH (*J. Amer. Chem. Soc.*, 1923, 45, 1901—1904).—The thermal data obtained by the authors for lead-sodium alloys (66.6 atomic % of sodium) differed appreciably from Mathewson's results (A., 1906, ii, 666); consequently they have determined the freezing-point data for alloys between 50 and 75 atomic % of sodium. It is shown that the pure compound separating from alloys of lead and sodium, the composition of which is between 58.8 and 76.6 atomic % of sodium, is Na_5Pb_2 , this compound forming solid solutions with both NaPb and Na_4Pb . Alloys containing 58.8 to 71.4 atomic % of sodium rearrange at 182° on cooling, the compound Na_5Pb_2 disappears and a new compound, Na_2Pb , is formed. The complete diagram of lead-sodium alloys is given corrected for the above results.
J. F. S.

The Crystal Structure of Sodium Chlorate. WILHELM KIBY (*Z. Physik*, 1923, 7, 213—250).—The work of Kolkmeijer, Bijvoet, and Karssen (A., 1921, ii, 200) and of Dickinson and Goodhue (A., 1922, ii, 145) on the determination of the crystal structure of sodium chlorate by Bragg's method of X-ray crystal analysis is briefly reviewed. Wulff (*Z. Kryst.*, 1922, 57, 190) employing Laue's method of analysis, calculated values of the parameters differing considerably from those found by the previous observers. The present paper contains the mathematical analysis of a method whereby the crystallographic parameters of a crystal of sodium chlorate are determined from a consideration of the distribution of intensities in the X-radiation diffracted in various directions by the crystal, as evidenced by the intensities of the photographic point images contained in the appropriate Laue X-ray diagram. In the case of a crystal of sodium chlorate, such a diagram contains 51 points in each quadrant. Employing the method of combination suggested by Schiebold, sixteen only of these points are required in the analysis. The following assumptions amongst others are made in the analysis: that the structure is close-packed; the oxygen atoms in the crystal structure lie each in contact with the appropriate chlorine atom and the two nearest sodium atoms and each lies in the plane defined by these three atoms; each chlorine atom is at an equal distance from each of the corresponding two sodium atoms referred to. With these assumptions, it is shown that the values of the parameters a , b , p , q , and r referring, respect-

ively, to the co-ordinates of a sodium atom, a chlorine atom, and the three oxygen atoms in a molecule of sodium chlorate, which enable the positions of all atoms within the structure to be calculated are a , 0.071; b , 0.429; p , 0.301; q , 0.473; r , 0.590. The values are in close agreement with those deduced from the work of Dickinson and Goodhue referred to. J. S. G. T.

The Properties of Ammonium Nitrate. VI. The Reciprocal Salt Pair Ammonium Nitrate and Potassium Sulphate. EDGAR PHILIP PERMAN and WILLIAM JOHN HOWELLS (T., 1923, 123, 2128—2134).

The Diffusion of Oxygen through Silver. LEO SPENCER (T., 1923, 123, 2124—2128).

The Crystalline Structures of Silver Iodide. R. B. WILSEY (*Phil. Mag.*, 1923, [vi], 46, 487—496).—Employing the powder-method of X-ray crystal analysis, the author has determined as follows the lattice structure, length of side of the elementary structure, and distance apart of the nearest atomic centres in the cases of the respective silver halides and metallic silver:—silver chloride: simple cubic of the sodium chloride type, 5.540, 2.770 Å.; silver bromide: simple cubic of the sodium chloride type, 5.768, 2.884 Å.; silver iodide: diamond cubic of the zinc sulphide type, 6.493, 2.812 Å.; and hexagonal of the zinc oxide type, 4.593, 2.813 Å.; metallic silver: face-centred cubic, 4.078, 2.884 Å. Most of the samples of silver iodide examined showed predominance of the hexagonal structure. In some cases the cubic structure alone was evident, whilst all samples exhibited this to some extent. The axial ratio of the hexagonal structure in the case of silver was found to be 1.633 ± 0.008 . J. S. G. T.

The Preparation of Barium Alloys. V. M. GOLDSCHMIDT (*Norg. Geol. Undersökelse, Statens Raastofkomite Publication*, 1922, No. 7).—Alloys of barium with lead have been prepared by the electrolysis of fused barium chloride (8 parts), potassium chloride (5 parts), and sodium chloride (3 parts) in a cell with a carbon anode and molten lead as the cathode. The preparation of an alloy containing 10% of barium requires a temperature of 600—650°, using 4—6 volts, with electrodes 1—1.5 cm. apart, and a current density not exceeding 3 amperes/cm.² at the anode and 1 ampere/cm.² at the cathode. Alloys have been prepared containing 18% of barium and less than 1% of sodium; alloys with zinc and tin, of low barium content, have also been obtained.

CHEMICAL ABSTRACTS.

Reduction of some Rarer Metal Chlorides by Sodium. M. A. HUNTER and A. JONES (*Amer. Electrochem. Soc.* [advance copy], 1923, 35—41).—The anhydrous chlorides of glucinum, chromium, uranium, vanadium, and zirconium when heated with sodium in a closed steel bomb are reduced to the metal, which is generally comparatively pure and in the form of small pellets. In the case of glucinum the beads contained 99.6% of metal, d 1.793, m. p.

in hydrogen 1370°. The metal could not be completely burnt in air; it is readily soluble in hydrochloric acid, but is not attacked by cold concentrated nitric acid. With chromium, the product was 99·86% pure, d 6·29—6·40; it is unattacked by cold hydrochloric or sulphuric acid, but is readily attacked by either acid when heated. It is unattacked by nitric acid. In the case of uranium, powdered metal of 99% purity was obtained which oxidised slowly in the air. Similarly, vanadium was obtained as a powder of d 5·97. Zirconium gave a yield of 76% of powdered metal of 93·2% purity, d 5·29. J. F. S.

A Double Salt of Magnesium Chloride and Carbonate. TSUNEKICHI NISHIMURA (*Rikwagaku Kenkyujo Ihô*, 1923, 2, 63—65).—The double salt, $\text{MgCl}_2 \cdot \text{MgCO}_3 \cdot 6\text{H}_2\text{O}$, was prepared by passing carbon dioxide into a mixture obtained by adding calculated amounts of magnesium chloride and carbonate to 27·5% or more concentrated solution of magnesium chloride. The double salt is decomposed at once by water, but is stable towards absolute alcohol. The salt purified with absolute alcohol and dried at 40° has d^{16} 1·679. Part of the water of crystallisation is lost at 50—60°; at 100° the salt has the composition $\text{MgCl}_2 \cdot 3\text{MgCO}_3 \cdot 7\text{H}_2\text{O}$. A similar double salt is not formed with calcium chloride and carbonate. K. K.

Separation of Common Lead into Fractions of Different Density. R. H. ATKINSON (*Nature*, 1923, 112, 282).—Fractional crystallisation of lead, followed by purification, yielded samples having d $11\cdot345 \pm 0\cdot005$ and $11\cdot313 \pm 0\cdot005$, respectively. It was observed that lead which has solidified slowly is not homogeneous as regards density, the portions which solidify first being the denser. A. A. E.

Comparison between Dilatation and Thermal Curves. L. LOSANA (*Gazzetta*, 1923, 53, i, 393—395).—The author has applied the dilatometer described by Montemartini and Losana (this vol., ii, 373) to the study of the changes occurring during the cooling of pure tin and of tin-lead, tin-lead-cadmium-bismuth, and lead-bismuth alloys and finds that, for temperatures up to 400°, the singular points are indicated as clearly as by the ordinary cooling or heating curves. For higher temperatures, a suitable liquid with the necessary continuity in thermal dilatation is lacking. T. H. P.

Complex Formation in Lead Nitrate Solutions. I. The Ternary Systems Lead Nitrate-Sodium Nitrate-Water, and Lead Nitrate-Potassium Nitrate-Water. SAMUEL GLASSTONE and HAROLD NICHOLAS SAUNDERS (T., 1923, 123, 2134—2140).

Rare Earth Elements in Triple Nitrites. V. CUTTICA and F. GALLO (*Gazzetta*, 1923, 53, i, 374—379; cf. this vol., ii, 497).—Cobalt, nickel, and copper form triple nitrites in which the other metals are an alkali metal and a metal of the cerium or yttrium group. In the cerium compounds now described, the cerous

nitrite exhibits the normal composition, $\text{Ce}(\text{NO}_2)_3$, which is not that of the isolated salt itself. Since, also, the normal nitrites of cobalt, nickel, and copper are not known, the following triple nitrites must be considered as true complex compounds.

$2\text{Co}(\text{NO}_2)_2, \text{Ce}(\text{NO}_2)_3, 5\text{KNO}_2$ forms a green powder and is decomposed by water, yielding cerous nitrite and potassium cobaltosonitrite. $2\text{Co}(\text{NO}_2)_2, \text{Ce}(\text{NO}_2)_3, 5\text{RbNO}_2$, which is also green and $2\text{Co}(\text{NO}_2)_2, \text{Ce}(\text{NO}_2)_3, 5\text{TlNO}_2$, which is deep brown, behave similarly towards water. These compounds, which are slowly attacked by cold, dilute acids, yielding $\text{R}_3\text{Co}(\text{NO}_2)_6$, may be represented by the general formula, $\left[\text{Co}(\text{NO}_2)_6 \right]_2 \text{Ce}(\text{La, Pr, Nd, Y}) \text{K}(\text{Rb, Tl})_5$.

As has been found in other cases, the following compounds, containing nickel or copper in place of cobalt, exhibit no general formula. $3\text{Ce}(\text{NO}_2)_3, 5\text{Ni}(\text{NO}_2)_2, 13\text{KNO}_2$ forms a flesh-red powder; $2\text{Ce}(\text{NO}_2)_3, 6\text{Ni}(\text{NO}_2)_2, 7\text{TlNO}_2$ (cf. this vol., ii, 77) has a pale chestnut colour; $3\text{Ce}(\text{NO}_2)_3, 4\text{Cu}(\text{NO}_2)_2, 15\text{NH}_4\text{NO}_2$ forms a black, crystalline precipitate, readily soluble in water to a green solution, remains unaltered for some time in a desiccator, but decomposes in the air with evolution of nitrous fumes; $\text{Ce}(\text{NO}_2)_3, 4\text{Cu}(\text{NO}_2)_2, 12\text{KNO}_2$ is similar in appearance to, but more stable in the air than, the preceding compound; $\text{Ce}(\text{NO}_2)_3, 3\text{Cu}(\text{NO}_2)_2, 5\text{TlNO}_2$ is the most stable of these copper complexes.

T. H. P.

Some Properties of Electrolytic Manganese. ALAN NEWTON CAMPBELL (T., 1923, 123, 2323—2327).

The Reaction between Ferrous Phosphate and Sulphur Dioxide in Phosphoric Acid Solution; the Nature of the Decomposition Products. SYDNEY RAYMOND CARTER and JOHN ALFRED VALENTINE BUTLER (T., 1923, 123, 2380—2384).

The System Ferric Oxide-Phosphoric Acid-Water. A New Phosphate. SYDNEY RAYMOND CARTER and NORMAN HOLT HARTSHORNE (T., 1923, 123, 2223—2233).

Electrolytic Reduction of Molybdic Acid Solutions. F. FOERSTER and E. FRICKE (*Z. angew. Chem.*, 1923, 36, 458—460).—The electrolytic reduction of molybdic acid solutions to the quinquevalent stage and the preparations of compounds of the type $(\text{MoOCl}_5)_2\text{M}_2$, where M is an alkali metal or ammonia, is described. Amalgamated lead anodes were replaced by platinised platinum wire netting, as the lead was found to go into solution. The solution can also be reduced to the tervalent stage by suitable choice of acid concentration and current density. The properties of complex salts of the type $[\text{MoCl}_5, \text{H}_2\text{O}]\text{M}_2$ and $[\text{MoCl}_6]\text{M}_3$ are described. The salt $[\text{MoBr}_5, \text{H}_2\text{O}](\text{NH}_4)_2$ was also prepared. Attempts to prepare the alums and complex oxalates of molybdenum, rubidium, and caesium were unsuccessful. Only the tervalent elements of lower atomic weight (Ti, V, Cr, Mn, Fe, Co) in this horizontal row of the periodic system appear to form easily crystallisable complex salts with bivalent anions, whereas the elements of higher atomic weight also give well crystallised complex salts with univalent

anions. The existence of the red salts, $(\text{MoCl}_6)_2\text{M}_2$ and $[\text{MoCl}_5, \text{H}_2\text{O}]_2\text{M}_2$ indicates that in the reddish-brown solutions of tervalent molybdenum an equilibrium exists between the tervalent kations and the complex ions, $(\text{MoCl}_5, \text{H}_2\text{O})''$ and $[\text{Mo}(\text{H}_2\text{O})_6]'''$, respectively. Considerations of static potential lead to similar conclusions. No confirmation was obtained of Chilesotti's hypothesis of an incipient reduction of tervalent to bivalent molybdenum taking place (A., 1906, ii, 263, 365). The presence of the ions MoCl_6''' , $(\text{MoCl}_5, \text{H}_2\text{O})''$, and $[\text{Mo}(\text{H}_2\text{O})_6]'''$ is held to account for the increased reducing power of the green tervalent molybdenum solution. The fact that solutions of molybdic acid in dilute hydrochloric acid can only be reduced to the quinquevalent stage, whilst solutions in more concentrated hydrochloric acid can be reduced electrolytically to the tervalent stage, is explained by assuming that the next stage to quinquevalent molybdenum is Mo''' -ions, which in the presence of a high concentration of Cl' -ions immediately form complex ions and the static potential of the solution is reduced below that necessary for the generation of hydrogen from platinised platinum electrodes. If the concentration of chloride-ions is low, however, comparatively few complex ions are formed, and the static potential of the solution remains higher than that necessary for the evolution of hydrogen. If polished platinum electrodes are used, however, owing to the much higher potential necessary for the evolution of hydrogen, the tervalent stage can be reached even in dilute hydrochloric acid solution. The electrolytic reduction of molybdenum shows changes of potential parallel with those occurring in vanadium and titanium solutions under similar conditions.

H. C. R.

Normal Thorium Molybdate, $\text{Th}(\text{MoO}_4)_2$. FERRUCCIO ZAMBONINI (*Atti R. Accad. Lincei*, 1923, [v], 32, i, 518–524; cf. A., 1916, ii, 249).—*Thorium molybdate*, $\text{Th}(\text{MoO}_4)_2$, obtained by fusing partly dehydrated thorium chloride with excess of anhydrous sodium molybdate, forms tetragonal crystals, $a : c = 1 : 0.73565$, $d^{75} 4.92$, which exhibit mutual miscibility in the solid state with cerous molybdate. The properties of the thorium salt are compared with those of other molybdates. The fact that thorium and cerium may replace one another isomorphically in such simple compounds as their normal molybdates supports the view that the element observed by Dauvillier in the mixture of rare earths containing Urbain's original celtium is identical with that encountered some months subsequently by Coster and Hevesy in certain zirconiferous minerals.

T. H. P.

Bismuth Tetroxide Prepared from Sodium Bismuthate. C. E. CORFIELD and ELSIE WOODWARD (*Pharm. J.*, 1923, 111, 80–82).—Attempts to prepare bismuthic acid and bismuth pentoxide by decomposing sodium bismuthate with nitric acid, under the most favourable conditions, were unsuccessful. If formed at all, these compounds appeared to be unstable and decomposed immediately into the tetroxide with loss of oxygen. The authors have obtained a hydrated tetroxide containing between $1\text{H}_2\text{O}$ and

$2\text{H}_2\text{O}$, but this could not be reduced to $1\text{H}_2\text{O}$ without simultaneous loss of oxygen. W. P. S.

Celtium or Hafnium ? (*Chemistry and Industry*, 1923, **42**, 784—788).—A review of the facts concerned in the controversy regarding priority of nomenclature of the element of atomic number 72. On the evidence so far published, it is held that Urbain's claim to priority of discovery and to the name "celtium" should be admitted. A. A. E.

Hafnium or Celtium ? BOHUSLAV BRAUNER (*Chemistry and Industry*, 1923, **42**, 884—885).—Polemical in support of Urbain's celtium. Attention is directed to the significance of the spectrographic observations of Exner and Hatschek in 1911. A. A. E.

Mineralogical Chemistry.

Chemical Relations between Humic Substances and Coal.

MAURICE PIETTRE (*Compt. rend.*, 1923, **177**, 486—488; cf. *ibid.*, 139).—Extraction of Brazilian, American, or Elsecar coals with boiling pyridine, and subsequent evaporation of the solvent, gives a residue which on extraction with alcohol-ether mixtures affords an insoluble, humus-like substance (nitrogen content 2.25—2.50%), and a soluble, brown resin. The latter may be separated, by extraction with alkalis, into acidic and tarry substances.

Cardiff coal gives no appreciable pyridine extract, and is therefore to be regared as a completely mature coal. On treatment with nitric acid (*d* 1.40), it affords a highly combustible nitrated product, which, after reduction in presence of alkali, gives a black substance (nitrogen content about 4.45%) possessing most of the properties of humus. This suggests a common origin for humus, peat, and coal.

E. E. T.

Japanese Minerals containing Rarer Elements. V. Analysis of Beryl from Ishikawa, Ishikawa Province. TAKU UYEMURA (*J. Chem. Soc. Japan*, 1923, **44**, 296—302).—The analysis of beryl produced in Ishikawa, Ishikawa Province, opaque, slightly green crystals, *d* 2.8, gave the following results :

SiO ₂ .	GIO.	Fe ₂ O ₃ .	Al ₂ O ₃ .	CaO.	MgO.	Alkali (as Na ₂ O).	Loss by heating.	Total.
49.60	19.31	0.11	24.09	0.79	0.14	3.65	2.81	100.50

By spectrum analysis silicon, glucinum, iron, aluminium, calcium, magnesium, scandium, and sodium, but not chromium were detected. The formula 4GIO, Al₂O₃, 4SiO₂ and a constitutional formula are proposed; in the latter, one molecule of silicic acid is expressed as ortho-acid. In the present case, Copaux's method (A., 1919, ii, 192) was useless for the estimation of glucinum.

K. K.

Clays. I. The Acidic Reaction of Japanese Acid Clays.

TSURUJI OKAZAWA (*Rikwagaku Kenkyujo Ihô*, 1923, 2, 189—221).—When treated with a neutral salt solution, Japanese acid clay gives an acidic reaction to the solution, a phenomenon which K. Kobayashi ("Japanese Acid Clay," Tokyo, 1922; *J. Chem. Ind. Japan*, 1923, 26, 289) has attributed to its large adsorptive action, but the author has put forward a different explanation. Clays may be classified into three kinds according to their reactivity with salt solutions and acids. The first group gives no dissolved part by treatment with salt solutions and only a slight amount with strong acids; the second yields none by the salt solution, but a large quantity by the acid; and the third, which includes Japanese acid clay, gives a large amount by both the solutions. When treated with salt solutions, clay particles absorb positive radicles, aluminium being dissolved as the corresponding salt, *e.g.*, $R:Al\cdot OH + MgCl_2 = RMg + AlCl_2\cdot OH$, and $AlCl_2\cdot OH + 2H_2O = Al(OH)_3 + 2HCl$. This reaction is therefore attributed partly to adsorption, but mainly to double decomposition, and the acidity is governed by the salt used, adsorptive and reactive affinities of the clay, stability of the reaction product, reaction velocity, etc.

The acidity is therefore not definitely determined by titrating with alkali solution, and reaction will be as follows (when a chloride is used as a salt): $AlCl_2\cdot OH + 2H_2O = Al(OH)_3 + 2HCl$; or $AlCl_3 + 3H_2O \rightleftharpoons 3HCl + Al(OH)_3$; $AlCl_2\cdot OH + 2NaOH = Al(OH)_3 + 2NaCl$; or $AlCl_3 + 3NaOH \rightarrow Al(OH)_3 + 3NaCl$. Aluminium hydroxide thus produced will further react with alkali.

When the clay is burned, the so-called acidity is decreased and almost completely removed in one hour at 700—800°. By the action of heat the state of molecular aggregation will be changed and the aluminium oxide in the clay will not be dissolved by salt solutions. But a reverse relation exists between the temperature of burning and the quantity of aluminium oxide dissolved by acids; the quantity dissolved attains a maximum value at about 700—800°, and decreases rapidly above 900°.

K. K.

Oxydase Reaction of Japanese Acid Clay, Fuller's Earth, and Florida Earth.

KYUHEI KOBAYASHI and KEN-ICHI YAMAMOTO (*J. Chem. Ind. Japan*, 1923, 26, 289—296).—Japanese acid clays, fuller's earth, and Florida earth, but not kaolin, kieselguhr, or volcanic ash, give the oxydase reaction with an alcoholic solution of guaiacum, and with other substances. It is supposed that the so-called Helmholtz double layer is formed around the surface of the clay when suspended in water and that it absorbs hydroxyl-ions, hydrogen-ions being liberated near the surface. The hydroxyl-ions thus absorbed combine directly, liberating one atom of oxygen and forming water. This active atom of oxygen may act on oxidisable reagents and give the oxydase reaction.

K. K.

Analytical Chemistry.

A New Colorimeter having Perfectly Symmetrical Light Distribution. K. BÜRKER (*Z. angew. Chem.*, 1923, **36**, 427—429).—Two parallel beams of light pass upwards through equal and variable thicknesses of, respectively, pure solvent and the coloured solution under examination, and then through 10 mm. of standard colour solution and pure solvent, respectively. They are brought together by means of an Albrecht-Hüfner hexagonal lens and appear in the eyepiece of the instrument as two semicircular fields separated by a narrow boundary line. [Cf. *J.S.C.I.*, 1923, Oct.]

W. T. K. B.

[Use of] the Gooch Crucible. ARCHIBALD CRAIG (*Chem. Age [N.Y.]*, 1923, **31**, 31—32).—The importance of rapidly filtering asbestos is emphasised. A modified form of bell-jar for filtering directly into a beaker is described. To enable a pencil to be used for marking crucibles, the surface of the porcelain is roughened by application of a paste of barium sulphate and hydrofluoric acid. For calculating results of gravimetric analyses, an empirical factor, dependent on the conditions of the estimation, should be used instead of the theoretical factor.

CHEMICAL ABSTRACTS.

A New Explosion Pipette. K. TIDDY (*Gas World*, 1923, **79**, 187).—A modification of the Hempel explosion pipette employed in gas analysis, which eliminates leakage of gas under the pressure developed by the explosion, and is more robust than the customary form, is described. In this, the U-shaped exit tube connected by a rubber joint with the capillary of the measuring vessel is replaced by a straight capillary tube and stop-cock. The device can be readily incorporated in a gas analysis apparatus of the Orsat type.

J. S. G. T.

Carbinols as Indicators. L. KARCZAG and R. BODÓ (*Biochem. Z.*, 1923, **139**, 342—344).—The colourless carbinols of certain triphenylmethane dyes (*e.g.*, red-violet, fuchsin-S, water-blue) may be utilised as indicators, since on the addition of acid they are immediately converted into the coloured ammonium bases. The carbinols were obtained by decolorising solutions of the dyestuffs with stick charcoal, and by using these with buffer solutions according to Sørensen's method it was found that water-blue has a range from p_H 5.0 to 6.2, the colour development being instantaneous at the higher hydrogen-ion concentration and requiring from ten to fifteen minutes at the lower value. Fuchsin-S showed a similar but more rapid change over a range from p_H 5.2 to 6.6.

J. P.

The Colorimetric Estimation of Hydrogen-ion Concentration by the Method of Michaelis, with One Colour Indicators, using Inorganic Comparison Solutions. I. M. KOLTHOFF (*Pharm. Weekblad*, 1923, **60**, 949—966).—In view of the

application of the method of Michaelis and his co-workers (A., 1921, ii, 56; *Biochem. Z.*, 1921, 109, 307) to the examination of urine, drinking-water, and other biologically important liquids, a critical examination has been made of his results. The low buffer capacity of his solutions renders the accuracy of his figures questionable, and the necessity of preparing for each series of determinations a great number of comparison solutions of the indicators makes his method cumbersome. The constants of the indicators have now been re-determined, using the buffer mixture solutions of Clark, which have also been checked potentiometrically.

The indicators 2 : 4-, 2 : 5-, and 2 : 6-dinitrophenol, *m*- and *p*-nitrophenol, and salicyl-yellow have thus been examined, and the constants with their temperature coefficients now determined show good agreement with those given by Michaelis, except in the case of *p*-nitrophenol, for which $p_H = 7.04$, a value considerably below the figures given in the literature.

In place of the alkaline solutions of the indicators themselves, solutions of potassium chromate (for 2 : 4-dinitrophenol and *p*-nitrophenol) and dichromate (2 : 5-dinitrophenol, *m*-nitrophenol, and salicyl yellow) and mixtures of the two (2 : 6-dinitrophenol) may be more conveniently employed as comparison solutions, and details are given of the concentrations and quantities corresponding with the colour of definite indicator solutions. S. I. L.

Estimation of Total Sulphur in Biological Material. MABEL STOCKHOLM and FRED C. KOCH (*J. Amer. Chem. Soc.*, 1923, 45, 1953—1959).—The dry fusion method for the estimation of sulphur in organic material tends to give low and irregular results when properly corrected for blanks; this is due to loss of reduced sulphur by volatilisation during the heating of the dry mixture, the loss being greater the more rapidly the temperature is increased (cf. Barlow, A., 1904, ii, 82). It is found that the following procedure gives the calculated value for cystine, and uniform results, usually higher than by the fusion method, with different biological materials containing organically combined sulphur. 0.5—2 G. of material and 10 c.c. of 25% sodium hydroxide solution are slowly evaporated on the steam-bath until almost dry; 5 c.c. of 30% hydrogen peroxide solution are then very gradually added, the heating being meanwhile continued. The partly oxidised material is now acidified by means of nitric acid, and concentrated more rapidly until crystallisation commences. The boiling solution is oxidised by the gradual addition of 10 c.c. of fuming nitric acid and 40—50 drops of bromine. In the analysis of lipin materials, *e.g.*, nerve-tissue or egg-yolk, the treatment with nitric acid and bromine is prolonged during twenty-four hours. The solution is evaporated almost to dryness, water is added, and the evaporation repeated, to remove most of the nitric acid. The aqueous solution, filtered if necessary, is neutralised by means of sodium hydroxide, diluted to about 600 c.c., and acidified by means of 10 c.c. of concentrated hydrochloric acid. The sulphate is estimated in the usual way, after the addition of 10 c.c. of 0.1*N*-sulphuric acid. This addition of a

standard quantity of sulphuric acid in estimations of sulphate, including blanks, is recommended, because in this way the complete precipitation of small traces of sulphate is promoted. W. S. N.

Detection of Nitrites by Rodillon's Test. HANS HELLER (*Chem. Ztg.*, 1923, 47, 701).—Leffmann's failure to obtain consistent results in Rodillon's test for nitrites in water (this vol., ii, 37) was due to his use of hot sulphuric acid for dissolving the resorcinol (*Amer. J. Pharm.*, 1923, 95, 110). If the cold acid is used and the reagent freshly prepared for each test trustworthy results are always obtained; on keeping, the solution slowly deposits crystals and is then useless. The following modification of the original method is recommended: 0.4 g. of resorcinol is shaken with 5 c.c. of cold, concentrated sulphuric acid and 1 c.c. of this solution is carefully poured below the surface of 5 c.c. of the water to be tested. At the interface between the liquids a green, violet, or blue colour appears, according to the concentration of the nitrite. The reagent crystallises after eight hours; for further use, a few drops of water are added and the whole is warmed until the crystals dissolve, and then cooled. A. R. P.

Estimation of Phosphorus in Light Aluminium Alloys. L. LOSANA and C. E. ROSSI (*Annali Chim. Appl.*, 1923, 13, 200—204).—The estimation of sulphur or phosphorus in aluminium alloys containing 1% of either copper or tin should be effected by the oxidation method and not by treating the metal with hydrochloric acid and estimating the hydrogen sulphide or phosphide liberated; zinc, however, does not interfere with the latter method. T. H. P.

The Micro-estimation of Phosphoric Acid. RICHARD KUHN (*Z. physiol. Chem.*, 1923, 129, 64—79).—The micro-estimation of phosphoric acid is best carried out gravimetrically by weighing the precipitate obtained on precipitation with ammonium molybdate. The alkalimetric titration is not satisfactory except with very small quantities of material. Separation of arsenic from phosphorus is best carried out by distillation of the arsenic in a stream of hydrogen chloride. The phosphorus is then estimated either gravimetrically or, if there is less than 0.04 mg., nephelometrically (cf. Kleinmann, *Biochem. Z.*, 1919, 99, 115, 150). W. O. K.

Chemistry of the Reinsch Test for Arsenic and Antimony and its Extension to Bismuth. B. S. EVANS (*Analyst*, 1923, 48, 357—367).—The tests were carried out by comparing the colour of the film deposited on a cleaned and polished surface of electrolytic copper suspended in the solution to be tested by means of a glass stirrup, with a standard copper-arsenic or copper-antimony alloy similarly suspended in the same beaker, but enclosed in a smaller interior beaker containing distilled water. The time taken for the electrolytic copper surface to assume the same appearance as the standard alloy under different conditions as regards concentrations of sodium chloride, sulphuric acid, arsenic, antimony, or bismuth, and cupric-ions was noted. For arsenic tests, a 70 : 50 copper-arsenic alloy polished and etched with nitric

acid ($d\ 1.2$) was used, and a 50 : 50 copper-antimony alloy, similarly treated, was used for the antimony tests. For the bismuth tests, a 90 : 10 copper-arsenic alloy, polished but not etched, was employed. The results of varying the factors mentioned above one at a time are given in a series of tables. Increase of sodium chloride concentration increases the rate of formation of the standard film markedly in the case of arsenic and antimony, less so in the case of bismuth. Increase of sulphuric acid concentration also increases the rate of formation of the film, but in all three tests there is a certain concentration of acid above which further additions are without influence on the rate of reaction. These concentrations are for arsenic, antimony, and bismuth, respectively, 5.47%, 2.74%, and 2.28%. The presence of cupric-ions in the solution retards the formation of the film to such an extent that any considerable concentration may be said to inhibit it, but cuprous-ions which are formed during the reaction itself have no such action. The film formed in the test for arsenic was analysed, and consisted chiefly of the compound Cu_5As_2 , with the addition of a little elementary arsenic deposited electrolytically. In the case of the bismuth reaction, only a trace of copper was found in the film. The separation of the antimony film presented great difficulty. The initial purple film probably consists of the compound Cu_2Sb , but the composition of the subsequently formed white film could not be determined.

H. C. R.

Estimation of Boric Acid by the Hönig-Spitz Method. HANS RATH (*Naturprodukte*, 1923, 134—139).—A detailed account of the method of titrating boric acid with sodium hydroxide in presence of glycerol.

E. H. R.

Estimation of the Content of Active Carbon Dioxide in Drinking Waters. P. LEHMANN and A. REUSS (*Z. Unters. Nahr. Genussm.*, 1923, 45, 227—236).—A consideration of the work of Schlöesing (*Compt. rend.*, 1872, 74, 1552; 75, 70) and the application of the law of mass action leads to the deduction of the following formula for calculating the combined carbon dioxide (c) in a sample of drinking water from the total carbon dioxide (t) determined in mg. per litre: $c = 27[\sqrt[3]{t} + \sqrt{t^2 + 5823} + \sqrt[3]{t} - \sqrt{t^2 + 5823}]$. If, however, t exceeds 200, a correction is necessary on account of the carbonate not being completely dissociated at higher concentrations. This correction factor is deduced to be $2772.9/(2886 - c)$. A table is given of the sums of combined and active carbon dioxide concentrations corresponding with experimentally determined total carbon dioxide concentrations, calculated by means of the above formula, the correction factor being applied where necessary. Details are given of methods of estimating the combined and free carbon dioxide by titrations with hydrochloric acid, using methyl-orange as indicator, and with sodium carbonate, using phenolphthalein as indicator, respectively. The active carbon dioxide in water containing calcium sulphate must be estimated directly by experiments on powdered

marble according to von Heyer's method (*Gesundheitsingenieur*, 1912, 35, 675; see also Kolthoff, A., 1921, ii, 59). H. C. R.

The Estimation of Alkalies in Rocks by the Indirect Method. FREDERICK WALKER (T., 1923, 123, 2336—2341).

Estimation of Potassium by the Perchlorate and Cobaltinitrite Methods, and the Removal of Sulphates. R. LEITCH MORRIS (*Analyst*, 1923, 48, 250—260; cf. A., 1920, ii, 707).—The perchlorate method is trustworthy for the estimation of potassium in the presence of phosphates, but sulphates and ammonium salts must be removed previously. It is recommended that the sulphate should be precipitated as barium sulphate from a strongly hydrochloric acid solution and that the barium sulphate precipitate should be ignited and extracted with hot hydrochloric acid, the acid extract being added to the main solution. The potassium perchlorate precipitate should be washed first with alcohol containing 0.2% of perchloric acid and then with this alcohol-perchloric acid mixture saturated previously with potassium perchlorate. Drushel's modification of the cobaltinitrite method (A., 1908, ii, 66) also yields trustworthy results provided that, in the oxidation of the precipitate, a considerable excess of permanganate solution is used and the mixture heated for ten minutes before the sulphuric acid is added; the heating should be continued for a further ten minutes before the oxalic acid is added.

W. P. S.

New Method of Analysing Sodium Hyposulphite. S. H. WILKES (*J. Soc. Chem. Ind.*, 1923, 42, 356—357T).—Sodium hyposulphite is estimated by determination of the amount of iodine liberated from excess of an iodate-iodide mixture according to the equation $3\text{Na}_2\text{S}_2\text{O}_4 + 4\text{KIO}_3 + 2\text{KI} = 3\text{I}_2 + 3\text{Na}_2\text{SO}_4 + 3\text{K}_2\text{SO}_4$. The iodine liberated is not titrated directly with thiosulphate, but excess of the latter is used and the quantity unused is determined by back titration with standard iodine. The method is not applicable to samples of hyposulphite containing soda-ash or decomposition products.

H. H.

Estimation of Calcium in Plasma. A. HIRTH (*Compt. rend. Soc. Biol.*, 1923, 88, 458—460; from *Chem. Zentr.*, 1923, ii, 1099).—The ash from 5 c.c. of plasma is dissolved in 2 c.c. of 7% hydrochloric acid. Four drops of 4% ferric chloride solution and one drop of bromine water are added, and the liquid is heated to boiling. After cooling and diluting to 15 c.c., ammonia is added until the liquid is alkaline to phenolphthalein. A slight excess of acetic acid is added and the ferric phosphate and basic ferric acetate are removed by filtration; the precipitate is washed with water containing ammonium acetate and acetic acid. The neutralised filtrate is concentrated to about 4 c.c. and the calcium precipitated as calcium oxalate.

G. W. R.

Estimation of Magnesium in Plasma. A. HIRTH (*Compt. rend. Soc. Biol.*, 1923, 88, 460—461; from *Chem. Zentr.*, 1923, ii, 1099).—The filtrate from the estimation of calcium (see pre-

ceding abstract) is evaporated to dryness and heated to remove ammonium compounds. The residue is dissolved in hydrochloric acid. After addition of ammonia solution, the magnesium is precipitated by addition of ammonium phosphate solution. The precipitate after washing is dissolved in nitric acid containing sulphuric acid. Ammonium molybdate is added to precipitate the phosphate (Lorenz-Pregl). The precipitate of ammonium phosphomolybdate is then dissolved in ammonia solution and precipitated with 2 c.c. of 10% barium chloride solution (Posternak). This precipitate after collection is incinerated and weighed. The factor used for conversion to magnesium is 0.00579. G. W. R.

A New Reaction for Zinc. G. SPACU (*Bul. Șoc. Științe Cluj*, 1922, 1, 348—351; from *Chem. Zentr.*, 1923, ii, 1052).—The reaction proposed depends on the insolubility of the compound $[\text{Zn}(\text{C}_5\text{H}_5\text{N})_2](\text{CNS})_2$. It takes place preferably in neutral solution or with a slight excess of pyridine. With great excess of pyridine the precipitate redissolves. One part of zinc in 200,000 parts of water may be detected. G. W. R.

Estimation of Cobalt in Special Steels. GIULIO FERRERI (*Giorn. Chim. Ind. Appl.*, 1923, 5, 339—340).—The tungsten and silicon are removed from the solution as oxides and the cobalt separated as potassium cobaltinitrite and estimated electrolytically. [Cf. *J.S.C.I.*, 1923, Oct.] T. H. P.

Estimation of Chromium in Presence of Organic Matter. G. GRASSER (*Z. Leder-u. Gerb.-Chem.*, 1922—1923, 2, 185—188).—The treatment of chromium residues with sulphuric acid and potassium permanganate to destroy organic matter prior to the iodometric estimation of the chromium gives concordant results, but not with iron alum solution. The Fresenius-Babo method of oxidising with sulphuric acid and potassium chlorate gives good results with iron alum and iodometrically. Potassium chlorate and hydrochloric acid, also chloric acid, have been used to oxidise the organic matter, in some cases completing the oxidation with ammonium persulphate. The quickest and best method of oxidation consists in heating a mixture of 10 parts of the chromium residue, 3 parts of potassium nitrate, and 1 part of calcined sodium carbonate to dryness and then fusing to oxidise the chromium to chromate. The fused mass is extracted with hot water, acidified, and the chromium estimated iodometrically or with iron alum.

D. W.

Uses of Amalgams in Volumetric Analysis. VIII. Estimation of Chromium and of Iron in the Presence of Chromium. NAOTSUNA KANO (*J. Chem. Soc. Japan*, 1923, 44, 37—46).—Chromium was estimated volumetrically after reduction with ferrous or titanous sulphate, which was prepared by reducing with zinc amalgam. A definite quantity of titanous sulphate was reduced to the titanous salt with zinc amalgam, potassium chromate was added until the colour of chromium-ion appeared, and the remaining ter-

valent titanium was titrated with about 0.1*N*-iron alum solution, using ammonium thiocyanate as indicator. Towards the end, the solution should be warmed at 50°. 0.1*N*-Potassium permanganate may be used instead of iron alum solution. A definite quantity of iron alum may be used instead of titanous sulphate and the remaining bivalent iron titrated with 0.1*N*-potassium permanganate solution. When the quantity of chromium is large, *e.g.*, 0.03 g. of the oxide in 100 c.c., the first method is the most accurate. When less chromium is present, a definite quantity of titanous sulphate can be reduced to titanous salt, a mixture of potassium chromate and iron alum in different proportions added, and the chromium titrated with potassium permanganate. Chromium may also be estimated by the same method, using iron alum instead of titanous sulphate. Iron in presence of chromium is estimated as follows. A mixture of iron and chromium salts is reduced with zinc amalgam in the presence of carbon dioxide. When reduction is complete, the carbon dioxide is replaced by air and the liquid shaken for a few minutes; chromium is completely changed into the tervalent form, and the bivalent iron is titrated with 0.1*N*-potassium permanganate solution; the quantity of chromium should be limited to 0.03 g. of the oxide in 100 c.c. of solution. K. K.

Uses of Amalgams in Volumetric Analyses. IX. Estimation of Titanium and of Iron in the Presence of Titanium. NAOTSUNA KANO (*J. Chem. Soc. Japan*, 1923, **44**, 47—53; cf. *ibid.*, 1922, **43**, 544, 547, 554, 555).—Titanium and iron are estimated volumetrically without separation. A mixture of iron alum and titanium sulphate is reduced with zinc amalgam and titrated with 0.1*N*-potassium permanganate, by which the sum (*s*) of the titanium and iron is determined. Next a definite volume (*a* c.c.) of the mixture of iron alum and titanium sulphate is reduced with zinc amalgam and titrated with the unreduced mixture (*b* c.c.) using ammonium thiocyanate as indicator; tervalent iron in the latter mixture oxidises tervalent titanium in the reduced mixture. Then the ratio of the concentrations $c_{Fe}/c_{Ti}=a/b$, and $c_{Ti}(1+a/b)=s$. K. K.

Estimation of Antimony and its Separation from Tin. P. WENGER and G. PARAUD (*Ann. Chim. Analyt.*, 1923, [ii], **5**, 230—232).—The methods of Henz (A., 1904, ii, 150), Wortmann and Metzel (A., 1905, ii, 655), Bunsen and Baubigny (A., 1897, ii, 351), and Classen for the estimation of antimony gave results varying between 99.34% and 99.79% of the theoretical. Rose's method, however, gave very low results and is not considered to be of any value for exact estimations. Wortmann and Metzel's and Classen's methods are the most convenient and rapid. In separating antimony from tin, Clarke's method (*Chem. News*, **21**, 124) and Tomula's method (A., 1922, ii, 74) were found satisfactory, but Rose's method is again useless. H. C. R.

Detection of Methyl Alcohol in Ethyl Alcohol. R. MEURICE (*Ann. Chim. Analyt.*, 1923, [ii], **5**, 204—205).—Ten c.c. of the

95% alcohol are mixed at 18° with 10 c.c. of 22% ammonium sulphate solution; in the case of pure ethyl alcohol, the mixture separates into two clear layers within about two minutes, but if the alcohol under examination contains 3% of methyl alcohol the lower layer is turbid and contains crystals of ammonium sulphate. In the presence of 10% of methyl alcohol, a voluminous precipitate of ammonium sulphate is formed. W. P. S.

The Detection of Methyl Alcohol in Alcoholic Liquids. VAN RIJN (*Pharm. Weekblad*, 1923, 60, 978—984).—Samples of spirits suspected to contain methyl alcohol were examined by (1) Mannich and Fendler's method, (2) method of Pfijl, Reif, and Hanner, and (3) Riche-Bardy's method, the results being checked by determination of the refractive indices of the absolute alcohol obtained by distillation over calcium oxide. All these methods gave parallel results, but owing to the time required for (3), the first two are more suitable.

From 500 c.c. of the original sample half was distilled, from the distillate half again, and so on until 15 c.c. only of distillate was left, each fraction and the original sample being tested by the three methods. In all cases positive results were obtained from the original sample, and sometimes from the first distillate, but never from the fourth and fifth distillates. Since methyl alcohol concentrates in the final fractions, as was confirmed by adding 0.5% to one sample, it is evident that positive results are given by substances other than this alcohol (higher alcohols or ethers ?), in testing for which, accordingly, it is necessary to fractionate repeatedly. The refractive index of the anhydrous alcohol affords a valuable check. S. I. L.

Critical Examination of Methods for the Estimation of Lævulose in the Presence of Dextrose. H. COLIN (*Bull. Assoc. Chim. Sucr.*, 1923, 40, 397—405).—The methods investigated were (1) the polarimetric method; (2) oxidation of the dextrose by bromine, (3) oxidation of the dextrose by iodine; (4) conversion of the dextrose into methyl glucoside; (5) destruction of the lævulose by heating at 100° for three hours with 7% hydrochloric acid; and (6) detection of lævulose by precipitating it as its calcium compound. All these methods yielded trustworthy results when applied to the pure sugars alone, but not in the case of complex mixtures such as plant extracts. The latter contain substances which interfere particularly with the polarimetric, bromine, and iodine methods. W. P. S.

Estimation of Starch. FRANZ TEMPUS (*Naturprodukte*, 1923, 52—58).—The difficulties attending the accurate estimation of starch in vegetable materials can be overcome by means of a preliminary heating with strong ammonia solution. This treatment brings about disruption of the cell-walls, frees the starch granules, and facilitates the removal of sugars, dextrin, hemicelluloses, and fats. A dried sample, not more than 2 g., is finely powdered and warmed for three hours in a stoppered glass vessel

at 40—45° with 50 c.c. of concentrated ammonia. It is then filtered through a linen filter on a Gooch crucible and washed well. The residue is then finely ground and the starch estimated by the diastase method.

E. H. R.

Estimation of Starch. II. Estimation of Starch in Potatoes. ARTHUR R. LING and W. J. PRICE (*J. Inst. Brewing*, 1923, 29, 732—734; cf. A., 1922, ii, 879).—A curve, similar to that given for barley and wheat starches, has now been obtained showing the dependence of the proportion of apparent maltose yielded by potato starch on the diastatic power of the malt used to effect the starch conversion. The two curves are almost parallel, the percentages of maltose being higher for potato starch than for barley and wheat starches.

To estimate the starch in potatoes, about 8 g. of the finely sliced tubers are weighed exactly and pounded in a glass mortar, the pulp being washed into a beaker with about 100 c.c. of water and left for thirty minutes with occasional stirring. The supernatant liquid is then decanted on to a No. 41 Whatman filter and another 100 c.c. of water are added to the pulp and decanted at the end of thirty minutes, the pulp and filter being well washed with water. The filter and its contents are boiled in the beaker containing the pulp with 100 c.c. of water for ten minutes, and the gelatinised starch is afterwards hydrolysed at 57° by treatment for an hour with 10 c.c. of the extract of a malt of known diastatic power. The liquid is then boiled, cooled, and made up to 200 c.c., an aliquot portion being then titrated with Fehling's solution.

T. H. P.

Estimation of the Eugenol Content of Volatile Oils by Titration. P. N. VAN ECK (*Pharm. Weekblad*, 1923, 60, 937—940).—A weighed quantity of clove or other eugenol-containing oil is heated with excess of standard ammoniacal silver nitrate solution, the excess of silver nitrate being estimated after filtration by titration with standard thiocyanate solution. One part of eugenol is found by experiment to cause the separation of 1.75 parts of silver.

S. I. L.

Estimation of Simple, Soluble Cyanogen Compounds, Making Use of the Principle of Aëration. JOSEPH H. ROE (*J. Amer. Chem. Soc.*, 1923, 45, 1878—1883).—An aëration process for estimating cyanides has been devised, in which the liberated hydrocyanic acid is swept by a current of air into a dilute solution of an alkali hydroxide and the mixture then titrated with standard silver nitrate solution, using a little potassium iodide solution as indicator. In the case of a soluble cyanide, the procedure is as follows: a quantity of the cyanide (0.05 g.) is dissolved in 100 c.c. of water and placed in a cylinder of 200 c.c. capacity fitted with a doubly bored stopper. Through one hole, a glass tube, which reaches to the bottom of the cylinder, is placed and a glass exit tube passes through the other hole. The exit tube is connected with a double bubbler apparatus containing about 100—150 c.c.

of 5% sodium hydroxide. A few drops of amyl alcohol are added to the cyanide solution to prevent foaming. The apparatus is connected to a water pump and a slow current of air drawn through, and at the same time 25 c.c. of saturated tartaric acid solution are added to the cyanide. Air is drawn through at the rate of 3 litres per minute for two to three hours. The alkaline solution is then treated with 10 drops of 10% potassium iodide and titrated with 0.01N-silver nitrate solution until a faint turbidity is produced. The method has been applied to the case of mercuric cyanide. In this case, a few crystals of sodium chloride are added to the solution of mercuric cyanide and then, in addition to the tartaric acid which is added as before, 10 c.c. of 5% stannous chloride are added and the process is carried out as described. The present method has many advantages over the older distillation methods, among which may be noted the absence of loss due to hydrolysis of the hydrocyanic acid and its power of estimating cyanides in the presence of ferrocyanides and ferricyanides. The results are highly accurate.

J. F. S.

Potassium Ferrocyanide as a Reagent in the Microscopic Qualitative Chemical Analysis of the Common Alkaloids.

HOWARD IRVING COLE (*Philippine J. Sci.*, 1923, **23**, 97—101).—Potassium ferrocyanide forms definite crystalline compounds with certain alkaloids (cf. Cumming, T., 1922, **121**, 1287) and may be used for their microchemical detection. A small drop (2 to 3 mm. diameter) of the solution of the alkaloid in hydrochloric acid is placed on the microscope slide near a smaller drop of a 5% solution of potassium ferrocyanide and a narrow channel between the drops is made by means of a platinum wire; after a short time the preparation is vigorously scratched with the wire to induce crystallisation. β -Eucaine yields, under these conditions, thin elongated hexagonal or rhombic plates which exhibit parallel and symmetrical extinction under crossed nicols; brucine gives highly refractive prisms arranged in rosettes and exhibiting strong polarisation; cinchonidine gives rosettes of yellow, curving, hair-like needles, cinchonine, yellow, irregular, trapezium-shaped crystals which polarise strongly, and cocaine, irregular, six-sided plates and prisms which grow much thicker, polarise more strongly, and are more irregular in shape than those of the β -eucaine compound. The coniine compound crystallises in rosettes of colourless needles, which polarise weakly, exhibiting oblique extinction, that of heroin in spheroidal crusts only from concentrated solutions and that of hydrastine in spheroidal crusts which are polarised under crossed nicols. The crystals obtained from quinoline are lemon-yellow rhombohedra exhibiting parallel and oblique extinction, those from sparteine are colourless rhombs giving symmetrical extinction, and those of stovaine are rosettes of needles showing parallel extinction. Potassium ferrocyanide in hydrochloric acid solution affords a very sensitive test for strychnine, with which it gives long, slender needles or spear-shaped crystals with serrated edges and exhibiting oblique extinction. Veratrine yields an amorphous

precipitate under these conditions and, although this crystallises slowly, the test is unsatisfactory in this case. A. R. P.

Evaluation of the Catalytic Power of Diastases. L. MATHIEU (*Bull. Assoc. Chim. Sucr.*, 1923, 40, 423—426).—The method proposed consists in mixing 10 c.c. of the diastase solution (vegetable or other extract) with 5 c.c. of hydrogen peroxide in a suitable apparatus and measuring the volume of oxygen liberated within one minute. It is suggested that the catalytic value be expressed as the ratio between the volume of oxygen thus found and that obtained when 1 g. of manganese dioxide is treated under the same conditions. The manganese dioxide used should pass a 100-mesh sieve; the hydrogen peroxide (12 vol.) should be treated previously with sodium hydroxide so that 90% of its acidity is neutralised. W. P. S.

Pancreatic Enzymes. IV. The Stalagmometric Estimation of Hydrolysis of Tributyrin by Lipase. RICHARD WILLSTÄTTER and FRIEDRICH MEMMEN (*Z. physiol. Chem.*, 1923, 129, 1—25).—The estimation of lipase may be carried out conveniently by measuring with a stalagmometer the change in a given time in the "drop-number" of a saturated aqueous solution of tributyrin. It is found that albumin inhibits the hydrolysis of tributyrin by lipase in acid and in alkaline media, whilst albumin inhibits the hydrolysis of olein in an acid and accelerates it in an alkaline medium. This is because the sodium oleate produced increases the rate of hydrolysis by lipase. The rate of hydrolysis of tributyrin is increased by the presence of sodium oleate or sodium glycocholate, but more particularly by calcium oleate. It is suggested that the inhibition due to albumin is caused by the adsorption of one component only (the lipase), whilst in the presence of soaps, both components are adsorbed. The measurements of the amount of lipase present, obtained by the tributyrin method, are not always identical with those obtained from the hydrolysis of olein, although they are approximately so for lipase from pig's or sheep's pancreas. A tributyrin unit is therefore suggested—the amount which will cause a decrease of 20 drops, *i.e.*, about half the difference between the drop number of pure tributyrin solution and of pure water, in fifty minutes under specified conditions. For such estimations, the lipase is activated by sodium oleate, calcium chloride, and albumin, and brought to p_H 8.6, and a temperature of 20°.

The polypeptide, leucylglycylglycine, very markedly increases the rate of hydrolysis of tributyrin by lipase. If albumin, calcium chloride, and sodium oleate, however, are there previously, the tripeptide has little effect. The hydrolysis of olein or methyl butyrate in presence of calcium oleate is markedly increased by albumin, but that of tributyrin under similar conditions is not.

W. O. K.

General and Physical Chemistry.

Some Refractive Indices of Benzene and cycloHexane. J. W. GIFFORD and T. M. LOWRY (*Proc. Roy. Soc.*, 1923, [A], 104, 430—437).—Values of the refractive indices of benzene and cyclohexane at 15°, for about twenty wave-lengths between 7701.92 and 2980.75 Å., have been determined to the seventh significant figure, by the method of the hollow prism. In the case of cyclohexane, the refractive index, n , corresponding with the wave-length λ , is, in the case of wave-lengths other than 3261.17 and 3252.65 Å., given with an average error equal to 0.00006, by the equation

$$n^2 = 2.011046 + 0.0102467/(\lambda^2 - 0.013977).$$

In the case of the two wave-lengths referred to, the respective differences between experimental and calculated values of n are +0.00121 and +0.00130. No corresponding relation holds in the case of benzene, a result which is in accord with the more complex chemical structure of this substance. J. S. G. T.

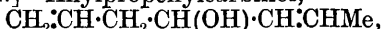
Spectrochemistry of Tropane Derivatives. K. VON AUWERS (*J. pr. Chem.*, 1922, [ii], 105, 102—119).—The following data are recorded. Tropane has $d_4^{10.5}$ 0.9386, $n_a^{10.5}$ 1.47950, $n_b^{10.5}$ 1.48187, $n_\beta^{10.5}$ 1.48845, $n_\gamma^{10.5}$ 1.49394, $d_4^{21.6}$ 0.9307, $n_a^{21.6}$ 1.47427, $n_b^{21.6}$ 1.47659, $n_\beta^{21.6}$ 1.48318, $n_\gamma^{21.6}$ 1.48854. Tropidine has $d_4^{18.4}$ 0.9535, $n_a^{18.4}$ 1.48752, $n_b^{18.4}$ 1.49037, $n_\beta^{18.4}$ 1.49793, $n_\gamma^{18.4}$ 1.50417, $d_4^{10.5}$ 0.9609, $n_a^{10.5}$ 1.49199, $n_b^{10.5}$ 1.49486, $n_\beta^{10.5}$ 1.50257, $n_\gamma^{10.5}$ 1.50898. Tropine has $d_4^{9.8}$ 1.0161, $n_a^{9.8}$ 1.47917, $n_b^{9.8}$ 1.48113, $n_\beta^{9.8}$ 1.48766, $n_\gamma^{9.8}$ 1.49269. Acetyl tropein has $d_4^{15.4}$ 1.0627, $n_a^{15.4}$ 1.47456, $n_b^{15.4}$ 1.47687, $n_\beta^{15.4}$ 1.48321. Propionyl tropein has $d_4^{19.6}$ 1.0399, $n_a^{19.6}$ 1.47208, $n_b^{19.6}$ 1.47434, $n_\beta^{19.6}$ 1.48069, $n_\gamma^{19.6}$ 1.48591. Tropinone has $d_4^{20.6}$ 0.9872, $n_a^{20.6}$ 1.45975, $n_b^{20.6}$ 1.46205, $n_\beta^{20.6}$ 1.46910. Ethyl tropane-2-carboxylate has $d_4^{20.5}$ 1.0408, $n_a^{20.5}$ 1.47272, $n_b^{20.5}$ 1.47562, $n_\beta^{20.5}$ 1.48197, $n_\gamma^{20.5}$ 1.48719, d_4^{15} 1.0468, n_a^{15} 1.47583, n_b^{15} 1.47805, n_β^{15} 1.48448, n_γ^{15} 1.48968. The methyl ester of *l*-ecgonine has $d_4^{20.5}$ 1.1468, $n_a^{20.5}$ 1.48474, $n_b^{20.5}$ 1.48765. Ethyl tropidine-2-carboxylate has $d_4^{21.3}$ 1.0625, $n_a^{21.3}$ 1.49173, $n_b^{21.3}$ 1.49480, $n_\beta^{21.3}$ 1.50300, $d_4^{11.7}$ 1.0721, $n_a^{11.7}$ 1.49615, $n_b^{11.7}$ 1.49930, $n_\beta^{11.7}$ 1.50768, $n_\gamma^{11.7}$ 1.51462. Ethyl tropinone-2-carboxylate has $d_4^{20.8}$ 1.1207, $n_a^{20.8}$ 1.49225, $n_b^{20.8}$ 1.49537, $n_\beta^{20.8}$ 1.50432, $d_4^{18.7}$ 1.1228, $n_a^{18.7}$ 1.49312, $n_b^{18.7}$ 1.49626, $n_\beta^{18.7}$ 1.50353. Trocacaine has $d_4^{100.1}$ 1.0426, $n_a^{100.1}$ 1.50440, $n_b^{100.1}$ 1.50801, $n_\beta^{100.1}$ 1.51840, $n_\gamma^{100.1}$ 1.52707. *d*- ψ -Cocaine has $d_4^{20.6}$ 1.1020, $n_a^{20.6}$ 1.49862, $n_b^{20.6}$ 1.50218, $n_\beta^{20.6}$ 1.51199, $n_\gamma^{20.6}$ 1.51959. (*d* + *l*)- ψ -Cocaine has $d_4^{20.5}$ 1.1026, $n_a^{20.5}$ 1.49867, $n_b^{20.5}$ 1.50209, $n_\beta^{20.5}$ 1.51193, $n_\gamma^{20.5}$ 1.51996. ψ -Pelletierine has $d_4^{20.5}$ 1.0014, $n_a^{20.5}$ 1.47351, $n_b^{20.5}$ 1.47596, $n_\beta^{20.5}$ 1.48289, $n_\gamma^{20.5}$ 1.48861. Ethyl *N*-methylpyrrolidine-2:5-diacetate has $d_4^{15.4}$ 1.0490, $n_a^{15.4}$ 1.45872, $n_b^{15.4}$ 1.46113, $n_\beta^{15.4}$ 1.46765, $n_\gamma^{15.4}$ 1.47035.

s-Copellidine has $d_4^{19.0}$ 0.8315, $n_a^{19.0}$ 1.44113, $n_b^{19.0}$ 1.44354, $n_\beta^{19.0}$ 1.44982, $n_\gamma^{19.0}$ 1.45524, and is converted by the action of methyl iodide into *N-methyl-2:4:6-trimethylpiperidine*, a colourless oil, which has b. p. 153—155°, $d_4^{19.7}$ 0.8231, $n_a^{19.7}$ 1.44063, $n_b^{19.7}$ 1.44299, $n_\beta^{19.7}$ 1.44952, $n_\gamma^{19.7}$ 1.45471. *N-Methyltetrahydroquinoline* has $d_4^{17.3}$ 1.0236, $n_a^{17.3}$ 1.57620, $n_b^{17.3}$ 1.58268, $n_\beta^{17.3}$ 1.60057. Bornyl acetate has $d_4^{22.6}$ 0.9833, $n_a^{22.6}$ 1.45998, $n_b^{22.6}$ 1.46225, $n_\beta^{22.6}$ 1.46827, $n_\gamma^{22.6}$ 1.47319. *isoBornyl acetate* has $d_4^{23.4}$ 0.9807, $n_a^{23.4}$ 1.45978, $n_b^{23.4}$ 1.46191, $n_\beta^{23.4}$ 1.46798, $n_\gamma^{23.4}$ 1.47275. Bornyl *isovalerate* has $d_4^{22.2}$ 0.9487, $n_a^{22.2}$ 1.45779, $n_b^{22.2}$ 1.46001, $n_\beta^{22.2}$ 1.46590, $n_\gamma^{22.2}$ 1.47068. Camphidine reacts readily with methyl iodide, giving *N-methylcamphidine*, a colourless oil, which gives a *picrate*, short, slender needles, m. p. 234°; it has b. p. 195—197°, $d_4^{19.0}$ 0.9011, $n_a^{19.0}$ 1.47378, $n_b^{19.0}$ 1.47625, $n_\beta^{19.0}$ 1.48308, $n_\gamma^{19.0}$ 1.48869, $d_4^{20.8}$ 0.8998, $n_a^{20.8}$ 1.47311, $n_b^{20.8}$ 1.47552, $n_\beta^{20.8}$ 1.48230, $n_\gamma^{20.8}$ 1.48767.

It is concluded that, in general, a molecule containing a seven- or eight-membered ring having a -NMe- group as a bridge, shows a depression in the values of the molecular refraction and molecular dispersion.

W. S. N.

Spectrochemistry of Compounds with Augmented Conjugations. K. VON AUWERS (*J. prakt. Chem.*, 1923, [ii], 105, 361—384).—The following data are recorded and discussed [With H. WESTERMANN].—Allylpropenylcarbinol,



has b. p. 61—62°/15 mm., d_4^{20} 0.8612, n_a^{20} 1.45089, n_{He}^{20} 1.45414, n_β^{20} 1.46191, n_γ^{20} 1.46840, and gives, when distilled with potassium hydrogen sulphate in a current of hydrogen, $\Delta^{4,7,8}$ -heptatriene, which has b. p. 113—114°, $d_4^{19.8}$ 0.7636 (hence d_4^{20} 0.764), $n_a^{19.8}$ 1.50786, $n_{\text{He}}^{19.8}$ 1.51604, $n_\beta^{19.8}$ 1.53754, $n_\gamma^{19.8}$ 1.55742, n_{He}^{20} 1.5160 (cf. Enklaar, A., 1913, i, 243).

[With J. HEYNA].—Ethyl β -vinylacrylate is prepared by the action of ethyl iodide on an ethereal solution of silver β -vinylacrylate; it polymerises very readily, and has b. p. 70—71°/31 mm., 59.9°/18 mm., or 57.2—57.5°/13 mm., $d_4^{23.3}$ 0.9348, $n_a^{22.9}$ 1.46948, $n_{\text{He}}^{22.9}$ 1.47504, $n_\beta^{22.9}$ 1.48928, $n_\gamma^{22.9}$ 1.50252, n_{He}^{20} 1.4764. Closely corresponding figures for d and n are quoted for other temperatures. Ethyl sorbate has b. p. 81°/15 mm., or 76.5°/12 mm., $d_4^{15.25}$ 0.9405, $d_4^{14.85}$ 0.9408, $n_a^{15.25}$ 1.49149, $n_{\text{He}}^{15.25}$ 1.49775, $n_\beta^{15.25}$ 1.51395, n_{He}^{20} 1.4956. Ethyl α -methylsorbate has $d_4^{16.5}$ 0.9501 (d_4^{20} 0.947), $n_a^{15.5}$ 1.49306, $n_{\text{He}}^{16.5}$ 1.49907, $n_\beta^{16.5}$ 1.51492, $n_\gamma^{16.5}$ 1.52998, n_{He}^{20} 1.4976. Ethyl α -ethylsorbate has $d_4^{15.3}$ 0.9345 (d_4^{20} 0.931), $n_a^{15.3}$ 1.49076, $n_{\text{He}}^{15.3}$ 1.49653, $n_\beta^{15.3}$ 1.51162, $n_\gamma^{15.3}$ 1.52605, n_{He}^{20} 1.4944. Ethyl γ -methylsorbate has $d_4^{15.6}$ 0.9499 (d_4^{20} 0.946), $n_a^{15.6}$ 1.49484, $n_{\text{He}}^{15.6}$ 1.50087, $n_\beta^{15.6}$ 1.51642, $n_\gamma^{15.6}$ 1.53138, n_{He}^{20} 1.4989. Ethyl $\beta\delta$ -dimethylsorbate has $d_4^{18.5}$ 0.9343 (d_4^{20} 0.933), $n_a^{18.5}$ 1.48301, $n_{\text{He}}^{18.5}$ 1.48823, $n_\beta^{18.5}$ 1.50175, $n_\gamma^{18.5}$ 1.51447, n_{He}^{20} 1.4876. Diethyl crotonylidenemalonate has b. p. 149°/15 mm., $d_4^{14.3}$ 1.0508 (d_4^{20} 1.045), $n_a^{14.3}$ 1.47867, $n_{\text{He}}^{14.3}$ 1.48353, $n_\beta^{14.3}$ 1.49629, n_{He}^{20} 1.4809.

Sorbyl chloride has $d_4^{18.75}$ 1.0666 (d_4^{20} 1.065), $n_a^{18.75}$ 1.54707, $n_{He}^{18.75}$ 1.55710, $n_\beta^{18.75}$ 1.58453, n_{He}^{20} 1.5566.

[With W. MÜLLER.]—The ethyl ester of the stable cinnamylideneacetic acid (Vorländer, A., 1906, i, 362), has m. p. 25–26°, $d_4^{41.6}$ 1.0299 ($d_4^{42.2}$ 1.0294, d_4^{20} 1.049), $n_a^{42.2}$ 1.60039, $n_{He}^{42.2}$ 1.61348, $n_\beta^{42.2}$ 1.65080, $n_\gamma^{42.2}$ 1.69311, n_{He}^{20} 1.6233. *Ethyl allocinnamylideneacetate* is a colourless, mobile oil, which decomposes when heated under 10 mm. pressure. It has $d_4^{16.3}$ 1.0473 (d_4^{20} 1.044), $n_a^{16.3}$ 1.60645, $n_{He}^{16.3}$ 1.61950, $n_\beta^{16.3}$ 1.65722, $n_\gamma^{16.3}$ 1.70002, n_{He}^{20} 1.6181. *Ethyl α -methylcinnamylideneacetate* is an oil which cannot be distilled. It has d_4^{22} 1.0391 (d_4^{30} 1.041), n_a^{22} 1.60324, n_{He}^{22} 1.61641, n_β^{22} 1.65401, n_{He}^{20} 1.6155. β -Methylcinnamylideneacetic acid has m. p. 156–157° (Kohler, A., 1910, i, 484, gives m. p. 153°); its *ethyl* ester is an oil, which cannot be distilled, and has $d_4^{25.1}$ 1.0384 (d_4^{20} 1.043), $n_a^{25.1}$ 1.58849, $n_{He}^{25.1}$ 1.59936, $n_\beta^{25.1}$ 1.63013, $n_\gamma^{25.1}$ 1.66379, n_{He}^{20} 1.6017. γ -Methylcinnamylideneacetic acid, short, thick prisms, m. p. 108–110°, is prepared by the condensation of malonic acid with α -methylcinnamic acid in the presence of hot pyridine, which is accompanied by elimination of carbon dioxide, or by dehydrating the hydroxy-ester formed by condensing α -methylcinnamic acid, ethyl bromoacetate, and zinc in benzene solution. *Ethyl γ -methylcinnamylideneacetate*, a colourless oil, which cannot be distilled, has $d_4^{20.3}$ 1.0387 (d_4^{20} 1.039), $n_a^{20.3}$ 1.59010, $n_{He}^{20.3}$ 1.60100, $n_\beta^{20.3}$ 1.63176, $n_\gamma^{20.3}$ 1.66551, n_{He}^{20} 1.6012. *Ethyl β -acetylacrylate* has $d_4^{18.1}$ 1.0387 (d_4^{20} 1.037), $n_a^{18.1}$ 1.44987, $n_{He}^{18.1}$ 1.45346, $n_\beta^{18.1}$ 1.46250, $n_\gamma^{18.1}$ 1.47081, n_{He}^{20} 1.4526. *Ethyl muconate* has $d_4^{28.8}$ 0.9832 (d_4^{30} 0.9829), $n_a^{28.8}$ 1.46178, $n_{He}^{28.8}$ 1.46755, $n_\beta^{28.8}$ 1.48259, $n_\gamma^{28.8}$ 1.49695. *Dimethyl β -methyl- $\Delta^{\alpha\gamma}$ -butene- $\alpha\delta$ -dicarboxylate* has $d_4^{34.8}$ 1.1006 ($d_4^{34.9}$ 1.1005, d_4^{20} 1.115), $n_a^{34.9}$ 1.50142, $n_{He}^{34.9}$ 1.50762, $n_\beta^{34.9}$ 1.52413, $n_\gamma^{34.9}$ 1.53993, n_{He}^{20} 1.5143. The corresponding diethyl ester has b. p. 163–164°/19 mm. (Stephen and Weizmann, T., 1913, 103, 276, give b. p. 170°/10 mm.), and does not solidify when strongly cooled. It has d_4^{17} 1.0586 (d_4^{20} 1.056), n_a^{17} 1.49515, n_{He}^{17} 1.50081, n_β^{17} 1.51560, n_γ^{17} 1.52985, n_{He}^{20} 1.4995. W. S. N.

Dispersion Accompanying Magnetic Double-refraction. G. SZIVESSY (*Z. Physik*, 1923, 18, 97–104).—Values of the phase difference, ψ , between the ordinary and extraordinary rays propagated in a magnetic field of strength $H=10,100$ gauss, and of the respective refractive indices n , at about 20° are tabulated for $\lambda\lambda$ 486, 520, 550, 589, 620, and 656 $\mu\mu$ in the cases of toluene, *p*-xylene, *m*-xylene, chlorobenzene, bromobenzene, quinoline, anethole, benzoyl chloride, benzyl alcohol, and benzonitrile. From the results the respective values of the Cotton-Mouton constant, C , and the Havelock constant, h , are calculated by means of the equations $\psi=ClH^2$ and $C=h(n^2-1)^2/n\lambda$, where l denotes the length of path traversed in the respective substances. In the case of any of the substances investigated, the respective values of h are found to be independent of the wave-length employed, in accordance with Havelock's theory.

J. S. G. T.

The Influence of Foreign Gases on the Secondary Spectrum of Hydrogen. S. BARRATT (*Phil. Mag.*, 1923, [vi], **46**, 627—629).—In continuation of previous work on the enhancement of lines in the secondary spectrum of hydrogen due to the presence of helium (A., 1922, ii, 461), the author finds that similar changes, evidently related although on a far smaller scale, are produced by argon, whilst oxygen exerts no influence of the kind. The secondary hydrogen lines $\lambda\lambda$, 6392.99 and 6111.08 Å., previously observed only in the presence of helium, were developed when argon was present.
J. S. G. T.

The Zeeman Effect associated with the Red and Blue Hydrogen Lines. K. FÖRSTERLING and G. HANSEN (*Z. Physik*, 1923, **18**, 26—33).—In a magnetic field of strength up to 20,000 gauss, each component of the doublets H_α and H_β in the hydrogen spectrum becomes a normal Zeeman triplet. Contrary to the conclusion of Erochin (*Ann. Physik*, 1913, [iv], **42**, 1054), the authors find that the central components of each pair of triplets arising respectively from H_α and H_β are displaced towards one another in the magnetic field, a result which is not in accord with any current theory of the Zeeman effect.
J. S. G. T.

Ultra-violet Resonance Spectra of Iodine Vapour. OTTO OLDENBERG (*Z. Physik*, 1923, **18**, 1—11).—Iodine vapour, excited by ultra-violet radiation of short wave-length emits a resonance spectrum comprising a series of lines characterised by the same regularity and nuclear vibration quanta as in the case of the resonance spectrum excited by the green mercury line. In the neighbourhood of the band λ 3250 Å., additional bands $\lambda\lambda$ 3169, 3191, 3212, 3237, 3261, 3285, 3311, 3338, 3364, 3394, 3417, 3442, 3466, 3495, 3495, 3525, 3559, 3596, 3640, 3680, 3720, 3765, 3813, 3866, 3925, and 4007 Å. are observed when extraneous light is carefully excluded. The frequencies, ν , of about thirty-five lines conforming with Stokes's law, and of three lines of shorter wave than that of the exciting radiation, are, in the case of excitation with the zinc line λ 1900, represented by the equation $\nu = 52630(1 - 0.00416n + 0.000017n^2)$, $n = 0, 1, 2, 3, \dots$. Toward the region of long wave-lengths, the resonance spectrum passes gradually into the ultra-violet fluorescence band spectrum of iodine vapour observed by McLennan (A., 1913, ii, 455; 1914, ii, 829), which corresponds fairly well with the ultra-violet bands in the spectrum emitted by iodine vapour under electrical excitation. It is concluded that the band spectrum is the long wave-length extension of the short wave-length resonance spectrum. The author discusses a possible origin of emission of the fluorescence spectrum, which is excited only by radiation of wave-length shorter than 1950 Å. It is shown conclusively, in agreement with McLennan's result, that the visible and ultra-violet fluorescence spectra are emitted by the iodine molecule and are not attributable to the presence of an impurity.
J. S. G. T.

Series Spectra in Oxygen and Sulphur. J. J. HOPFIELD (*Nature*, 1923, **112**, 437—438).—The series for oxygen previously

reported (*Physical Rev.*, 1923, **21**, 710) have been extended from two to seven and from one to six members, respectively. No second member of the third series was found. Gaseous sulphur dioxide has a strong absorption band extending from λ 2500 to λ 1700, and another from λ 1650 indefinitely into the ultra-violet. The spark spectrum of sulphur extends to λ 350; the arc spectrum contains a number of triplets of wide separation and constant frequency difference which have been classified in series by analogy with oxygen. In the cases of both oxygen and sulphur, the intensities and separations observed are inverted as compared with the known spectra of these elements in the visible and ultra-red. One stable and two metastable forms of each of the elements atomic oxygen and atomic sulphur appear to exist. The resonance and ionising potentials, respectively, for the stable forms are calculated to be: oxygen, 9.11 and 13.56 volts; sulphur, 6.50 and 10.31 volts.

A. A. E.

The Carbon Arc Spectrum in the Extreme Ultra-violet.

II. F. SIMEON (*Proc. Roy. Soc.*, 1923, [A], **104**, 368—375).—In continuation of previous work (this vol., ii, 45), the author has shown that the spectrum of the carbon arc in vacuum extends as far in the extreme ultra-violet as that of the spark, with the exception of a very faint line at λ 360.5 Å. The wave-lengths and relative intensities of twenty-five new lines in the region between λ 976.7 and λ 371.5 Å. are tabulated. In agreement with a deduction from the quantum theory, it is found that a potential of between 30 and 40 volts is sufficient to excite the *L*-series of carbon lines. Reasons are advanced for attributing the lines $\lambda\lambda$ 1751.8, 1760.6, 2297.1, 2509.5, and 2512.4 Å., excited at 30 volts to the carbon spark spectrum, and the remainder to the arc spectrum. J. S. G. T.

Structure of the Spectrum of Neon. A. LANDÉ (*Z. Physik*, 1923, **17**, 292—294).—It is shown that certain lines in the neon spectrum analysed by Paschen (A., 1920, ii, 69, 718), which, according to Grotrian (A., 1922, ii, 179) may be regarded as *L*₁ and *L*₂ terms derived by extrapolation of the *L*-series of doublets in the Röntgen spectrum of neon, can be classified as the first components of a system of quintuplets, two systems of triplets, and a system of singlets. In the latter classification, both *L*₁ and *L*₂ terms originate by the displacement of electrons from 2₂ orbits. J. S. G. T.

Excitation of the Spark Spectra of Lithium. E. VON ANGERER (*Z. Physik*, 1923, **18**, 113—119).—The literature of the excitation of spark spectra is briefly reviewed, and experimental details of attempts made by the author to excite the spectra of Li^{II} and Li^{III} are given. The following lines, hitherto unrecorded, and possibly attributable to Li^{II}, were observed in the vacuum spectrum: 3143.7, 3028.5, 3024.6, 2988.5, 2959.5, 2899.66, 2869.90, 2866.45, 2704.60, 2635.20. J. S. G. T.

Spectra and the Periodic Classification. M. A. CATALÁN (*Anal. Fis. Quím.*, 1923, **21**, 321—329; cf. this vol., ii, 104, 105, 356).—Further data are given for the spectrum of the manganese. The

relation of ionisation potentials to the periodic classification is discussed. Well defined maxima are shown for zinc and cadmium and a less marked maximum for calcium. G. W. R.

The α -Lines in the K-Series Tungsten Spectrum. CHARLES CROFUTT (*Proc. Iowa Acad. Sci.*, 1921, **28**, 117—118; cf. Duane and Shimizu, *Physical Rev.*, 1919, **13**, 306; Duane and Patterson, A., 1921, ii, 363; *Proc. Nat. Acad. Sci.*, 1920, **6**, 509; Duane and Stenström, *ibid.*, 1920, **6**, 477).—Experiments with a crystal of thickness 0.015 cm., a front slit 0.005 cm. wide, and a prolonged exposure did not reveal the α_3 -line, which is therefore assumed to have an intensity less than one-tenth of that of the α_2 -line, or to differ from it in wave-length by less than 0.05%.

CHEMICAL ABSTRACTS.

The Absorption Spectra of some Metallic Vapours. WALTER GROTRIAN (*Z. Physik*, 1923, **18**, 169—182).—In continuation of previous work (this vol., ii, 106), the author has investigated the absorption of visible radiation and radiation extending into the ultra-violet as far as about λ 2350 Å. by the vapours of copper, silver, gallium, lead, tin, bismuth, antimony, and manganese. In the case of copper vapour, in a tube 30 cm. long, absorption of the first members of the doublet principal series, $\lambda\lambda$ 3247 and 3274 Å., was observed at about 1050°. Under similar conditions, absorption of the corresponding lines $\lambda\lambda$ 3280 and 3383 Å. in the case of silver vapour was observed at about 900°. In the case of gallium, absorption of the first members of the subordinate series was observed at 850° in the case of the $2p_2$ -lines $\lambda\lambda$ 2874 and 4033 Å., whilst in the case of the $2p_1$ lines $\lambda\lambda$ 2943.7, 2944.2, and 4172 Å. absorption was first observed at about 900°. Absorption of the line λ 2833 Å. by 30 cm. of lead vapour was observed at 550°. At temperatures above 950°, the line broadened unsymmetrically, the centre being displaced towards the red end of the spectrum. At 1200°, a continuous absorption band, about 10 Å. wide, relatively sharply defined towards the blue and indefinite towards the red end of the spectrum, was observed. The broadening is attributable to the formation of lead molecules, probably Pb_2 . From the position of the line 2833 in the series proposed for the lead spectrum by Thorsen (*Naturwiss.*, 1923, **11**, 78), the ionisation potential of the lead atom is found to be 7.38 volts. As the normal condition of the lead atom corresponds with a p -term, it is concluded that the 82 electrons associated with the atom are arranged in a 6_2 orbit. Absorption of other lines was observed at higher temperatures, in accordance with theoretical considerations. The partial pressure of the atoms exhibiting absorption was of the order 10^{-5} mm. In a tube 15 cm. long, absorption of the lines $\lambda\lambda$ 3009.2, 2863.4, and 2706.6 Å. by tin vapour was observed at 1,050°. Bismuth exhibited typical absorption of the line 3067 Å. at 650°. At higher temperatures, bands were strongly developed. It is suggested that the molecule of bismuth vapour is partly polyatomic. Absorption of the manganese triplet 2794.82, 2798.27, and 2801.07 by manganese vapour was observed at about 850°, whilst absorption of the triplet 4030.76,

4033·07, and 4034·49 occurred at about 880°. The results are considered to justify the assumption by Catalán (A., 1922, ii, 726) of the $1S$ term as the normal condition of the manganese atom.

J. S. G. T.

Röntgen Spectroscopy. Absorption Spectra in the L -Series Relating to the Elements from Lanthanum (57) to Hafnium (72). D. COSTER, Y. NISHINA, and S. WERNER (*Z. Physik*, 1923, **18**, 207—211).—The authors have determined the respective wave-lengths of the heads of absorption bands L_I , L_{II} , and L_{III} in the L -series relating to the elements of atomic numbers 57, 58, 64, and 68 to 72. The results confirm the existence, suggested by Bohr and Coster (this vol., ii, 110) of an anomaly in the level curves in the region of the rare earths.

J. S. G. T.

Influence of the Aperture of the Spectrometric Slit on the Form of the Absorption Curves of the Infra-red. G. B. BONINO (*Gazzetta*, 1923, **53**, 591—597).—A mathematical paper which does not lend itself to abstraction.

T. H. P.

Spectrochemistry in the Ultra-red. G. B. BONINO (*Gazzetta*, 1923, **53**, 555—575).—The author gives a summary of previous publications on this subject and describes the apparatus and methods of observation employed in his own investigations (see succeeding abstracts).

T. H. P.

Spectrochemistry in the Ultra-red. II. Absorption of the Alcohols. G. B. BONINO (*Gazzetta*, 1923, **53**, 575—582; cf. preceding abstract).—From the results of investigations on the absorption of alcohols in the ultra-red region between 2·5 and 3·8 μ , Henri and Wurmser (Henri, "Études de Photochimie," 1919, 45) deduced a linear relation between the molecular coefficient of maximum absorption and the chemical composition. The author finds, however, that, if the slit of the spectrometer used is gradually made narrower, the absorption curves of the alcohols are not so simple as is represented by Henri and Wurmser's results, the value of which is questionable.

Compounds containing hydrogen united to a single other element exhibit in the ultra-red a simple absorption band of constant spectral position under ordinary dispersive conditions, whereas compounds containing hydrogen atoms united to two different elements present, in the same region of the spectrum, two distinct bands. In the case of the alcohols, the maximum of one of these bands coincides with that shown by the hydrocarbons, and that of the other with the maximum of the band exhibited by water. It appears, then, that the position of the maximum for these bands is to be attributed to the hydrogen and varies, in one and the same spectral region, according to the nature of the linking (cf. Puccianti, A., 1900, ii, 585).

On the assumption that the bands in question are to be attributed to the partial field of the valency electron of the hydrogen (cf. Stark, "Prinzipien der Atomdynamik," 1915), Planck's elementary law, $h\nu = E$, where ν is an infra-red frequency, h Planck's constant, and E the energy of the field or a measure of the work necessary to

rupture the bond between the valency electron of the hydrogen and the other atom, indicates that the frequency ν should be proportional to the energy value of the bond. With hydrofluoric, hydrochloric, and hydrobromic acids the author finds that this is very nearly the case. Moreover, Haber's relation, $\nu_{uv}/\nu_{ir} = \sqrt{M/m}$, where ν_{uv} and ν_{ir} are, respectively, the ultra-violet and infra-red characteristic frequencies, m the mass of the electron, and M that of the vibrating atom, is found to hold satisfactorily for the hydrocarbons if the mass of the hydrogen atom is put in place of M and the total mass of the electrons forming the bond of Stark's hypothesis in place of m .

With different compounds, the molecular absorption coefficient for the band in the infra-red varies in the same sense as the number of hydrogen atoms in the molecule, and in a homologous series the coefficient of maximum absorption varies, approximately and with certain limitations, proportionally with the number of hydrogen atoms in the molecule. It may thus be assumed that $d\epsilon = Kd\rho/\rho$, where ρ is the ratio between the numbers of hydrogen atoms and molecules present, K a constant, and ϵ the coefficient of absorption divided by the number of g.-mols. present. Integration of this expression between two limits corresponding with the ratios of two definite homologous compounds having, respectively, n_1 and n_2 molecules of hydrogen per molecule yields, $\epsilon_2 = \epsilon_1 + C \log_{10} n_2/n_1$. Thus from the value of ϵ for one compound that of a homologous compound can be calculated. Excellent agreement is obtained in this way with the lower monohydric aliphatic alcohols and with certain higher members of the ethylene series. T. H. P.

Spectrochemistry in the Ultra-red. III. Absorption of certain Solutions. G. B. BONINO (*Gazzetta*, 1923, **53**, 583—590; cf. preceding abstracts).—The author has investigated the molecular coefficient of infra-red absorption ϵ of solutions of methyl alcohol in carbon tetrachloride under dispersion conditions analogous to those of Henri's experiments ("Études de Photochimie," 1919), the values of ϵ being calculated by means of the expression $I = I_0 10^{-\epsilon cd}$, in which c is the number of g.-mols. of the substance per litre of the liquid examined, d the thickness of the liquid layer in cms., and I_0 and I the respective intensities of the radiation emerging from the cell charged with the solvent and the solution. The results obtained show that the value of ϵ increases with the dilution of the alcohol.

The case of the alcohols being complicated by the appearance in the infra-red spectrum of a double band with maxima presumably attributable to the hydroxyl group and the hydrogen united with carbon, similar measurements have been made on benzene and its solutions in carbon tetrachloride. Here, too, the molecular coefficient for the position of maximum absorption increases with the dilution of the benzene. Both in this instance, and also with the carbon tetrachloride solutions of methyl alcohol, the curve connecting the logarithm of the molecular absorption coefficient with the logarithm of the volume in litres of solution containing 1 g. mol. of the solute is sensibly linear at relatively high concentrations,

but at lower concentrations a constant value of the former logarithm is approached. For the benzene solutions, especially the more dilute ones, the experimental values are in moderately good agreement with those calculated from the expression given by Baly and Tryhorn (A., 1916, ii, 278). T. H. P.

The Absorption Spectra of the Vapours and Solutions of Various Ketones and Aldehydes. JOHN EDWARD PURVIS (T., 1923, 123, 2515—2521).

Absorption Spectra and Molecular Phases. I. RICHARD ALAN MORTON and HARRY BARNES (T., 1923, 123, 2570—2572).

A Theory of Colour Production. I and II. JULIUS STIEGLITZ (*Proc. Nat. Acad. Sci.*, 1923, 9, 303—308, 308—312).—I. All organic dyes have the property of being reducible to a so-called leuco-compound which can in turn be oxidised again to the dye. Fundamentally, oxidation consists in the removal of electrons from an atom, through which process it acquires the power of attracting electrons. The author traces colour production in dyes to electronic vibrations brought about by the oxidising power of an oxidised atom exerting its influence on a neighbouring atom in the molecule having strong reducing properties. In the case of indophenol, $O=\text{C}_6\text{H}_4=\text{N}-\text{C}_6\text{H}_4\text{OH}$, which exemplifies the theory, the carbon atom of the quinonoid nucleus attached to the nitrogen atom is fully oxidised and consequently has a strong attraction for the electrons attached to the corresponding carbon atom in the strongly reducing phenolic nucleus. These electrons, being “largely freed from intra-atomic restraints,” have their vibrational orbits so modified that absorption of white light results. The known fact that the reducing power of organic compounds such as quinol or *p*-aminophenol is greatly increased by strong bases can be correlated with the deepening effect of such bases on the colour of indophenol. Similarly, the fact that basic dyes such as pararosaniline have their maximum colour depth and intensity when combined with acid may be due to the known effect of acids in intensifying the oxidising power of oxidising agents. The electronic vibrations postulated must be intra-atomic, and must not involve any actual transference of electrons from one atom to another, as this would involve the migration of the hydrogen atom of the hydroxyl group in indophenol from one nucleus to the other. There is positive evidence that such migration does not take place in the dimethylmurexides, of which two can be prepared. The one is prepared from dimethyluramil and alloxan, the other from uramil and dimethylalloxan, and in both cases the original components can be recovered by decomposition of the dye. The source of colour cannot therefore be migration of the electrons, as this would, in the case under consideration, involve migration of the methyl groups.

II. The ideas developed in the preceding section are applied to inorganic compounds, and it is concluded that colour in these compounds must be ascribed to intra-atomic or inter-atomic oxida-

tion-reduction potentials of sufficient force to make possible vibrations of electrons in the reducing component long enough to absorb visible light waves. Combination of a strong oxidising kation with a strong reducing anion leads to strong colour, as in PtI_4 . In permanganates and chromates the source of colour lies in the tendency of the valence electrons of the oxide oxygen atoms to pass to the strongly oxidising atoms Mn^{++++} and Cr^{+++} . Intense colour is produced by the association of atoms of a given element in two conditions of oxidation, as in ferrosferrie oxide, ferrous ferri-cyanide, and red lead. The colour of chromic salts must be due to intra-atomic forces caused by the presence in the atom Cr^{+++} of three valence electrons. Aluminium and gallium salts contain no such valence electrons and are colourless. A number of other examples are discussed.

E. H. R.

Röntgenographic Investigations of Systems Capable of Luminescence. ARTHUR SCHLEEDE and HANS GANTZCKOW (*Z. physikal. Chem.*, 1923, **106**, 37—48).—Substances capable of phosphorescence are considered, and it is shown that the power of luminescence is never connected with glass-like substances, but only with crystalline substances, provided that a few of the metallic atoms of the fundamental substance are replaced by atoms which are foreign to the lattice of the fundamental substance. The various types of luminescence phenomena, cathodic luminescence, fluorescence, phosphorescence, in one and the same fundamental substance prepared in various ways, depend in all probability on various conditions of deformation of the lattice.

J. F. S.

Radiochemistry and Fluorescence. JEAN PERRIN (*Compt. rend.*, 1923, **177**, 612—618).—The author re-discusses previous ideas on the radiation theory of chemical change (cf. A., 1922, ii, 628), more particularly in connexion with the recent work of Levaillant (this vol., ii, 597). The rate of decolorisation of new methylene-blue and fluorescent-blue in glycerol solution is appreciably increased by rise in temperature. Thus, for the former blue, at temperatures from 19—55°, the velocity of disappearance of colour under the influence of orange rays is multiplied by 1.3 for an increase, by one-thirtieth, of the absolute temperature. From this, the author concludes that the infra-red rays producing the critical molecules of glycerol (the cause of the reduction of the colouring matter) have a frequency of 5×10^{13} and a wave-length of 6μ . Fluorescent-blue gave similar results, but neither solution underwent change in absence of light. At 150°, however, New methylene-blue solutions are slightly decolorised in the dark.

E. E. T.

Luminescence of Organo-magnesium Halides. R. T. DUFFORD, S. CALVERT, and DOROTHY NIGHTINGALE (*J. Amer. Chem. Soc.*, 1923, **45**, 2058—2072).—An investigation of the luminescence of organo-magnesium halides. It is shown that Grignard reagents in ethereal solution exhibit chemi-luminescence on oxidation by oxygen only when the magnesium is attached to an unsaturated

carbon atom. This holds for both aromatic and aliphatic compounds in all the cases (60) investigated. The nature of the solvent affects the intensity of the luminescence but not the wave-length. Zinc and mercury organic halides give no luminescence. Both the intensity and the wave-lengths of the luminescence are affected by the nature of the reacting halogen. The wave-length and the intensity are affected by the nature of the organic radicle involved, and especially by the nature of the substituting groups in cyclic compounds. The effect depends on the position of the substituting group and its chemical character. But it is definitely shown that the mass of the substituting group is not the controlling factor. Certain cases of very bright chemi-luminescence are described and that of magnesium *p*-chlorophenyl bromide is believed to be the brightest yet recorded. A new method of preparing chlorine-containing Grignard compounds is described; this consists in carrying out the Grignard reaction in *isoamyl* ether and using either iodine or ethyl bromide as catalyst. Many Grignard compounds emit light when treated with chloropicrin or with bromopicrin. This light is not the same as that emitted on oxidation with oxygen. Many Grignard compounds, and especially their oxidation products, are found to be fluorescent in ultra-violet light. Tables are given of the luminescent properties of sixty Grignard compounds.

J. F. S.

Rotatory Polarisation in an Orthorhombic Crystal [Triphenylbismuthine Dichloride] Exhibiting Crossed Axial Dispersion. GILBERT GREENWOOD (*Min. Mag.*, 1923, 20, 123—130).—Circular polarisation, if any, in optically biaxial crystals is masked by the double refraction, but when they exhibit crossed axial dispersion they are optically uniaxial for a certain colour, and the effects of the circular polarisation can then be observed in light of that colour. In crystals of triphenylbismuthine dichloride (orthorhombic-holoaxial class, $a : b : c = 0.774 : 1 : 0.409$), the acute positive bisectrix is perpendicular to (010), and for red to green light the axial plane is (100), whilst for green to violet it is (001). For green light of wave-length $510 \mu\mu$, the crystal is uniaxial at 17° . A section perpendicular to the acute bisectrix does not extinguish between crossed nicols in parallel white light, but transmits light of a bright green colour: this was examined spectroscopically. The optic axial angles for different wave-lengths were determined at two temperatures (17° and 35°). Similar phenomena are shown by potassium sodium tartrate. A salt of one part of sodium potassium tartrate and two parts of sodium ammonium tartrate is uniaxial in the green, whilst a salt of equal proportions is uniaxial in the blue.

L. J. S.

Absorption and Anomalous Rotation Dispersion of Camphorquinone. NINA WEDENEWA (*Ann. Physik*, 1923, 72, 122—140).—Measurements of the rotation, the ellipticity, and the absorption of a solution of camphorquinone in toluene (0.6913 g. in 200 c.c.) have been made in the regions of the absorption bands. The results are discussed from the point of view of Drude's theory,

and the activity coefficients have been calculated. A method of measuring the phase difference and the dichroism is described.

J. F. S.

Models for the Illustration of some Propositions of the Rules of Symmetry in the Exposition of Stereochemistry.

ERNST MOHR (*J. pr. Chem.*, 1922, [ii], **105**, 93—101).—The author describes paper or cardboard models by means of which various types of molecular symmetry may be demonstrated. The original does not lend itself to abstraction, and must be consulted for details.

W. S. N.

Specific Action of Luminous Rays of Various Colours in Photosynthesis.

V. LUBIMENKO (*Compt. rend.*, 1923, **177**, 606—608).—For most plants, the amount of photosynthesis in red light (λ 760—600 $\mu\mu$), as measured by the carbon dioxide exchange, is greater than that in bluish-violet light (λ 480—400 $\mu\mu$), although with a few plants, accustomed to diffused daylight, photosynthesis is nearly as great in bluish-violet as in red light.

E. E. T.

Influence of Drying on Photochemical Reactions.

HEINRICH TRAMM (*Z. physikal. Chem.*, 1923, **105**, 356—401).—An apparatus is described by means of which the purification and drying of gases may be carried out at the temperature of liquid air. No drying agents are used, and a degree of dryness greater than that represented by a pressure of water vapour less than 0.004 mm. is achieved. The photochemical formation of ozone, hydrogen chloride, sulphuryl chloride, and carbonyl chloride and the photochemical decomposition of hydrogen chloride, hydrogen bromide, and hydrogen iodide in the presence of various quantities of moisture have been investigated. It is shown that a highly desiccated mixture of hydrogen and chlorine free from oxygen does not combine to a measurable extent under the influence of light. A mixture of carbon monoxide and oxygen which has been dried to the point where it ceases to be explosive and at high temperatures reacts very sluggishly in the dark, when exposed to ultra-violet light exhibits the same velocity of reaction as a similar moist mixture. This shows that the reversal of the photo-decomposition of carbon dioxide by ultra-violet light in the presence of traces of moisture as demonstrated by Coehn and Sieper (*A.*, 1916, ii, 281) is not due to an acceleration of the formation of carbon dioxide, but to a retardation of the decomposition. Traces of sulphur dioxide retarded the decomposition of carbon dioxide by ultra-violet light in exactly the same way as water. Against the assumption that the accelerating action of water vapour on the reaction between carbon monoxide and oxygen under the influence of heat is due to the formation of formic acid as an intermediate product, it is shown that mixtures of oxygen and formic acid do not explode, whilst an equivalent mixture of hydrogen, oxygen, and carbon monoxide does so. A mixture of hydrogen and oxygen so dry that it does not explode in a vessel heated to a red heat but only combines slowly when exposed to ultra-violet light reacts at exactly

the same rate as the undried mixture. The author has been unable to dry hydrogen chloride and ammonia to such an extent that they do not combine.

J. F. S.

The Influence of Ultra-violet Radiation on the Reactivity of Halogen attached to the Nucleus in the Presence and Absence of Catalysts. K. W. ROSENMUND, K. LUXAT, and W. TIEDEMANN (*Ber.*, 1923, **56**, [B], 1950—1957).—The reactivity of halogen atoms attached to aromatic nuclei is greatly enhanced by ultra-violet radiation; this is more particularly the case when copper is present as catalyst. Thus, for example, the chlorine atom of *p*-chlorobenzoic acid is removed quantitatively when its solution in aqueous potassium hydroxide (35%) is boiled for six hours in the presence of copper and ultra-violet light. The enhanced reactivity appears to be due to the effect of the radiation on the organic molecule, and not on the catalyst. The reaction between halogen compounds and alkali hydroxides under these conditions does not lead smoothly to the expected hydroxy-compounds, but the process is well adapted to the production of ethers from halogen compounds and alkyl oxides, and to that of acids from halogen compounds and cyanides: $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CO}_2\text{H} + \text{KCN} + 2\text{H}_2\text{O} \rightarrow \text{KCl} + \text{NH}_3 + \text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$. Copper precipitated in the solution appears to be more effective than Ullmann's copper powder or Piccard's copper (A., 1922, ii, 216).

The reactions are carried out in small flasks of clear silica exposed to the light of a Heraeus mercury lamp. The following examples are cited: phenyl *iso*amyl ether, b. p. 210—215°, from bromobenzene and sodium *iso*amyloxide; phenyl *n*-propyl ether, from bromobenzene and sodium *n*-propoxide; *p*-tolyl *iso*amyl ether, b. p. 232—235°, from *p*-bromotoluene and sodium *iso*amyloxide; *o*-tolyl *iso*amyl ether, b. p. 213°, from *o*-bromotoluene and sodium *iso*amyloxide; *p*-anisyl *iso*amyl ether, b. p. 234—237°, from *p*-bromoanisole and sodium *iso*amyloxide. α -Bromonaphthalene and sodium *iso*amyloxide unexpectedly yield naphthalene in almost quantitative yield.

Potassium *p*-chloro- or *p*-bromo-benzoate and potassium cyanide in aqueous solution, in the presence of cuprous cyanide, give terephthalic acid in 70% yield. *p*-Bromobenzenesulphonic acid yields *p*-sulphobenzoic acid (yield 75%), whilst *p*-bromotoluene-*o*-sulphonic acid is similarly transformed into the corresponding carboxylic acid.

The formation of nitriles from alkyl halides and potassium cyanide is appreciably facilitated by the presence of cuprous cyanide and ultra-violet light.

H. W.

The Protective Action of Antioxidising Substances [Polyphenols] against Fading of Dyed Fibres in the Light. P. SISLEY (*Bull. Soc. chim.*, 1923, [iv], **33**, 1079—1081).—It is found that certain polyphenols exercise a protective action on some dyes on the fibre, in that the latter are rendered more stable to the action of light and, sometimes, of oxygen. It is not possible, however, to draw any general theoretical conclusions from the results observed,

because it is found that a polyphenol which protects one dye may even accelerate the fading of a closely related dye. Tannin, for instance, has a well-marked protective action on methylene-blue dyed on silk, but has practically no effect on auramine. Hydroxylamine sulphate, again, protects methylene-blue, but accelerates the fading of phloxine, whilst thiocarbamide protects the latter, but accelerates the fading of the rhodamines. H. H.

Some Biochemical Effects of Polarised Light. ELISABETH SIDNEY SEMMENS (*Chemistry and Industry*, 1923, 42, 954).—The hydrolysis of starch in the mustard seed, and also of starch grains when acted on by diastase in vitro, is accelerated by exposure to plane polarised light. It is suggested that the influence of polarised light brings about some change in the starch granules prior to the rupture of the membrane. C. H. R.

Influence of the Wave-length on the Energy Change in Carbon Dioxide Assimilation. OTTO WARBURG and ERWIN NEGELEIN (*Z. physikal. Chem.*, 1923, 106, 191—218).—Making use of the method previously described (A., 1922, i, 1097) for measuring the energy changes accompanying the assimilation of carbon dioxide, the authors have investigated the change in the following spectrum ranges: infra-red, 800—900 $\mu\mu$, red, 780—700 $\mu\mu$; 690—610 $\mu\mu$; yellow, 578 $\mu\mu$; green, 546 $\mu\mu$; blue, 436 $\mu\mu$, and ultra-violet, 366 $\mu\mu$. There is no decomposition of carbon dioxide in the infra-red region and the decomposition in the ultra-violet and the long wave red 780—700 $\mu\mu$ has proved to be unsuitable for quantitative experiments. The absorption coefficient of a methyl alcohol extract of the colouring matter of the alga *Chlorella* has been determined for the four spectral regions and it is found that the value is smallest for the green line ($\alpha=0.09$), 1.8 times as large for the yellow, 9 times as large in the red, and 20 times as large in the blue. The assimilation experiments were carried out with *Chlorella* stems, and show that the yield in the carbon dioxide assimilation decreases with decreasing wave-length. No relationship between the yield and the wave-lengths of the absorption bands can be found; the yield in the red, a region of strong absorption, is greater than that in the green, a region of very weak absorption, whilst the yield of this is greater than that in the blue, the region of strongest absorption. J. F. S.

The Photoelectric Conductivity of Cinnabar. B. GUDDEN and R. POHL (*Z. Physik*, 1923, 18, 199—206).—Whilst the results obtained by the authors (A., 1921, ii, 145; this vol., ii, 528) and by Rose (*Z. Physik*, 1920, 3, 174) are in substantial agreement in regard to the spectral distribution of the photo-sensitivity of cinnabar, they exhibit differences greater than the possible experimental error. These differences are now attributed to differences in the experimental conditions—direction and intensity of illumination, voltage applied to the crystal—whereby the increased conductivity of the crystal when illumined originates in a primary or secondary effect, or a combination of both effects, produced by the incident

radiation. The current produced by the secondary effect arises in somewhat the same manner as ionisation in a gas is produced by collisions. In an electric field transverse to the direction of illumination, the secondary current constitutes a greater proportion of the total current than is the case in a longitudinal field. The same considerations are applied to the discussion of selective maxima of sensitivity exhibited more especially by powders in strong electric fields. The energy relations observed in connexion with the photo-sensitivity of cinnabar are held to support, in a general manner, the truth of the photo-chemical equivalence law.

J. S. G. T.

The Passage of Corpuscular Radiation through Matter, and Atomic Constitution. II. W. BOTHE (*Jahrb. Radioaktiv. Elektronik*, 1923, 20, 46—84).—The literature of the scattering and absorption of α - and β -rays, and of the production of secondary radiation and of ionisation by the passage of these rays through matter is critically reviewed.

J. S. G. T.

The Period of Protactinium. JOHN H. MENNIE (*Phil. Mag.*, 1923, [vi], 46, 675—685).—From a comparison of the α -activities of ionium and protactinium, separated from several kilograms of uranyl nitrate, the author has found the average life period of protactinium to be 18,000 years, in substantial agreement with the period of half-change, 12,500 years, found by Hahn and Meitner (*A.*, 1921, ii, 150).

J. S. G. T.

Radioactive Disintegration Series and the Relation of Actinium to Uranium. A. S. RUSSELL (*Phil. Mag.*, 1923, [vi], 46, 642—656).—Regarding a disintegration series as made up of three types of successive changes, the author deduces that there are probably only four such series which are independent, these corresponding, respectively, with the values 222, 221, 220, and 219 for the respective atomic weights of components of the series having an atomic number 86. Of these, the series 221 is new. The series 222, 220 refer, respectively, to the uranium and thorium series, and it is shown that series 219 is the actinium series. Simple empirical relations between the periods of substances related by the expulsion of at least four α -particles without the expulsion of separate β -particles, and of substances related by the expulsion of an α -particle followed by two β -particles in succession and then an α -particle are given. It is deduced that the actinium series originates from an isotope of uranium having an atomic weight 239 (actin-uranium-I), present to the extent of about 5% in ordinary uranium. Estimates of the periods of the substances preceding protoactinium in this series are given. Radioactive isotopes are compared with those of inactive elements, and it is suggested that thallium and bismuth, in addition to isotopes of lead, may form end-products of radioactive series.

J. S. G. T.

The Short-lived Radioactive Products of Uranium. WILLIAM GEORGE GUY and ALEXANDER SMITH RUSSELL (*T.*, 1923, 123, 2618—2631).

Long-range Particles from Radium Active Deposit. L. F. BATES and J. STANLEY ROGERS (*Nature*, 1923, **112**, 435—436; cf. Kirsch and Pettersson, this vol., ii, 675).—Radium active deposit, $B+C$, on a brass disk was found to emit particles with ranges in air ($15^\circ/760$ mm.) of 9.3, 11.1, and 13.2 cm., respectively, as well as particles (presumably hydrogen particles) of range >18 cm., in quantities of 380, 126, 65, and 160, respectively, compared with 10^7 of α -rays of range 6.97 cm. It was ensured that the long-range particles were not produced by collisions of the 6.97 cm. α -particles with air molecules, or by excitation in the mica sheets; they appeared to be independent of the metal on which the deposit was formed. It is considered possible that Kirsch and Pettersson's (*loc. cit.*) 12, 13, and 10 cm. hydrogen particles are actually long-range α -particles emitted by the active deposit. A. A. E.

Method for Photographing the Disintegration of an Atom, and a New Type of Rays. WILLIAM D. HARKINS and R. W. RYAN (*J. Amer. Chem. Soc.*, 1923, **45**, 2095—2107).—The rarity of a collision between a fast helium nucleus (α -particle) and the nucleus of an atom in a gas through which it is passing increases greatly as the directness of the collision increases. In three cases the authors have obtained photographs which show the rebound of the α -particle, and taking account of the number of photographs obtained and the fact that the α -particle has passed through about 12 billion atoms in air, this alone indicates that the nucleus of an atom of nitrogen or oxygen is of the order of slightly more than 10^{-13} cm. in radius. A more accurate value can be obtained by a mathematical analysis of all of the deflections of the α -particle through smaller angles. In an ordinary collision, three tracks meet in a point, one for the particle before collision, and a second for the same particle after collision. Should the oxygen or nitrogen nucleus disintegrate, then at least four tracks should meet, the additional track being due to a fragment, such as an electron, a hydrogen, or a helium nucleus disrupted from the bombarded nucleus. The chance of such a disintegration increases rapidly with the directness of the collision and with the speed of the α -particle. The authors have obtained a photograph in which the fourth track appears, and this should characterise an atomic disintegration. That this track starts from the proper point in space is shown by two projections obtained simultaneously. These give two views at an angle of 90° . Rays of a new type, designated by the authors ζ -rays, have been photographed. In this case, the α -particle evidently drives particles from two widely separated atoms in its path. It is remarkable that the two tracks thus obtained lie in almost parallel planes, both are highly curved and almost parallel lines, and both have a sharp retrograde motion. It seems probable that the ζ -rays are due to electron emission. The particles must be very light, since the direction of the α -particle is not materially affected by the emission, and the tracks of the particles are moderately long, very much longer than those of the previously recorded δ -rays. The apparatus used by the authors

in this work records 3,000 photographs per hour, and 40,000 such photographs have been secured. It is shown that in no case does an oblique impact effect a disintegration. The argon nucleus remains intact even under the sharp impact of a helium nucleus from thorium-C'.

J. F. S.

The Values of the Electrical Moments of the Atoms and their Connexion with other Quantities. R. D. KLEEMAN (*J. Franklin Inst.*, 1923, **196**, 479—493).—Assuming that atoms and molecules in their interactions are characterised by possessing definite electrical moments, which at 0° (absolute) are approximately independent of the density of the substance, the author shows from a consideration of the values of the internal heat of vaporisation of various substances that the electrical moments of atoms and molecules are, respectively, equal to $10^{-19}N^{2/3}$ and $10^{-19}\Sigma N^{2/3}$, in which N denotes the atomic number of the atoms concerned. The distance of separation of the electrical charges in the representative atomic doublet is shown to be equal to $2.09 \times 10^{-10}N^{-1/3}$ cm., which is much smaller than the diameter of the atom. It is suggested that, in the case of the hydrogen atom, the nucleus is situated at a point distant 2.09×10^{-10} cm. from the centre of the circular path of the rotating electron and in a plane at right angles to the plane of motion. The doublet effect in the case of the more complicated atomic structures is probably attributable to the nuclei not occupying the foci of the electronic paths. It is shown that in the case of a number of substances, the respective values of the internal specific heat, c_i , at 0° , are related to the atomic weights a_w of the atoms constituting the molecules, by the equations $\log c_i = h_1 \Sigma N^{2/3} = h_2 \Sigma a_w^{1/2}$, where h_1 and h_2 are constants. More generally, at corresponding temperatures T_1 the relation takes the form $\log c_i = \phi(T/T_c) \Sigma N^{2/3}$, where T_c denotes the absolute critical temperature and $\phi(T/T_c)$ denotes a function of T/T_c . The application of the doublet effect to the subject of specific inductive capacity is briefly discussed.

J. S. G. T.

Formation of Gaseous Ions in the Oxidation of Nitric Oxide. A. K. BREWER and FARRINGTON DANIELS (*Trans. Amer. Electrochem. Soc.* [advance copy], 1923, 171—182).—Experiments with a special form of chamber show that when nitric oxide is oxidised between oppositely charged electrodes a current of electricity passes through the gases. The current is of the order of 10^{-14} amperes for the oxidation of 50 c.c. of nitric oxide per minute reacting in a field of 450 volts per cm. This corresponds with about one ion for every million molecules reacting. The current is directly proportional to the voltage and to the number of molecules reacting. No evidence of a saturation current could be detected. Various hypotheses to explain the results are advanced.

J. F. S.

Motion of Electrons in Helium. J. S. TOWNSEND and V. A. BAILEY (*Phil. Mag.*, 1923, [vi], **46**, 657—664).—In continuation

of previous work (A., 1922, ii, 43, 277, 494, 836), the authors have determined the velocities of translation and of agitation of electrons in helium submitted to the action of a uniform electric force, at various pressures ranging from 5 to 240 mm. of mercury. Values are deduced for the mean free path of the electron at 1 mm. pressure, and the proportion of energy lost by an electron on collision. The results indicate that, so calculated, the free path of an electron in helium is about twice that in hydrogen. The mean free path is approximately constant and equal to about 0.05 cm. for velocities between 10^8 and 5×10^7 cm. per sec. Moreover, the increase in the free path as the velocity diminishes occurs for smaller velocities in helium than in argon. The proportion of energy lost by an electron due to collision is approximately constant and equal to 2.5×10^{-4} for velocities ranging between 2×10^7 and 10^8 cm. per sec. For velocities greater than 10^8 cm. per sec., the proportion increases considerably owing to ionisation produced by the collision.

J. S. G. T.

The Motion of Electrons in Carbon Monoxide, Nitrous Oxide, and Nitric Oxide. M. F. SKINKER and J. V. WHITE (*Phil. Mag.*, 1923, [vi], 46, 630—637).—In continuation of previous work, the authors have investigated the velocities of translation and of agitation of the electrons under various electrical forces and at various pressures, in the cases of the gases carbon monoxide, nitrous oxide, and nitric oxide. The results indicate that in the case of carbon monoxide the electrons in the stream do not tend to form ions by adhering to molecules of the gas, whilst such ions are produced in nitrous oxide and nitric oxide. Values of the mean free path of the electrons, the effective radius of the molecules, and the proportion of energy lost in collision between an electron and a molecule are tabulated.

J. S. G. T.

Problems of Hydrone and Water: the Origin of Electricity in Thunderstorms. HENRY E. ARMSTRONG (*Nature*, 1923, 112, 537—538).—If it is assumed that changes in the size of particles of water can, in the absence of conducting electrodes, give rise to free electricity, it is held that the coalescence of small drops is more likely to induce electrical phenomena than is the reverse process, in that energy is thereby liberated (cf. this vol., ii, 542). Chemical interchanges are believed to account for observations recorded by Simpson (*Phil. Trans.*, 1909, [A], 209, 379) and Lenard (*Ann. Phys. Chem.*, 1892, [ii], 46, 584).

A. A. E.

Electrical Conductivity of Dilute Aqueous Solutions of Hydrogen Chloride. HENRY C. PARKER (*J. Amer. Chem. Soc.*, 1923, 45, 2017—2033).—The electrical conductivity of aqueous solutions of hydrochloric acid has been determined at 25° for concentrations between 0.04 and 3.0 millimols. per litre. The solutions were made up by weight and were accurate to a few hundredths %, and the water had a specific conductivity of 0.1×10^{-6} . The values for the equivalent conductivity show a slight maximum in the region of 0.1 millimol. per litre, due to the influence

of the impurities in the water, which apparently cause a somewhat greater effect than in the case of iodic acid (this vol., ii, 7). Comparison with the results of other investigators confirms the conclusions of Kraus and Parker (*loc. cit.*) regarding the considerable influence of the impurities in the water and of the alkali in glass cells on the electrical conductivity of dilute solutions of acids. Values have been interpolated for rounded concentrations from the results for hydrochloric and iodic acid. The data for iodic acid cover the range $0.05 \times 10^{-3}N$ to $0.5N$. The cell constant was determined by an intercomparison with three standard cells, over a considerable range of concentrations, with potassium chloride as electrolyte. The unusual results of this intercomparison may be explained by assuming the presence of an adsorbed layer in contact with the electrodes, the resistance of which is greater or less than that of the bulk of the solution, according to whether the electrolyte is negatively or positively adsorbed. One of the intercompared cells apparently has a greater correction for this adsorbed layer than the cell used in the measurements with hydrochloric acid, whilst the other two have a smaller correction. On the supposition that hydrochloric acid will be positively adsorbed and will consequently have but slight correction for this effect, a value for the constant was selected at the minimum point of the cell constant curve, which value is assumed to remain fixed in the measurements of the acid solutions. Extrapolation of the results on the assumption that the law of mass action is approached as a limiting form at infinite dilution gives a value of Λ_0 for hydrochloric acid of 425.69. Assuming that the value of Λ_0 for the chloride-ion at 25° is 75.8, a value of 349.89 is obtained for the hydrogen-ion at that temperature. Comparison of this with the value 349.93 obtained by Kraus and Parker (*loc. cit.*) for iodic acid leads to the value 349.89 ± 0.05 as the most probable value for the hydrogen-ion at 25° , since the basis for the cell constant is more firmly established for the measurements with hydrochloric acid. The mass-action constant corresponding with this extrapolation has a value 0.105.

J. F. S.

Electrical Conductivity Measurements on Dilute Aqueous Salt Solutions at 0° , 18° , and 100° . P. WALDEN and HERM. ULLICH (*Z. physikal. Chem.*, 1923, **106**, 49—92).—Very exact electrical conductivity determinations have been made at 0° , 18° , and 100° with solutions of potassium chloride, nitrate, and perchlorate, sodium chloride and nitrate, caesium nitrate, lithium perchlorate and picrate, tetraethylammonium picrate, potassium picrate, chlorate, bromate, and iodate in concentrations down to the most dilute. The limiting conductivity has been deduced by means of P. Hertz's hypothesis, and values have been found which confirm the hypothesis. Electro-conductivity-concentration curves have been drawn, and in the case of the less soluble salts it is found that regular deviations from the Hertz curve occur. Lithium picrate and tetraethylammonium picrate follow Stokes's law with sufficient exactitude in the temperature range examined. This result makes

it possible to determine the ionic mobility at 100° with satisfactory accuracy. In the case of the perchlorate-ion, ClO_4' , the mobility at 18° equals 58.4 , a value which is lower than the older measurements indicated.

J. F. S.

Simple Determination of the Limiting Value of the Molecular Conductivity of Strong Electrolytes. C. DRUCKER (*Z. physikal. Chem.*, 1923, **105**, 472—475).—A criticism of Lorenz and Landé's papers (this vol., ii, 9, 284), in which it is shown that the statement that α is a constant characteristic of the substance is at variance with facts; the author shows that α expresses in its variability the accepted variability of the transport number. Consequently the suggested new extrapolation process is not applicable.

J. F. S.

The Theory of Electrolytes. II. P. DEBYE and E. HÜCKEL (*Physikal. Z.*, 1923, **24**, 305—325).—In continuation of previous work (this vol., ii, 459), the authors present a mathematical analysis of the effect on the electrical conductivity of a completely ionised solution due to the presence of, and the mutual electric forces between, the ions. Ionic and electrophoretic forces are investigated, attention being directed to the following, among other matters: potential distribution around the moving ions, the motion of the solvent, and velocity and pressure distribution in the neighbourhood of the ions. An expression for the conductivity coefficient, f_λ , is derived in the form $1-f_\lambda = (4\pi\epsilon^2\nu/DkT)^{1/2}[\epsilon^2w_1/6DkT + bw_2]$, in which ϵ is the electronic charge, ν the total number of ions, n the number of molecules dissolved per c.c., D the dielectric constant of the solvent, k , Boltzmann's constant, T the temperature, w_1 and w_2 are complex valency factors, expressions for which are given, and b the mean diameter of the ions. This expression agrees with the conclusion of Kohlrausch (A., 1907, ii, 600), that in the case of dilute solutions, $1-f_\lambda \propto c^{1/2}$, c denoting the concentration. Results deduced from the expression are compared with experimental results in the cases of aqueous solutions of univalent and multivalent salts, and of non-aqueous solutions. Generally, the agreement between calculated and experimental results is satisfactory.

J. S. G. T.

Relative Measurement of the Electrical Resistance of Thallium in the Region of the Temperature of Liquid Helium. H. KAMERLINGH ONNES and W. TUYN (*Arch. Néerland*, 1923, [iii], **6**, 284—292).—The electrical resistance of thallium has been determined at the temperature of liquid air, liquid hydrogen, and liquid helium with the object of ascertaining whether thallium is a super-conductor like mercury and lead. It is found that at 2.32°K all resistance has disappeared.

J. F. S.

Relative Measurements of the Electrical Resistance of Ordinary Lead and Lead from Uranium at Temperatures Below 14°K . H. KAMERLINGH ONNES and W. TUYN (*Arch. Néerland*, 1923, [iii], **6**, 293—300).—The electrical resistance of ordinary lead and lead from uranium (radium-*G*) has been deter-

mined and the point at which the resistance disappears ascertained. It has been found that pure lead (at. wt. 207.20) and uranium lead (at. wt. 206.06) have the same point of disappearance of resistance within 0.025°.

J. F. S.

Electrical Resistance of Phenol-Water Systems, and the Application of [the Properties of] such Systems to Biological [Processes]. MARTIN H. FISCHER (*Kolloid Z.*, 1923, 23, 131—147).—After a discussion of the theory of the colloidal condition, in which the lyophilic colloidal condition is defined as the product of two mutually soluble substances and is compared with the system phenol-water, the author describes a number of measurements of the electrical resistance of the system phenol-water to which various additions of acids, bases, salts, and non-electrolytes have been made. In these systems, the phenol phase is regarded as comparable with protoplasm, and the physico-chemical properties of this phase are regarded as of importance in the elucidation of the characteristic properties of living substance. Pure hydrated phenol has a very high electrical resistance, which is reduced by the addition of acids and alkalis. The addition of neutral salts also reduces the resistance, but not to so marked an extent. In all these cases, the amount of reduction is dependent, not only on the concentration of the added substance, but also on its chemical nature. The reduction caused by the addition of salts of constant concentration is not the same in all cases, and it is deduced that an "antagonism" exists in certain cases. Some non-electrolytes, such as the lower alcohols, also lower the resistance, but not so strongly as the electrolytes. The behaviour of hydrated phenol is parallel with that of cells and animal fluids under the same conditions. The presence of various electrolytes and non-electrolytes in mixtures of phenol and water changes the volume of the hydrated phenol phase. Acids slightly reduce the volume, whilst alkalis increase it considerably, that is, they bring about a swelling of the phenol. Salts reduce the volume in proportion to their concentration. This behaviour is parallel with the absorption and loss of water in living cells, which is usually attributed to changes in osmotic pressure. Protoplasm is not, as is so generally held, a solution of protoplasmic materials in water, like phenol in water, but a system of the opposite type, namely, water dissolved in protoplasmic material, like water in phenol. The physico-chemical laws which apply to the latter type of system alone hold for living material.

J. F. S.

Single Potential of Arsenic and its Power to Replace other Metals in Solutions. LOUIS KAHLENBERG and JOHN VERNON STEINLE (*Trans. Amer. Electrochem. Soc.* [advance copy], 1923, 203—226).—The single potential of arsenic has been determined in a number of different electrolytes, including arsenic trichloride, triiodide, arsenious oxide, *p*-aminophenylarsinic acid, *p*-hydroxyphenylarsinic acid, *p*-glycinoaminophenylarsinic acid, *p*-acetamidophenylarsinic acid, and di-*p*-aminophenylarsinic acid, and in general the results of previous investigators have been confirmed. In making

the single potential measurements, the arsenic electrodes were prepared in a number of different ways. It was found that a solid arsenic electrode, sawn from a large piece of arsenic, gives trustworthy results, and offers on the whole the best form of electrode for making the determinations. Electrodes prepared by electroplating arsenic on other metals were found to yield untrustworthy results, in that they do not develop the true potential of pure arsenic. Metallic arsenic was used to displace the metals silver, copper, and mercury from their compounds. The reaction which occurs in these cases may be represented by $6MX + 2As + 3H_2O = 6M + 6HX + As_2O_3$. Arsenic has been displaced [from its compounds by other metals, including sodium, magnesium, aluminium, zinc, cadmium, iron, cobalt, nickel, lead, tin, bismuth, and antimony. In many of these cases the replacement could not have been predicted from a knowledge of the single potentials of the metals concerned. The authors are of the opinion that in the case of arsenic the power of a metal to replace this metal is a highly specific property which depends on the individual nature of the metals in question and also on the liquids used in the experiments.

J. F. S.

Electric Potential of Antimony-Lead Alloys. S. D. MUZAFFAR (*Trans. Faraday Soc.*, 1923, **19**, 56—58).—Measurements of the electric potential of antimony-lead alloys against a calomel electrode in *N*-potassium hydroxide, *N*-lead nitrate, and acid potassium antimony tartrate solutions showed that up to 98% of antimony the potentials were identical with that of lead, thus demonstrating that, in the antimony-lead series, there are no solid solutions and no compounds formed.

A. R. P.

Oxidation-Reduction. III. Electrode Potentials of Mixtures of Indophenol-1-Naphthol-2-Sulphonic Acid and the Reduction Product. W. MANSFIELD CLARK and BARNETT COHEN (*U.S. Pub. Health Rep.*, 1923, No. 834, 3—28; cf. this vol., ii, 677).—A new indophenol, 4-indophenol-1-naphthol-2-sulphonic acid, $HO \cdot C_6H_4 \cdot N \cdot C_{10}H_5(SO_3H) \cdot O$ or $O : C_6H_4 \cdot N \cdot C_{10}H_5(OH) \cdot SO_3H$, has been synthesised by grinding 14.2 g. of quinone chloroimide with 25 g. of water and a quantity of ice, then with continual grinding adding 24.6 g. of sodium 1-naphthol-2-sulphonate in 75 c.c. of 4*N*-sodium hydroxide. The solution is kept for an hour. A cold saturated salt solution is then added, when a thick precipitate is formed. This is filtered and washed with cold saturated salt solution. The material is extracted with water and filtered. The filtrate is cooled and precipitated with carbon dioxide. The precipitate, after drying on porous plates, is recrystallised from alcohol, when a red sodium salt of the above-named compound separates. The reduction potentials of this compound in equilibrium with its reduction product at different P_H values have been determined at 30°. It is found that the measurements conform fairly with the equation $E_h = 0.5440 - 0.03006 \log [S_r]/[S_o] + 0.03006 \log (K_r K_s [H'] + K_r [H']^2 \dots + [H']^3) - 0.03006 \log (K_o + [H'])$, where S_r is the concentration

of the total reductant, $[S_0]$ that of the total oxidant, K , the dissociation constant of that phenolic group in the reductant which is possessed by the oxidant, K_0 is the dissociation constant of the same group in the oxidant, and K_2 is the dissociation constant of the phenolic group created by the reduction. The following values are obtained: $K_0=2.09 \times 10^{-9}$, K , 8.01×10^{-10} , and $K_2=2.00 \times 10^{-11}$. The hypothetical normal potential is +0.5440 volt. It is shown that an 80—90% reduction of 4-indophenol-1-naphthol-2-sulphonic acid within the ordinary physiological range of P_H indicates a reduction potential about 0.52 volt more positive than the hypothetical hydrogen electrode potential of the solution, and it is suggested that the reduction of this dye should indicate minute degrees of physiological reduction.

J. F. S.

Reduction Potentials of Quinones. I. The Effect of the Solvent on the Potentials of certain Benzoquinones. JAMES B. CONANT and LOUIS F. FIESER (*J. Amer. Chem. Soc.*, 1923, **45**, 2194—2218; cf. A., 1922, ii, 547; this vol., ii, 9, 285).—The reduction potentials of various alkyl and chloro-derivatives of benzoquinone have been measured in alcoholic and in aqueous solution. A method has been devised whereby the free energy of reduction of a quinone, and the reduction potential, referred to the solid state, can be found. A cell is constructed consisting of a hydrogen electrode, immersed in a given solvent, connected with a half-cell containing an inert electrode immersed in the same solvent saturated with both the quinol and the quinone, and containing both solid substances. From the potential of this combination it is possible to calculate directly the free energy of reduction, referred to the solid states. This method cannot be used, however, if a quinhydrone is formed; the following procedure is then adopted. Two separate combinations are investigated. In one the half-cell contains a solution saturated with the quinone and the quinhydrone; in the other, the solution is saturated with the quinol and the quinhydrone. The algebraic mean of the potentials of the two combinations is the required reduction potential referred to the solid states, whilst the difference between the potentials is a measure of the free energy of the formation of the solid quinhydrone from its solid components. The results obtained show that, either in solution or referred to the solid states, the introduction of methyl groups into the quinone nucleus decreases the reduction potential, whilst the introduction of chlorine atoms at first raises the potential and then lowers it. Essentially the same relationships are found between the reduction potentials of different substances in aqueous and alcoholic solution, but the potentials referred to the solid states are not entirely parallel to those measured in solution. The temperature coefficient of the reduction potential (solid states) has been measured for all the quinones investigated, and the total energy of reduction calculated. Comparison with previous thermochemical measurements reveals, probably owing to errors inherent in the latter, great discrepancies in the figures for the polychloroquinones.

W. S. N.

Membrane Potentials Considered as Diffusion Potentials.

E. B. R. PRIDEAUX and W. E. CROOKS (*Chemistry and Industry*, 1923, **42**, 955).—Measurements of conductivities, viscosities, diffusion, and membrane potentials in solutions of potassium benzoate and potassium salicylate with parchment membranes, show a definitely diminished mobility of the organic anions in the parchment; this retardation accounts for the increase of the diffusion potential with such salts. C. R. H.

Behaviour of Cuprous Oxide Photo-voltaic Cells.

ALLEN D. GARRISON (*J. Physical Chem.*, 1923, **27**, 601—622).—The formation of cuprous oxide electrodes and the conditions under which they have both a positive and a negative light effect are described and the general characteristics of each effect discussed. The positive photo-potential is found to be approximately proportional to the logarithm of the light intensity and to increase with increasing hydrogen-ion concentration. The maximum negative photo-potential is proportional to the intensity of the light for low intensities and constant at high intensities, whilst the positive recoil following the negative maximum increases with the intensity. The maximum negative photo-potential decreases with increasing hydrogen-ion concentration. For large effects, the negative photo-potential decreases and for small effects increases with increasing cupric-ion concentration. The characteristics of the cuprous oxide electrodes which are now known are all explained by the established laws of electro-chemistry by the assumption that the light displaces the equilibrium constant of the reaction, $\text{Cu}_2\text{O (solid)} \leftrightarrow \text{Cu}_2\text{O (dissolved)} \leftrightarrow 2\text{Cu}^+ + \text{O}''$, causing the cuprous oxide to behave as though its solubility was increased in the light. The results are what would be expected if Einstein's photo-chemical law applied to this reaction in a qualitative manner. The active frequencies have not yet been determined. The theory is also applicable to the silver halide electrodes as well as to the copper electrodes, since they behave in the same way, and is opposed to the theory that the primary effect of radiation is either photoelectric in its nature or causes a direct separation of the uncharged elements. The hypothesis that the effect of the light is a separation of the charged elements as ions or thereby an increase in the solubility of the salt and that the decomposition is made complete only by electro-chemical equilibrium is supported by the experimental fact that perfectly dry salts are stable in light. J. F. S.

The Electromotive Behaviour of Magnesium. II.

A. SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1923, **26**, 395—407; cf. A., 1921, ii, 402).—The effect of amalgamation on the *E.M.F.* of the magnesium electrode was studied. From theoretical considerations it was found that the magnesium electrode cannot possibly behave as an oxygen or hydrogen electrode, but that the explanation of its low *E.M.F.* is to be found in the fact that the formation of a layer of hydroxide on the surface of the metal hinders the establishment of the metal-hydrogen inner equilibrium. Activation by means of mercury causes the true inner equilibrium

to be approached more closely. By actual measurement it was found that the potential of a magnesium half-element containing *M*/10-magnesium sulphate was -1.902 volt with respect to a normal calomel electrode, but that on the addition of 3% of a saturated solution of mercuric chloride it fell to -1.740 volt. On removing the magnesium, washing with distilled water, and immersing in *M*/10-pure magnesium sulphate, it showed immediately an *E.M.F.* of -1.898 volt, and, after five minutes, one of -1.956 volt.

H. H.

Electrolysis with an Aluminium Anode the Anolyte being :
I. Solutions of Sodium Nitrite. II. Solutions of Potassium Oxalate. F. H. JEFFREY (*Trans. Faraday Soc.*, 1923, **19**, 52—55).—Electrolysis of solutions of sodium nitrite in concentrations varying from normal to saturated resulted in the formation of much aluminium hydroxide and in the evolution of nitric oxide, whilst nitric acid was found in the anolyte. Probably the primary product at the anode is aluminium nitrite, which is immediately hydrolysed to aluminium hydroxide and nitrous acid. The latter compound then decomposes into nitric oxide and nitric acid.

Electrolysis with potassium oxalate solution as the anolyte resulted in the aluminium anode dissolving; on evaporation of the liquid, well-developed, colourless crystals of potassium aluminium-oxalate, $K_3Al(C_2O_4)_3 \cdot 3H_2O$, were obtained analogous to potassium chromi-oxalate.

A. R. P.

The Electron in the Chemistry of Solutions and in Electrochemistry. I. The Paths of Electrons in Solutions during Electrolysis with a Spark Cathode. L. V. PISARSHEVSKI and (Mlle) M. ROSENBERG (*J. Russ. Phys. Chem. Soc.*, 1923, **54**, 533—547).—A solution of *N*/4-potassium iodide was electrolysed, keeping the cathode 3—4 cm. above the surface of the liquid so that a spark was produced. The addition of phenolphthalein causes the appearance of a red stream in the liquid along the path of the spark through the liquid; a blue stream is observed under the same conditions if starch be added instead of the phenolphthalein, whilst the colour of the stream is violet if both indicators are added together. Under the standard conditions adopted, the stream was usually visible to a depth of about 9 cm., and widened at the end, and it was observed that the red streams were somewhat more tortuous and irregular than the blue ones. The streams are deflected by the introduction of a magnetic field, and are due to a pencil of electrons, unaccompanied by matter, being projected into the liquid from the cathode. These electrons encounter ions of iodine and cause them to lose their electrons or become oxidised, the atomic iodine then reacting with the starch in the usual way. A secondary process is the reduction of potassium-ions, which acquire an additional electron and become atomic potassium; this then reacts with water, producing potassium hydroxide, which ionises and is detected by the red coloration of the phenolphthalein. It appears likely that the reduction of the potassium-ions is due both to the electrons lost by the iodine-ions and those of the cathode stream. These experiments

are thus a demonstration of the fact that the process of oxidation is the loss of an electron, whilst reduction involves the acquisition of an electron by an ion.

G. A. R. K.

The Electron in the Chemistry of Solutions and in Electrochemistry. II. The Electrons of Radium as a Reducing Agent and α -Particles as an Oxidising Agent. L. V. PISARSHEVSKI (*J. Russ. Phys. Chem. Soc.*, 1923, **54**, 548—570).—Aqueous solutions of hydrogen iodide (0.5*N*) and ferrous chloride were kept in contact with a radium preparation for about a year; the radium preparation was introduced directly into the solution in some cases and in others was contained in a separate glass vessel sufficiently thick to absorb all α -particles; control solutions were also kept. It was found that oxidation took place to an appreciable extent in solutions containing the radium preparation, iodine being liberated and ferrous-ions being converted into ferric-ions. No decomposition of the solvent was observed, doubtless because the oxygen and hydrogen produced were immediately acted on by the dissolved substances. It is shown by calculation that the results obtained can only be explained on the assumption that the ions of ferrous iron and iodine are oxidised, that is, they lose a valency electron, when they collide with α -particles derived from the radium salt. It was found that hydrogen iodide exposed to bombardment by β -particles (or electrons) alone showed slight but definite signs of decomposition; the action is explained by the absorption of the electrons by the ions of iodine. In solutions containing radium, this reducing process goes on concurrently with the oxidation due to α -particles, but the latter process predominates owing to the fact that α -particles are given out in far greater number than β -particles. In connexion with these experiments, the nature of chemical and electrochemical processes is discussed.

G. A. R. K.

The Electron in the Chemistry of Solutions and in Electrochemistry. III. The Electronic Nature of Ionic Reactions and their Capacity to Produce a Current. L. V. PISARSHEVSKI and (Mlle) M. ROSENBERG (*J. Russ. Phys. Chem. Soc.*, 1923, **54**, 570—600).—When two unequal platinum plates are dipped in a solution in which a chemical reaction is proceeding and the plates are connected together through a sensitive galvanometer, the passage of a current is observed. The current is due to the following causes. Every ionic reaction, such, for instance, as oxidation or reduction (cf. preceding abstract), involves the passage of electrons to and fro in the reacting medium. Some of these encounter the platinum plates dipping in the liquid and communicate an electric charge to them by virtue of a two-fold process; some electrons will encounter atoms of platinum with force sufficient to remove valency electrons from them, that is, causing the ionisation of the metal, whilst other electrons will merely enter the plates, increasing the concentration of electrons within it (the two processes are evidently mutually opposed). If it now be assumed that the electronic concentration in the two plates is not the same, it is clear that a current must be produced when they are joined by a wire; it is proved that if

the plates are of unequal dimensions, such is actually the case, and if the potential is due to the electrons acquired from the solution the larger plate is negatively charged whilst the smaller one is positive. The converse is, however, the case, if the chief process depends on the loss of electrons by the plates, favoured by the presence in the solution of some reagent ready to unite with the electrons set free. The larger plate then becomes positive and the current flows from the smaller plate to the larger; this is particularly noticeable in reactions involving oxidation and reduction, in accordance with the authors' view of these processes (preceding abstracts). Processes of ionic dissociation also produce an appreciable current under these conditions, and it is significant that the current is increased if pure water be added to the solution so as to cause increased ionisation of the electrolyte. The direction of this current is, however, dependent on the existence and relative magnitude of two processes, the ionisation of the electrode when brought into contact with the solution and the dissociation of the solute with a consequent movement of electrons; these two processes cause changes in opposite directions, and therefore the current between two unequal platinum plates dipped in a salt solution may pass in either direction, according to circumstances.

The influence of a radioactive substance on the phenomenon is described, and the observations of Schtschukarev (A., 1916, ii, 172) bearing on some aspects of the subject are discussed. G. A. R. K.

Electro-endosmosis and Electrolytic Water Transport. HEINRICH REMY (*Z. Elektrochem.*, 1923, 29, 365—370).—The author has determined the electrolytic transport of water as well as the water transported by electro-endosmosis for a number of normal and decinormal solutions. The water carried electrolytically is that which forms a layer round the ions, and in consequence is carried along with them. The amount of water carried in this way furnishes a measure of the number of molecules of water associated with each ion. The results show that the amount of water associated with the alkali-ions including ammonium follows the same order as has been previously calculated by the author from a comparison of the mobilities of these ions (A., 1915, ii, 310). The positive electrolytic water transport of the acids examined shows that the hydrogen-ions are sheathed in a small amount of water. The amount of water connected in this way lies between one and two molecules for each hydrogen-ion on the assumption that the water sheath of the chlorine-ion contains between three and nine molecules. J. F. S.

Velocity of Migration of Isomeric Ions. I. H. LEY and H. DIEKMANN (*Z. physikal. Chem.*, 1923, 106, 161—177).—The authors have redetermined the electrical conductivity of the sodium or potassium salts of *o*-hydroxybenzoic acid, *p*-hydroxybenzoic acid, *p*-cresotic acid, 6-hydroxy-*m*-toluic acid, *o*-hydroxybenzenesulphonic acid, *p*-hydroxybenzene sulphonic acid, anisic acid, and *o*-methoxybenzoic acid at 25° for a number of dilutions, and the molecular conductivity at infinite dilution has been obtained in each case. From these values, on the basis of $\lambda_{Na^+}=50.2$, the ionic

mobility of the anions has been deduced and the following values obtained: $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2'$ $[\alpha] \lambda_a=36.8$; $[p] \lambda_a=31.5$. $\text{OH}\cdot\text{C}_6\text{H}_4\text{Me}\cdot\text{CO}_2'$, $[\text{Me}:\text{OH}:\text{CO}_2'=1:3:4] \lambda_a=34.4$; $[\text{Me}:\text{OH}:\text{CO}_2'=1:2:3] \lambda_a=34.4$; $[\text{Me}:\text{OH}:\text{CO}_2'=1:3:6] \lambda_a=30.5$. $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2'$ $[\alpha] \lambda_a=33.5$; $[p] \lambda_a=33.3$; $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3'$ $[\alpha] \lambda_a=35.5$; $[p] \lambda_a=33.9$. The results are discussed in connexion with the orientation of the compounds. J. F. S.

The Constitution of Soap Solutions: Migration Data for Potassium Oleate and Potassium Laurate. JAMES WILLIAM McBAIN and RICHARD CHARLES BOWDEN (T., 1923, 123, 2417—2430).

Crystalline Form of Electro-deposited Metals. WILLIAM BLUM and H. S. RAWDON (*Trans. Amer. Electrochem. Soc.* [advance copy], 1923, 245—267).—A simple hypothesis of the mechanism of crystal formation in electro-deposition is put forward, according to which the cathode discharge of metal-ions and the formation of crystals constitute one and the same process, and any given ion is discharged at the point at which the lowest discharge potential is required. The discharge potential is a function of the solution pressure of the metal and the "effective" metal-ion concentration adjacent to it. The single potential and solution pressure of a metal are the resultant of the "primary single potential," which is defined in terms of the solution pressure of a single unorientated atom, and the "orientation potential," which is a measure of the diminution in solution pressure and corresponding algebraic increase in single potential caused by the arrangement or orientation of the adjacent metal atoms. A higher potential is required to discharge an ion in a position unrelated to those of previously discharged atoms than on an existing crystal, and similarly a higher potential is required to discharge an ion on a small crystal than on a large one. Typical structures of electrode deposits are classified into three major groups: those in which all, or practically all, of the initial nuclei continue to grow, those in which only a part of the initial nuclei continue to grow, and those in which none of the initial nuclei grow. The factors which determine the character of the crystals are discussed and the direction of the change produced by any change in operating conditions is predicted and illustrated. J. F. S.

Passivity. GERHARD C. SCHMIDT (*Z. physikal. Chem.*, 1923, 106, 105—154).—Attempts to measure the solubility of hydrogen and oxygen in iron, platinum, chromium, nickel, gold, and copper have been made by liberating these gases electrolytically on one side of a metal electrode and measuring the potential of the other side against a normal calomel electrode. The effect of leading hydrogen and oxygen over surfaces of copper, iron, nickel, chromium, platinum, and gold on the potential of these metals in various solutions has also been determined. The effect of roughening and polishing the surface of chromium, iron, molybdenum, nickel, tantalum, vanadium, and platinum on the potential of these metals has been determined. The results of the above determinations are

discussed in connexion with the passivity phenomena of the metals. It is shown that Warburg's hypothesis (*Ann. Phys. Chim.*, 1889, [iii], 38, 321) that the change of potential brought about by the passage of hydrogen or oxygen over a metal is due to changes of concentration in the surrounding solution is not confirmed by the present experiments. On the other hand, the hypothesis which states that gases dissolved in metals change the potential on account of their solution pressure is found to be in agreement with the experiments. No sure conclusions with respect to activity or passivity can be drawn from potential measurements alone, since the potential depends for the most part on whether the gas is dissolved or not in the metal. Chromium, nickel-chromium-steel, molybdenum, and tantalum after polishing give a very low potential which reaches the normal value again in fifty minutes with chromium, thirty minutes with molybdenum, and twenty minutes with tantalum. In the case of nickel, cobalt, and vanadium the change of potential is nothing like so great as in the above cases and it regains its normal value much more rapidly. Platinum, copper, antimony, aluminium, and iron exhibit a still smaller change of potential on polishing and in the case of zinc, tellurium, magnesium, cadmium, tin, and lead the change of potential is so small as to be scarcely detectable. The presence of gases or polarisation take no part in these changes. A complete parallelism exists between the amount of the change of potential, the time required for the metal to regain its normal potential, and the hardness of the metal. Thus the hardest metal, chromium, exhibits the largest change in potential and requires the longest time to regain its normal potential. This phenomenon is attributed to the diminution of the surface tension. Passive nickel becomes active when its surface is chemically attacked; this can occur by means of electrolytes such as sulphuric acid or by chlorine, bromine, or iodine. On account of the passivity of nickel, iodine separates at first in the electrolysis of potassium iodide solutions, but when the surface of the nickel has been attacked, nickel iodide is formed and the metal is then active. Nickel can also be activated by the removal of gases from its surface and by mechanically roughening the surface. Passive chromium becomes active by disturbing the surface, by scratching, knocking, and so on, but in nitric acid it remains permanently passive. Activated chromium placed in dilute hydrochloric or sulphuric acid remains permanently active. On removal from the acid, however, it becomes passive again after a short time, even although oxygen is rigorously kept away. Chromium heated in a vacuum or in nitrogen is active. In hydrochloric acid at 100° it is also active, and at this temperature chlorine, bromine, and iodine attack chromium and activate it, solely because the surface is disturbed. When hydrogen is evolved from one side of a sheet of iron the other side becomes active; diffusing oxygen acts in the same way. Even in a solvent in which iron does not dissolve, for example, a solution of potassium nitrate, it may be activated as above. This fact is in direct opposition to the oxidation and oxygen-alloy hypotheses. In addition to its activating action, oxygen also shows a passivating action. Iron becomes

passive in a solution of chromic acid which contains a trace of sulphuric or hydrochloric acid; it may be activated by diffusing hydrogen or by disturbing the surface. The passivity of metals is therefore to be attributed to a large surface tension, for when the surface tension is reduced the metal becomes active. Reduction of the surface tension can be brought about by attacking the surface chemically, by disturbing the surface mechanically, or by causing gases to escape from the surface. Oxygen passivates and hydrogen activates.

J. F. S.

Relation between Current, Voltage, and the Lengths of Carbon Arcs. II. A. E. R. WESTMAN and W. J. CLAPSON (*Trans. Amer. Electrochem. Soc.* [advance copy], 1923, 87—100).—Conditions have been found under which steady arcs can be maintained with currents from 120 to 700 amperes and voltages from 15 to 60. The appearance of steady arcs and of the various unsteady arcs that were encountered are described. A technique for accurately determining the relationship between current, voltage, and the length of carbon arcs has been developed, and has led to results which are tabulated in the paper. These results lead to the conclusion that $e=0.99L$, where e is the voltage over the arc and L the length in millimetres from the tip of the cathode to the bottom of the anode crater.

J. F. S.

Spectroscopic Magnetron Numbers. A. SOMMERFELD (*Physikal. Z.*, 1923, 24, 360—364).—The author considers the physical reality of the magneton, in accordance with the ideas of Gerlach (*Physikal. Z.*, 1923, 24, 275) and of Epstein (*Science*, 1923, 57), to be definitely established from a consideration of the series of multiplets in the spectra of chromium and manganese. It is shown that whereas in the transition from group to group in the periodic classification of the elements the value of the atomic magnetic moment associated with the atomic condition responsible for the emission of the lines of greatest multiplicity increases by one unit, the mechanical moment or the internal quantum number corresponding thereto increases by half a unit only. This result the author considers to be the basis of the explanation of certain apparent magneto-optic and magneto-mechanical anomalies, including the Richardson effect.

J. S. G. T.

Determination of the Isothermals of Hydrogen and Helium at Low Temperatures, made with the Object of examining whether the Compressibility of these Gases is Influenced by the Quanta. J. PALACIOS MARTINEZ and H. KAMERLINGH ONNES (*Arch. Néerland.*, 1923, [iii], 6, 253—276).—With the object of ascertaining whether or no the compressibility of hydrogen and helium is influenced by the quanta, the authors have determined the isothermals of these two gases at 20–50°. The values of δ_A and pv_A have been calculated, and it is shown that the product pv_A is practically a linear function of the density δ_A . It is concluded from this fact that the quanta exert no influence on the form of the isothermals, a result which is contrary to the demands of the hypothesis advanced by Sackur and by Keesom.

J. F. S.

Isothermals of Oxygen at 0° and 20°. H. A. KUYPERS and H. KAMERLINGH ONNES (*Arch. Néerland.*, 1923, [iii], 6, 277—283).—The isothermals of oxygen have been determined at 0° and 20°, and the values of pv_A , d_A , and p tabulated and compared with the calculated value of pv_A . The experimental values when plotted lead to a parabolic curve represented by the equation $pv_A = A_A + B_Ad_A + C_Ad_A^2$, for which the constants have been ascertained in the usual manner. These have the values for 0°, $A_A = 1.000956$, $B_A = -0.95803 \times 10^{-3}$, $C_A = 2.0608 \times 10^{-6}$ and for 20°, $A_A = 1.07426$, $B_A = -0.80379 \times 10^{-3}$ and $C_A = 2.0591 \times 10^{-6}$. By means of these coefficients the coefficient of dilation under constant pressure has been calculated and the following values have been obtained: $p=20$, $[\alpha_{p,0}]_0 = 0.00393$, $p=40$, $\alpha = 0.00425$, and $p=60$, $\alpha = 0.00449$.
J. F. S.

Influence of Small Variations of Temperature on the Conductivity of Solid Salts and the Rôle of Humidity in the Phenomenon. P. VAILLANT (*Compt. rend.*, 1923, 177, 637—639).—The temperature-conductivity curves for heating and cooling are identical when the material examined has been previously powdered and dried. With compressed, ground material (sodium chloride), not previously dried, or with a crystalline layer of material (Iceland spar), the conductivity at first rises rapidly with increase of temperature, reaches a maximum and then decreases steadily, the decrease continuing on cooling. At the original temperature, the material shows a smaller conductivity than at the outset. A second heating gives similar results, but the conductivity variations are smaller, whilst a third heating is accompanied by no variations. The loss of conductivity is, however, temporary, for on leaving the material exposed for some hours, it not only regains its conductivity, but then possesses a greater conductivity, and the above temperature effects are more pronounced than before. The conductivity in these cases is apparently a surface effect; it is decreased or increased by exposure of the material to a dry or wet atmosphere respectively.

E. E. T.

Melting Point of Ice on the Absolute Scale. LEIGHTON B. SMITH and ROBERT S. TAYLOR (*J. Amer. Chem. Soc.*, 1923, 45, 2124—2128).—The value, T_0 , the absolute temperature of melting ice, from the nitrogen volume and pressure expansion coefficients gives a mean value of 273.12° (see this vol., ii, 755). The mean value obtained by using the data of other gases including the Joule-Thomson coefficient is $273.13 \pm 0.01^\circ$.
J. F. S.

The Use of Rast's Camphor Method for Micro-determinations of the Molecular Weight of Liquids. J. HOUBEN (*J. pr. Chem.*, 1922, [ii], 105, 27—30).—Rast (A., 1922, ii, 421) has determined the molecular weight of four solid substances, by measuring the depression in the freezing point of camphor, using small quantities of material, and determining the freezing point by the capillary tube method. It is now shown that this procedure may be adopted to determine the molecular weight of any liquid

of fairly high boiling point. Excellent agreement with the theoretical figures is obtained for *n*-heptyl alcohol, geraniol, terpineol, methyl salicylate, methyl anthranilate, aniline, *n*-decyl alcohol, benzyl benzoate, ethyl benzoate, methyl nonyl ketone, benzonitrile, and tetrachloroethane. W. S. N.

Azeotropic Mixtures. SYDNEY YOUNG (*Proc. Roy. Irish Acad.*, 1922, [B], 36, 22—30).—The question whether two or three given liquids are likely to form a binary or ternary azeotropic mixture, of minimum or maximum boiling point, is discussed. No ternary azeotropic mixture of maximum boiling point has yet been discovered. Values of the boiling points of members of the methyl alcohol series from methyl to *n*-octyl alcohol inclusive are tabulated. The following are the values of the boiling points of binary and ternary azeotropic mixtures of the respective alcohols with water (represented by the symbol *w*), hexane (symbol *h*) benzene (symbol *b*), and toluene (symbol *t*), so far as these have been determined: methyl: *h*, 50·0°; *b*, 58·35°; ethyl: *w*, 78·15°; *h*, 58·7°; *b*, 68·25°; *t*, 76·7°; *h*, *w*, 56·6°; *b*, *w*, 64·85°; *t*, *w*, 74·55°; *iso*-propyl: *w*, 80·37°; *h*, 61·0°; *b*, 71·9°; *t*, 80·6°; *h*, *w*, 58·2°; *b*, *w*, 66·5°; *t*, *w*, 76·2°; *tert*.-butyl: *w*, 79·9°; *h*, 63·7°; *b*, 73·95°; *h*, *w*, 58·9°; *b*, *w*, 67·3°; *n*-propyl: *w*, 87·7°; *h*, 65·65°; *b*, 77·1°; *t*, 92·6°; *h*, *w*, 59·95°; *b*, *w*, 68·5°; *t*, *w*, 80·05°; *sec*.-butyl: *w*, 88·5°; *h*, 67·5°; *b*, 79°; *h*, *w*, 61·1°; *tert*.-amyl, $\text{CMe}_3\text{Et}\cdot\text{OH}$: *w*, 87° (?); *h*, 68·5°; *t*, 99·2°; *t*, *w*, 82°; *isobutyl*: *w*, 89·9°; *h*, 68·1°; *b*, 79·85°; *t*, 101·15°; *t*, *w*, 83°; *n*-butyl: *w*, 92·25°; *t*, 105·5°; *iso*amyl, $\text{CHMe}_2\text{CH}_2\text{CH}_2\text{OH}$: *w*, 95·15°; *t*, 110·5°; *n*-octyl: *w*, 98°. Methyl alcohol forms no azeotropic binary mixtures with water, benzene, or toluene, and no azeotropic ternary mixtures with the respective systems hexane–water, benzene–water, or toluene–water. *iso*Butyl alcohol forms no azeotropic ternary mixture with the system hexane–water. It is possible that the amyl alcohol, $\text{CMe}_3\text{CH}_2\text{OH}$, may form an azeotropic mixture with hexane, but much less probable that the amyl alcohol, $\text{CHMe}_2\text{CHMe}\cdot\text{OH}$, forms such a mixture. It may be regarded as certain that none of the alcohols with higher boiling points do so. No alcohol with a higher boiling point than 108° should form a ternary azeotropic mixture with hexane and water, nor form a binary mixture with benzene. It is uncertain whether *sec*.-butyl alcohol forms a ternary mixture with benzene and water; it is almost certain that *tert*.-amyl alcohol does not. Alcohols of higher boiling point cannot form ternary azeotropic mixtures with benzene and water. The existence of a binary methyl alcohol–toluene azeotropic mixture is doubtful. The b. p. of the amyl alcohol, $\text{CMe}_3\text{CH}_2\text{OH}$, is probably 112°. J. S. G. T.

Vapour Pressure Thermometer. ALFRED STOCK (*Z. Elektrochem.*, 1923, 29, 354—358).—A full description of the method of making and filling of a vapour pressure thermometer previously described by Henning and Stock (*A.*, 1921, ii, 432). The original must be consulted for details and dimensions. The thermometer filled with carbon disulphide has a range from the ordinary temper-

ature to -10° , with sulphur dioxide -10° to -40° , with ammonia -30° to -77° , with carbon dioxide -75° to -100° , hydrogen chloride -85° to -111° , ethylene -100° to -150° , methane -150° to -185° , and with oxygen -180° to -200° . A very complete table of vapour pressures from about 1,000 mm. downward with the corresponding temperatures is given for all the gases named above. The thermometer is capable of an accuracy sufficient for most purposes.

J. F. S.

The Vapour Pressures of Concentrated Sucrose Solutions.

EDGAR PHILIP PERMAN and HORACE LEONARD SAUNDERS (*Trans. Faraday Soc.*, 1923, **19**, 112—116).—The curves showing the relation between the vapour pressure of sucrose solutions and the concentration of the sugar at 70° and 90° have been determined and found to be smooth curves and not straight lines as previously found by Perman and Price (*A.*, 1913, ii, 20). From these curves the value of the hydration factor a in Callendar's formula, $p'/p = (N - an)/(N - an + n)$, is found to be 5 between concentrations of 20 and 65 g. of sugar per 100 c.c. Babo's law holds for sugar solutions up to a concentration of 80% of sugar.

A. R. P.

Improved Methods of Evaporation in the Laboratory.

H. G. BECKER (*Sci. Proc. Roy. Dubl. Soc.*, 1923, **17**, 241—248).—Experiments were made to determine the rate of evaporation of distilled water at different temperatures in still air and in air currents of different speeds. Using an open dish in an oil-bath, a bath temperature of 100° gives a water temperature of 70° in still air and of 54° in a strong draught. To maintain the water at 100° , bath temperatures of 170° and 215° are needed in still air and a strong draught respectively. The rate of evaporation increases very rapidly at higher temperatures, and between 90° and 100° each degree rise is about six times as effective as between 30° and 40° . The air current is relatively more effective at lower temperatures, on account of its greater cooling effect at high temperatures. The normal rate of evaporation on a water-bath in still air is 0.01 c.c. per minute per sq. cm. This can be increased without difficulty to 0.07 c.c. per sq. cm. by raising the dish temperature to 95° and using an air draught of 500 feet per minute. An effective apparatus for evaporating solutions is described, consisting of a glass bulb blown in a wide-bore tube, mounted horizontally and rotated whilst heated with a gas burner. A current of air may be passed through the bulb, or it may be evacuated. In this apparatus superheating is entirely avoided, and such substances as ferric chloride may be readily crystallised.

E. H. R.

Calorimetric Micro-bomb. M. PADOA and B. FORESTI (*Gazzetta*, 1923, **53**, 493—498).—Heats of combustion may be determined with a high degree of accuracy by means of a small bomb calorimeter inserted in an ice calorimeter of the Bunsen form. Only 0.03—0.06 g. of the substance is required, this being weighed on a microbalance. [Cf. *J.S.C.I.*, 1923, 1045A.] T. H. P.

The Heat of Combination of the Metals of the Alkaline Earths with Oxygen, Hydrogen, and Nitrogen. A. GUNTZ and F. BENOIT (*Ann. Chim.*, 1923, [ix], 20, 5—33; cf. this vol., ii, 126).—The following heats of formation were determined: Strontium hydride, 42.2 cal.; barium hydride, 40.9; strontium nitride, 31.8; barium nitride, 31.3; calcium amide, 93.0; lithium amide, 86.7 (for 2LiNH_2); strontium amide, 84.3; barium amide, 80.24; lithium imide, 52.6; barium imide, 54.4. In each case the measurement depended on the heat developed when the substance is dissolved in dilute hydrochloric acid. The purity of the material used was verified in some cases by analysis of the reaction products. The above results together with others quoted (without references) lead to the conclusions that heats of formation of the oxides, hydrides, nitrides, and amides decrease with rise of atomic weight and that lithium occupies from the thermochemical point of view a position between calcium and strontium. The authors point out that lithium and barium easily yield amides and stable imides by direct action of the metal on ammonia, whilst the calcium and strontium compounds are only obtainable indirectly by decomposition of the corresponding nitride, which is a matter of some difficulty. A comparative table embodying both original and quoted results is given. H. J. E.

Heats of Vaporisation of Mercury and Cadmium. MAYOR F. FOGLER and WORTH H. RODEBUSH (*J. Amer. Chem. Soc.*, 1923, 45, 2080—2090).—The importance of directly measured heat data as a supplement to vapour pressure data is discussed. The heat of vaporisation of mercury has been determined at 142° , and as a mean of 25 determinations the value 14490 ± 50 cal. is obtained. The value calculated for 298.1°K is 14670 ± 50 cal. A number of vapour pressure measurements have been made for cadmium at temperatures from 754.0°K to 867.6°K and from these data the value 25350 ± 100 cal. is obtained as the latent heat of vaporisation at 594.1°K . The generalisations regarding the entropies of monatomic gases, and relating vapour pressures to heats of vaporisation are confirmed for zinc, cadmium, and mercury. J. F. S.

Study of Solutions at Different Temperatures. I. The Capacity for Heat of Aqueous Solutions of Hydrogen Chloride and Ammonia. M. S. VREVSKI and A. I. KAĖGORODOV (*J. Russ. Phys. Chem. Soc.*, 1923, 54, 335—347).—The capacities for heat of aqueous solutions containing from 0.6 to 37.7% of hydrogen chloride, and from 1.47 to 32.3% of ammonia were determined at about 3° , 20° , 40° , and 60° . The determinations were carried out in a closed vessel to eliminate the effect of vaporisation at higher temperatures; the method of heating was electrical. The values obtained for the heat capacities at room temperature agree substantially with those of Thomsen, Marignac, and others.

The results of the investigation are expressed in the form of curves and it is shown that the heat capacity of hydrogen chloride solutions diminishes with increasing concentration, this being

observed at all temperatures. The heat capacity of ammonia solutions at low temperatures (2.4°) at first diminishes with increasing concentration and reaches a minimum at about 25% NH_3 ; it then begins to rise again. The curve for the same solutions at 20.7 shows a horizontal portion between 0 and 8% NH_3 , the heat capacity being equal to that of pure water; it then increases for higher concentrations. At higher temperatures the heat capacity rises in proportion to the concentration.

Weak solutions of hydrogen chloride (below 3%) and ammonia (below 5%) exhibit a minimum of heat capacity similar to that observed for pure water by Callendar and Barnes (Kaye and Laby, "Chemical and Physical Constants," London, 1919, p. 56).

The heat capacity of hydrogen chloride solutions is lower than the calculated value, whilst the converse is observed for ammonia solutions.
G. A. R. K.

Study of Solutions at Different Temperatures. II. The Heat of Solution of Hydrogen Chloride and Ammonia at Different Temperatures. M. S. VREVSKI and N. N. ZAVARICKI (*J. Russ. Phys. Chem. Soc.*, 1923, 54, 348—360).—The molecular heats of solution of hydrogen chloride and ammonia in water were determined at various temperatures. The method used consisted in the direct absorption of the gas in water, carried out in several stages; this is shown to be more accurate than the method of dilution.

It is found that the heat of solution rises rapidly in strong solutions, less so in weak solutions. With rise of temperature the heat of solution of hydrogen chloride rises, whilst that of ammonia diminishes. The heat of solution of hydrogen chloride at all temperatures increases with dilution; that of ammonia is remarkably constant for all concentrations below 12 or 15%.

G. A. R. K.

Study of Solutions at Different Temperatures. III. The Determination of the Density and Composition of the Vapour of Aqueous Solutions of Hydrogen Chloride and Hydrogen Bromide at Various Temperatures. M. S. VREVSKI, N. N. ZAVARICKI, and L. E. SCHARLOV (*J. Russ. Phys. Chem. Soc.*, 1923, 54, 360—375).—Using a specially constructed apparatus, the pressure and composition of the vapour in equilibrium with aqueous solutions at various temperatures were determined. Dry nitrogen was bubbled through the solution under investigation and the amount of water and acid carried away estimated. It is shown that the total vapour pressure of the solution diminishes with increasing concentrations of acid and reaches a minimum, then rises again; this minimum is more marked in solutions of hydrogen bromide and is greatest at low temperatures.

The partial pressure of the acids greatly depends on the concentration of the solution and is practically zero for solutions containing less than 10 % HCl and 20 % HBr at 19.9° . With rising concentration, the partial pressure rises rapidly and for solutions

containing more acid than the constant-boiling mixture the vapour consists of pure acid, the curve expressing the composition of the vapour rising very steeply.

A rise of temperature causes an increase in the partial pressure of the acid in solutions weaker than the constant-boiling mixture, whilst the converse is observed in stronger solutions; the effect of the temperature appears to be greatest for strong solutions. The experimental data referring to the composition of constant-boiling mixtures agree with the older data in the literature.

The results are shown to support the authors' view that for solutions the vapour pressure curve of which shows a minimum, the composition of the vapour and that of the constant-boiling mixture changes in opposite directions with change of temperature.

G. A. R. K.

Study of Solutions at Different Temperatures. IV. The Vapour Density and Heats of Formation of Solutions of Gases. M. S. VREVSKI (*J. Russ. Phys. Chem. Soc.*, 1923, **54**, 376—401).—A theoretical paper in which the results obtained in the three preceding papers are discussed from a mathematical point of view.

G. A. R. K.

Titrimetric Method for the Estimation of Density by Means of Floating Bodies. DOEMENS (*Svensk. Bryggmästare-Tidning*, 1923, 1; *Z. Ges. Brauwesen*, 1923, **46**, 23—29; from *Chem. Zentr.*, 1923, ii, 1201).—A method for the estimation of the density of a liquid consists in the addition of water to a known volume of the liquid until a glass float of known density sinks to the bottom of the vessel containing the liquid.

G. W. R.

Piezochemical Studies. XXI. Calculation of the Coefficient of Compressibility. A. L. TH. MOESVELD (*Z. physikal. Chem.*, 1923, **105**, 442—449; cf. this vol., ii, 537).—A theoretical paper in which a method is described whereby equations may be deduced which enable the pressure relationship of the mean and actual compressibility to be calculated. For amyl alcohol, the two equations are: $\beta_m = 101.5 - 36.3 \times 10^{-9}p + 7.47 \times 10^{-12}p^2$, and $\beta_w = 101.5 - 72.6 \times 10^{-9}p + 22.41 \times 10^{-12}p^2$, where β_m and β_w are the mean and true compressibilities, respectively, and p is the pressure. The calculated and observed values are in good agreement. J. F. S.

Piezochemical Studies. XXII. Compressibility of Mixtures of Alcohol and Water. A. L. TH. MOESVELD (*Z. physikal. Chem.*, 1923, **105**, 450—454; cf. preceding abstract).—The mean compressibility of various mixtures of water and ethyl alcohol at 25° has been determined over the pressure range 0—1,500 atm. An equation has been evolved, which represents the mean compressibility of these mixtures as a function of the pressure, and also equations which represent the mean compressibility as a function of the concentration over the same pressure range. Tables of the experimental and calculated compressibilities are given which show a good agreement between the two sets of values. The

mean compressibility in terms of concentration is given by the following equations for the pressure ranges indicated: $10^6 \beta_c^0 = 44.5 - 0.5443c + 0.01754c^2 - 0.06585 \cdot 10^{-3}c^3$; $10^6 \beta_c^{0-500} = 42.2 - 0.4514c + 0.01395c^2 - 0.05234 \cdot 10^{-3}c^3$; $10^6 \beta_c^{0-1000} = 39.4 - 0.3457c + 0.01049c^2 - 0.03773 \cdot 10^{-3}c^3$; $10^6 \beta_c^{0-1500} = 37.1 - 0.3253c + 0.00962c^2 - 0.03762 \cdot 10^{-3}c^3$.

J. F. S.

Relation between Young's Modulus and Atomic Volume.

ALBERT PORTEVIN (*Compt. rend.*, 1923, **177**, 634—636).—An equation recently given by Peczalski (*ibid.*, **176**, 500), connecting Young's modulus (E) and atomic volume, is identical with that given by Fessenden (*Chem. News*, 1892, **66**, 206). The latter equation held for the common metals, but is useless where the value of E is high (rhodium tantalum and tungsten). In these cases, more satisfactory results are obtained with the equation $E = kT^a/V^b$, where T = absolute temperature, and a and b are, respectively, about 1 and 2. The various equations connecting coefficients of elasticity (modulus of compressibility, etc.) with surface tension, cubic expansibility, and specific heat are obviously simply modifications of the above type of formula. Some calculations are made (of E) for various minerals, using existing compressibility data.

E. E. T.

Velocity of Sound in Nitrogen Tetroxide. A Lower Limit of its Velocity of Dissociation. E. GRÜNEISEN and E. GOENS (*Ann. Physik*, 1923, [iv], **72**, 193—220).—The velocity of sound in nitrogen tetroxide has been measured at various pressures and temperatures by Thiessen's method of closed cylindrical resonators. It is shown that up to frequencies of the order $15,000 \text{ sec.}^{-1}$ there is no indication that the velocity of sound depends on the frequency, as should be the case if the time required for setting up the dissociation equilibrium were comparable with the vibration period of sound. The absolute value of the velocity of sound agrees much better with the assumption that the time required for the setting up of a dissociation equilibrium is small in comparison with the vibration period. It can be stated from the most exact measurements at 25° and 760 mm. that the velocity constant of the decomposition, k , under the experimental conditions is certainly larger than 10,000. That is, every molecule of nitrogen tetroxide dissociates on the average at least once in every 10^{-4} sec. J. F. S.

Capillary Phenomena manifested at Surface of Separation of Water and Liquid Vaseline in Presence of Fatty Acids and Alkalis. RENÉ DUBRISAY and PIERRE PICARD (*Compt. rend.*, 1923, **177**, 589—591; cf. A., 1918, ii, 368).—Alkali carbonates, like alkali hydroxides, diminish the interfacial tension between liquid vaselin and water, although to a much less extent. Alkali hydrogen carbonates have a slighter effect still. Neutral salts decrease the interfacial tension between mixtures of liquid vaselin and oleic acid and dilute soap solution, probably owing to their decreasing the solubility of soap and thus favouring its separation at the surface of separation.

E. E. T.

Separation of Gas Mixtures by Diffusion into Steam under Pressure. FRANZ FISCHER, HANS SCHRADER, and ALBERT JAEGER (*Brennstoff-Chem.*, 1923, 4, 289—296).—The gas mixture and steam are passed in opposite directions on either side of a porous earthenware division, and thence, through water condensers, to gas receivers. The best separation of light and heavy constituents is obtained with a medium gas and steam velocity and a relatively low steam pressure. Similar results are obtained by replacing the earthenware division by a layer of Raschig rings. For example, an illuminating gas containing 44—45% of hydrogen gave a diffusate containing 70—74% of hydrogen, and this was increased by a second diffusion to 95%. Using a diffusion zone of sand or a large number of narrow tubes, rather less satisfactory results are obtained. [Cf. *J.S.C.I.*, 1923, Nov.] W. T. K. B.

Calculation of Molecular Weights of Associated and Non-associated Liquid from the Critical Data. W. HERZ (*Z. Elektrochem.*, 1923, 29, 394—395).—A theoretical paper in which it is shown that Berthelot's formula, $M = 11.4dT_k/p_k(2 - T/T_k)$, yields at low temperatures fairly accurate values for the molecular weights of non-associated liquids and absolutely correct values at high temperatures. In the case of associated liquids, the molecular weights calculated by this formula are considerably too large at ordinary temperatures and only at very high temperatures are accurate figures obtained. Associated and non-associated liquids pass gradually into one another. J. F. S.

Mechanical Theory of Solutions. C. DIETERICI (*Ann. Physik*, 1923, [iv], 72, 241—264).—A theoretical paper in which, by means of an empirical approximation, the author demonstrates the applicability of van der Waals's internal pressure equation to liquids, without making any assumptions with regard to van der Waals's quantities π and b . The author considers that the statement, that in the liquid phase of pure liquids over a wide range of temperature and pressure a constant value of the volume correction is always obtained, and that this same value of the volume correction is again found for all solutions in which no association or compound formation takes place, is fully confirmed on the mechanical basis considered. Further, the dimensions of cohesion pressure and its dependence on volume and temperature are also confirmed on the same basis. J. F. S.

Selective Solvent Action by the Constituents of Aqueous Alcohol. II. The Effect of some Alcohol-soluble Semi-solutes. ROBERT WRIGHT (*T.*, 1923, 123, 2493—2499).

The Increased Solubility of Phenolic Substances in Water on Addition of a Third Substance. CHARLES REYNOLDS BAILEY (*T.*, 1923, 123, 2579—2590).

Furthering of the Separation of Crystals and Gases from Supersaturated Solutions by Means of Fresh Surfaces and other Causes. R. FRICKE and C. ROHMANN (*Z. Elektrochem.*, 1923, 29, 400—402).—From a large number of experiments with super-

saturated solutions of potassium hydrogen tartrate it has been shown that the formation of a fresh surface or a surface partly separated from its surface film favours the separation of crystals. The effect of rubbing the vessel walls with a glass rod appears therefore to act in this way by forming a fresh surface. From a large number of experiments on solutions saturated with carbon dioxide, it is shown that the formation of a fresh surface also causes the separation of the gas, but here the nature of the substances in the surface is of importance, for some organic substances are active even with old surfaces, whilst others are not active. The presence of bubbles of another gas also favours the separation of the gas. J. F. S.

The Alleged Anomalous Reflection of X-Rays in Crystals.

RALPH W. G. WYCKOFF (*Amer. J. Sci.*, 1923, [v], 6, 277—287).—The “X-peak reflections,” recorded by G. L. Clark and W. Duane (this vol., ii, 468) from spectrometric observations on potassium iodide, are not confirmed by Laue photographs taken through the cube faces of crystals of this salt, there being no spots developed in the required positions. The photographs conform completely with the sodium chloride arrangement of the atoms; and the only anomalous effect to be observed is a slight hazy diffraction quite close to the central spot, due, perhaps, to distortion in the crystal or to “asterism.” L. J. S.

The Law of Distribution of Particles in Colloidal Suspensions with Special Reference to Perrin's Investigations.

II. ALFRED W. PORTER and J. J. HEDGES (*Trans. Faraday Soc.*, 1923, 19, 1—3).—In an emulsion of paraffin in distilled water, made by shaking the two liquids together for some hours and filtering, the change in concentration occurs at the bottom of the vessel and an increase of concentration takes place towards the surface of the liquid. The concentration n varies with the depth y according to the equation $\log_e n/(1-bn) + 1/(1-bn) = Ky + A$, the values of the constants A , b , and K being, respectively, 83.23, 9.7×10^{-7} , and -235 . A. R. P.

The Penetration of Electrolytes into Gels. V. Diffusion of Mixtures of Chlorides in Gels.

WALTER STILES (*Biochem. J.*, 1923, 17, 530—534).—There is no antagonism between the chlorides employed in regard to their diffusion through agar and gelatin. The rate of diffusion of mixed chlorides is a little higher than would be expected from the values of the coefficients of diffusion of the respective salts in pure solution. S. S. Z.

Water-line Corrosion.

KENNETH M. WATSON (*Trans. Amer. Electrochem. Soc.* [advance copy], 1923, 195—202).—Experiments have been carried out to ascertain the cause of water-line corrosion. Strips of zinc, copper, and brass were partly submerged in various corrosive liquids such as hydrochloric acid and solutions of sodium chloride, potassium nitrate, ammonium nitrate, calcium chloride, chromic, formic, acetic, phosphoric, hydrofluoroboric, and hydrofluorosilicic acids, and the conditions under which water-line corrosion occurs investigated. The results indicate that although the de-

polarising effect of oxygen is necessary for the corrosion of many metals in certain solutions, the contact of air with the upper surface of a liquid is never directly responsible for the occurrence of water-line corrosion. This phenomenon is caused by the slow downward flow of the heavier film of corrosion products along the surface of the metal, which draws in at the upper surface of the liquid a fresh supply of solution. Since all the metal except that at the surface of the liquid is in contact with partly exhausted solution, corrosion is most rapid at the water line. Although there is an even greater circulation of solution down the face of anodes used in the plating and refining of metals, water-line corrosion does not occur. In this work, the rate of corrosion is determined by the distribution of current over the anode surface, which depends on Ohm's law, and is only slightly affected by the amount of corrosion products contained in the film of solution that touches the anode. J. F. S.

The Distribution of Normal Fatty Acids between Water and Benzene. FREDERICK STANLEY BROWN and CHARLES E. BURY (T., 1923, **123**, 2430—2434).

The Liesegang Phenomenon—an Historical Note. J. R. I. HEPBURN (*Nature*, 1923, **112**, 439).—A claim for priority on behalf of Ord ("The Influence of Colloids upon Crystalline Form and Cohesion," London, 1879) over Liesegang in respect of the discovery of the phenomenon of stratified precipitation in gels. A. A. E.

A Method of Measuring the Velocity of Very Rapid Chemical Reactions. H. HARTRIDGE and F. J. W. ROUGHTON (*Proc. Roy. Soc.*, 1923, [A], **104**, 376—394).—A form of apparatus is described suitable for measuring the velocities of very rapid chemical reactions, such as the velocities of unimolecular reactions of which the half reaction is completed in as short a time as 1/300 sec. The fluids to be mixed are brought together at a high velocity within a restricted space by forcing them under considerable pressure through jets entering the space tangentially. The mixture thereafter flows with uniform velocity within a glass tube in such manner that estimations of the composition of the fluid at any cross section of the tube can be made by measuring the colour opacity, spectral absorption, optical activity, etc., of the fluid thereat. By using as fluids to be mixed *N*/10-solutions of sodium hydroxide and hydrochloric acid, the former being coloured with phenolphthalein, it is shown that with rates of flow through the observation tube equal to 400 cm. per sec., not more than 1% of the fluid remains unmixed. Various factors (nature of the flow in the observation tube, specific gravities of the liquids, surface tension) which might possibly influence the results obtained are discussed, and their effects shown to be negligible. J. S. G. T.

Mechanism of the Reduction of Permanganate and its Physico-chemical Basis. V. Mechanism of the Reduction of Manganate and its Dependence on the Alkalinity. JOSEF HOLLUTA (*Z. physikal. Chem.*, 1923, **106**, 276—294; cf. A., 1922, ii, 448, 628, 700, 771).—The reduction of manganate by formate

has been investigated in respect of its relation to the hydroxyl-ion concentration. It is shown that the velocity coefficients at low hydroxyl-ion concentrations change in inverse proportion to the square root of the hydroxyl-ion concentration. The effect of the hydroxyl-ion concentration on the velocity constant and on the pressure of oxygen liberated from the manganate is strictly in accord with the theory. It is shown to be probable that hydrated derivatives of manganese peroxide are the end-product of the reduction of manganate at high hydroxyl-ion concentrations. These compounds have a salt-like character. The importance of the adsorptive properties of the precipitated products on the further course of the reaction is discussed, and it is shown that in many cases a further reduction of the quadrivalent manganese takes place, which disturbs the normal course of the reaction when its velocity is very small. The retarding effect of low concentrations of hydroxyl-ion is overcome by an accelerating action at high alkali concentration which is found to be directly proportional to the hydroxyl-ion concentration.

J. F. S.

Velocity of Formation of Chloride from Chloroform and Alkali. E. ABEL (*Z. Elektrochem.*, 1923, 29, 391—394).—The velocity of formation of potassium chloride from potassium hydroxide and chloroform in ethyl alcohol solution at 25° has been investigated. The results show that the velocity is proportional to the chloroform concentration, but it is not proportional to the alkali concentration. The velocity increases much more rapidly than the concentration of alkali in the sense that starting with very dilute alkali solutions the apparent order of the reaction with respect to alkali is unity, but this increases with increasing alkali concentration.

J. F. S.

The Velocity of Reaction in Mixed Solvents. VI. The Velocity of Saponification of certain Methyl Esters by Potassium Hydroxide in Methyl Alcohol-Water Mixtures. WALTER IDRIS JONES, HAMILTON MCCOMBIE, and HAROLD ARCHIBALD SCARBOROUGH (*T.*, 1923, 123, 2688—2698).

Rate of Hydrogenation of Cinnamic and Phenylpropionic Acids. ERIC KEIGHTLEY RIDEAL (*Trans. Faraday Soc.*, 1923, 19, 90—97).—The mechanism of the hydrogenation of sodium cinnamate and sodium phenylpropionate in aqueous solution in the presence of a palladium sol stabilised with gum arabic has been examined. In the presence of sufficient catalyst, the rates at which *M*/10-solutions of the salts are hydrogenated are practically the same and proportional to the square of the shaking speed within very wide variations, the reaction velocity being of the zero order. For small quantities of catalyst, the reaction velocity is proportional to the palladium concentration, independent of the concentration of the salt within limits, and, above certain critical limits, of the shaking speed, but the rate of hydrogen absorption by the phenylpropionate is twice that by the cinnamate. The reaction velocity in all cases depends on the age of the sol; with freshly prepared sols, the

curve is of the zero order practically throughout the reaction. As the age of the sols increases the proportion of the curve of zero order becomes gradually less, the reaction finishing as one of the first order, until with very old and inactive sols the reaction throughout is of the first order. It is shown that the salt is adsorbed on the surface of the catalyst together with the hydrogen, and that it remains adsorbed until completely hydrogenated; this explains the fact that both salts are hydrogenated at the same rate, the phenylpropiolate taking up 2 mols. of hydrogen whilst the cinnamate is taking up 1 mol. A. R. P.

Piezochemical Studies. XXIII. Influence of Pressure on the Velocity of Reaction in Homogeneous Liquid Systems.

V. Liquid Mixtures. A. L. TH. MOESVELD (*Z. physikal. Chem.*, 1923, **105**, 455—471; cf. this vol., ii, 740).—The velocity reaction between 0.01*N*-sodium hydroxide and 0.01*N*-ethyl *o*-methoxycinnamate in 31 and 42.5 weight % ethyl alcohol at 25° has been determined at 1, 500, 1,000, and 1,500 atm. pressure. It is shown that in both solvents the velocity increases considerably as the pressure is increased. At 1,500 atm., the velocity constant is 2.34 and 2.15 times as large, respectively, as under 1 atm. pressure. The pressure coefficient of the velocity increases very much with increase in pressure. J. F. S.

The Kinetics of Hæmoglobin. II. The Velocity with which Oxygen Dissociates from its Combination with Hæmoglobin. H. HARTRIDGE and F. J. W. ROUGHTON (*Proc. Roy. Soc.*, 1923, [A], **104**, 395—430).—In continuation of previous work (this vol., ii, 229), the authors have determined the rate of reduction of oxyhæmoglobin by sodium hyposulphite, employing for this purpose the form of apparatus described in a previous paper (this vol., ii, 744). The chemical composition of the solution at any section of the observation tube through which it flowed from the mixing chamber was determined by means of the reversion spectroscope (this vol., ii, 105), using an auxiliary trough containing a solution of hæmoglobin saturated with carbon monoxide. It was shown that the velocity of reduction due to sodium hyposulphite was practically identical with that found when the reduction was effected by suitable physical means. For this and other reasons, it was concluded that the dissociation was not appreciably retarded by any back reaction between oxygen and reduced hæmoglobin. The results obtained indicate that the reduction of oxyhæmoglobin is a unimolecular reaction obeying the law of mass action. Hydrogen-ion concentration has a marked effect on the velocity of the reaction. On the alkaline side of p_H 7.7, the velocity is constant, and on the acid side of p_H 6.3, the velocity is probably also constant, having a value about seven times that corresponding with p_H 7.7; between p_H 6.3 and p_H 7.7 there is a gradual change from the one rate to the other. The interpretation of the p_H effect and the legitimacy of adopting a single velocity equation are discussed in detail. The effect of temperature on the velocity constant is in accord with Arrhenius's equation (A., 1889, 1103). At p_H 6.3

and p_H 7.7, the value of the temperature coefficient of the velocity of reaction is 3.8. At the low concentrations of hæmoglobin used, variations in the salt content of the solution are without effect on the velocity of reduction.

J. S. G. T.

Catalysis by the Action of Subdivided Metals. I. Heat of Adsorption of Hydrogen on Finely-divided Nickel. B. FORESTI (*Gazzetta*, 1923, 53, 487—493).—The author obtains values lying between 10957.6 and 11977.2 cal. for the molecular heat of adsorption at 0° of hydrogen at constant volume by nickel reduced from its oxide at 300°. The mean value, 11430.8 cal., is in satisfactory agreement with that calculated by Rideal (T., 1922, 121, 309). The amount of the gas adsorbable by the metal varies with different samples of nickel, and is considerably affected by the extent of the vacuum attained during the evacuation of the metal prior to the experiment and by the period of contact of the metal with the gas at reduced pressure. The values found by Gauger and Taylor for the heat of adsorption of hydrogen (this vol., ii, 398) are lower than the true values.

T. H. P.

Behaviour of certain Metals as Catalysts. II. C. SANDONNINI (*Gazzetta*, 1923, 53, 453—461).—Investigation of the changes occurring in hydrogen-oxygen mixtures at various temperatures and in presence of either reduced nickel, or purified sugar carbon containing 0.65% of ash, or mixtures of these two catalysts (cf. A., 1922, ii, 557) shows that carbon does not act on detonating gas as an energetic catalyst and that at 300—350° it absorbs oxygen, which at higher temperatures it gives up as carbon monoxide and dioxide. Nickel, however, exerts marked catalysing influence on the union of hydrogen and oxygen and also on the reactions resulting in the oxidation of the carbon. Formation of hydrocarbons was observed in none of the experiments.

T. H. P.

Catalytic Decomposition of Hydrogen Peroxide in a Bromine-Bromide Solution. II. Rate Measurements in Dilute Solutions and in the Absence of Sulphate, and their Interpretation as a Function of the Activity Product of Hydrobromic Acid. ROBERT S. LIVINGSTON and WILLIAM C. BRAY (*J. Amer. Chem. Soc.*, 1923, 45, 2048—2058; cf. this vol., ii, 473).—A continuation of previous work in which the catalytic decomposition of hydrogen peroxide in solutions of sulphuric acid and potassium bromide, more dilute than previously examined, has been investigated at 25° with the object of determining the reason why the value of k increased as the acid concentration was decreased below 0.2*N*. It is shown that the steady state rate of the bromine-bromide catalysis approaches a definite finite value as the concentration of the sulphuric acid is indefinitely decreased. The steady state rate has also been measured in solutions of hydrobromic acid, hydrobromic acid-perchloric acid, hydrobromic acid-potassium bromate, hydrobromic acid-barium bromide, and perchloric acid-potassium bromide. The rate constants obtained

from measurements in these various solutions are all slightly larger than those obtained in sulphuric acid solutions more concentrated than 0.2*N*. At the steady state in hydrobromic acid and hydrobromic acid-perchloric acid solutions of ionic strength less than 0.25 and in many of the experiments in the absence of sulphate, the rate of decomposition of the peroxide is represented by the following expression within the limits of experimental error, 1%—2%: $-d(\text{H}_2\text{O}_2)/dt = 0.0437(\text{H}_2\text{O}_2)(\text{H}^+)(\text{Br}')\gamma_{\text{HBr}}^2$. The activity coefficient, γ_{HBr} , in solutions containing sulphuric acid and potassium bromide has been estimated from the rate measurements in these solutions on the assumption that the above equation is true. The application of the "activity rate" hypothesis and of Brönsted's hypothesis to the present experiments is discussed. J. F. S.

Catalytic Dehydroxidation of Formic Acid. II. ERICH MÜLLER and JOHANNES KEIL (*Z. Elektrochem.*, 1923, 29, 395—399; cf. A., 1922, ii, 558).—The catalytic decomposition of formic acid into carbon dioxide and hydrogen by means of metallic osmium is connected very largely with the degree of dispersion of the metal. The necessary degree of dispersion is obtained when a compound of osmium (osmium tetroxide, potassium osmate, or potassium chloro-osmate) is acted on by formic acid itself. The osmium thus produced enters in the highly dispersed condition with the acid practically in statu nascendi, and exhibits a hitherto unobserved catalytic action. The catalyst loses its activity rapidly, because the degree of dispersion is reduced. The retardation of the catalysis can be largely prevented by the addition of a protective colloid, such as gelatin. The catalysis of the decomposition of formic acid by osmium shows a large induction period which is removed very largely by the presence of a little metallic osmium. The catalytic decomposition of formic acid in the presence of an osmium compound and gelatin takes place more easily, more certainly, and more completely than in the presence of metallic osmium which has been prepared by the reduction of the tetroxide by means of hydrogen.

J. F. S.

Isotopes. F. W. ASTON (*Chemistry and Industry*, 1923, 42, 935).—Measurements of the masses of the atoms or isotopes of elements not hitherto examined have now been made by a new method. The following elements are found to be simple: scandium, 45; titanium, 48; vanadium, 51; chromium, 52; manganese, 55; cobalt, 59; strontium, 88; yttrium, 89. Gallium has two isotopes, 69 and 71, germanium has three, 74, 72, and 70, and silver has two, 107 and 109. The atomic masses and isotopes of the first forty elements and a few others are now known. With the exception of nitrogen, every odd element has an odd atomic weight, and no atomic weight, excepting that of hydrogen, is less than twice the atomic number.

E. H. R.

A Calculation of the Atomic Weights of Isotopes. A. S. RUSSELL (*Nature*, 1923, 112, 588—589; cf. this vol., ii, 719).—Rules have been formulated from radioactive data whereby the

atomic weights of the principal isotopes of common and radioactive elements may be calculated. It is deduced solely from radioactive evidence that isotopes probably do not differ by more than 8 units of atomic weight; that only end-products of radioactive series or radio-elements emitting α -particles should be considered when a comparison is made between common and radioactive isotopes; that all elements are limited to two isotopes of odd atomic weight, differing by 2 units only; that elements of odd atomic number have odd isotopes only, the lighter being likely to be the more stable and abundant; that even elements may have both even and odd isotopes, the former usually being at least twice as numerous as the latter, and the lightest or heaviest not being odd; that isobares of common elements may be of even atomic weight only; that an element of atomic number $[?] 4n+3$ has an isotope of atomic weight $4n+1$ and vice versa; and that an even element has always one isotope a unit of atomic weight higher than one of the isotopes of the element next below it. The rules, some of which have already been formulated by Aston, do not apply in their entirety to elements below nickel and cobalt. Branching according to an unknown plan, and indecisive radioactive evidence concerning which mass-numbers are unstable and which are possible isobares, prevent the determination by calculation of all the isotopes of every element. The atomic weights of isotopes calculated in this way are quoted, and shown to agree closely, although not absolutely, with Aston's results. The complexity of an element appears to be a simple function of the atomic number $16n$. It is considered probable that elements of atomic numbers $16n+7$, $16n+10$, and $16n+11$ are simple; that $16n+3$, $16n+5$, $16n+13$, and $16n+15$ have two isotopes; that $16n+8$, and $16n+14$ have no odd isotopes; and that $16n$, $16n+2$, and $16n+12$ have odd isotopes

A. A. E.

The Periodic Law. P. I. PETRENKO-KRITSCHENKO (*J. Russ. Phys. Chem. Soc.*, 1923, **54**, 447—454).—A theoretical paper in which certain seemingly anomalous chemical facts such as the effect of accumulation of hydroxyl groups in organic acids, the heats of combination of elements with oxygen, etc., are discussed, and an attempt is made to demonstrate an element of periodicity in connexion with these facts. The arguments do not lend themselves to condensation.

G. A. R. K.

Active Cross-section of Gas Molecules for Slow Electrons.

II. CARL RAMSAUER (*Ann. Physik*, 1923, [ii], **72**, 345—352; cf. A., 1921, ii. 324).—In the earlier paper (*loc. cit.*), methods were described for the determination of the total active cross-section of gaseous molecules for slow electrons as a function of the velocity of the electrons. Using the same method, the work has been continued with krypton and xenon. It is shown that whilst for hydrogen, nitrogen, helium, and argon the active cross-section and the absorbing cross-section are practically the same for the smallest electron velocities, there are indications that these two quantities for argon, krypton, and xenon commence to differ for velocities between 30 and 70 volts; the divergence between the two commences

sooner the larger the atomic number. All inactive gases show the same peculiarity in comparison with the other gases (nitrogen, hydrogen, and carbon dioxide) investigated namely that the active cross-section reaches a maximum and then falls with decreasing electron velocity. The gases argon, krypton, and xenon exhibit the above peculiarity very markedly in two respects; the active cross-section increases to a maximum which is four to five times as large as the kinetic gas cross-section and then falls to one-seventh of the kinetic cross-section for velocities of 0.75 volt. Below this velocity no definite statements can be made. The gases neon, argon, krypton, and xenon show a definite progression in respect of the position and height of their maxima, with increasing atomic number (10, 18, 36, 54) the maxima increase strongly (active cross-section in cm^2/cm^3 for 0° and 1 mm. mercury, 13, 82, 98, 141), and in addition are displaced to smaller electron velocities ($\text{volt}_{\text{max.}} = 25, 13.2, 11.3, 6.4$).
J. F. S.

Structure and Deformation of Electron Sheaths and their Significance for the Optical and Chemical Properties of Inorganic Compounds. K. FAJANS (*Naturwiss.*, 1923, **11**, 165—172; from *Chem. Zentr.*, 1923, iii, 2—3).—The author discusses the hypothesis that in the activation of ions, and consequently of atoms and molecules, the deformation of electron sheaths is an important factor.

[With G. JOOS.]—Optical properties are a measure of deformability. The deformation of inert gas electron sheaths increases with increase of atomic size, anions being more deformable than kations, particularly when associated with a hydrogen nucleus.

[With H. BEUTLER.]—It appears from colour phenomena that the electron path of the anion is deflected to the kation. This is illustrated by compounds of copper. With kations of the inert gas type, the colour effect is the greater the more highly charged is the kation and the smaller its radius.

[With A. SCOTT.]—A deformed anion will approach more closely to a kation than will a rigid anion of equal magnitude. This is illustrated by data for heats of formation and lattice energies of salts. In general, the lattice energy of a salt with a heavy metal (without inert gas sheath) exceeds that of a salt of an equally charged kation of the inert gas type the more deformable the associated anion is.

[With A. HOLSTAMM.]—The behaviour of alkali metal halides shows that the ions compete for water in solutions. When acids dissociate in aqueous solution it is supposed that the hydrogen-ion associates with water to form H_3O^+ .

It is concluded from a study of the colour of the halides of titanium and silicon and of other compounds that extreme deformation results in a compacting rather than a loosening of electron paths.
G. W. R.

Co-ordination and the Electrons. T. MARTIN LOWRY (*Chemistry and Industry*, 1923, **42**, 1004—1007).—The factors which have led to delay in the universal acceptance of Werner's

theory of co-ordination are discussed. The view that the development of conjugated rings is an important factor in promoting co-ordination is maintained, in view of the strong experimental evidence on which it is based.

Kinetic Foundation for Chemical Affinity. J. K. SYRKIN (*Z. physikal. Chem.*, 1923, **106**, 243—254).—A theoretical paper in which it is shown that a kinetic representation of chemical affinity can be developed from considerations of molecular collisions on the assumption that not all the molecules are active, but only a portion of them, which is determined by a definite energetic condition furnished from considerations of statistical mechanics. An equation for chemical equilibrium is deduced on this basis and has the form $\log k = \log n_1!n_2!/n_1'n_2' - Q/RT - \Sigma n$, where k is the equilibrium constant, Q is the heat change of the reaction, n_1 and n_2 are the number of molecules of each kind reacting, n_1' and n_2' are the number of molecules of each product, and n is the total number of reacting molecules, $n = n_1 + n_2$. A kinetic equation is developed for reactions of any given order (2 or higher); this has the form $K = (\sqrt{0.8}\pi R\sigma^{n-1}n_1!n_2!r)N_0^{n-1}\sqrt{(n_1/M_1 + n_2/M_2 + \dots)/(n_1 + n_2)}\sqrt{T}e^{q/RT}$, where K is the velocity constant, σ is the sphere in which collision can occur, r is the radius of the reaction sphere, M_1 and M_2 are the molecular weights, and the other symbols have their usual meanings or those given in the first equation. J. F. S.

Measure of Chemical Affinity. RUDOLF WEGSCHIEDER (*Z. physikal. Chem.*, 1923, **106**, 18—36).—A theoretical paper in which it is shown from a measure of affinity that it must be demanded that it shall depend on the momentary state of the system alone and not on the conditions under which the following change takes place. This condition is satisfied only by the measurement of the affinity from the maximum obtainable work reduced by that required for overcoming the external pressure. Consequently, the volume energy is not to be regarded as a constituent of the chemical energy, nor is the opposing pressure which stops a reaction a measure of the affinity. On the other hand, the work of mixing is only to be deducted when the mixing takes place independently of the reaction itself, but it must not be deducted for the chemical processes which occur in galvanic elements in which actually no mixing takes place. The affinity is dependent on the condition of the system and consequently can, in general, not be defined by any work done by a finite change, but only by the differential quotient. These views are expressed by equations and elaborated by means of definite examples. Here, among other things, a new method is used for proceeding from the unmixed reactants to the unmixed products in a chemical reaction. Previous definitions of affinity refer to processes leading to equilibria (reaction and opposing reaction). The author discusses whether or no the forces of a single reaction can be defined. J. F. S.

Early Greek Chemistry. J. R. PARTINGTON (*Nature*, 1923, **112**, 590).—Comments on Berthelot and Ruelle's "Collection des

anciens alchimistes grecs" and Stéphanidès's emendations thereof (*Rev. études grecques*, 1922, **35**, No. 162). A. A. E.

Glass to Metal Joint. CYRIL H. MEYERS (*J. Amer. Chem. Soc.*, 1923, **45**, 2135—2136).—Glass to metal joints may be made by coating the metal part with tin or solder and cleaning the surface thoroughly with zinc chloride. The glass part is cleaned with chromic acid and water and then dried. The metal part is then heated until the solder or tin just melts and the glass, which has been previously warmed, slowly inserted. It is essential that the surfaces of both glass and metal should be clean and that the temperature reached in the soldering does not exceed that required to melt the solder. J. F. S.

A Simple Attachment for Gas Generators. L. SPIEGEL (*Ber.*, 1923, **56**, [B], 2068).—A device for attachment to the lower end of the tap funnel used in ordinary gas generators, to prevent a back-rush of gas through the tap. It consists of a U-tube with the longer leg closed except for a small hole at the top. The short limb is attached to the lower end of the dropping funnel by means of a well-greased ground joint. The result is that the U-tube becomes full of liquid, which effectually prevents a back-rush of gas. H. H.

Cellulose Acetate as a Material for the Preparation of Ultra-filters. R. FRICKE and P. KLEMP (*Kolloid Z.*, 1923, **23**, 164—168).—Ultra-filters may be made from cellulose acetate as follows: A solution of cellulose acetate (3—10 g.) in a mixture of one volume of 96% ethyl alcohol and nine volumes of chloroform is poured uniformly on a glass plate and allowed to dry in the air. The plate and filter are then placed in 96% alcohol for a short time to dissolve out the last traces of chloroform. The filter is loosened at one side and stripped from the plate and preserved in cold water. Such filters are durable and of suitable density, they may be bent without breaking and are best used inside a filter-paper. A number of examples of the use of cellulose acetate filters is given in the paper. J. F. S.

Inorganic Chemistry.

Electrolytic Generator for Pure Hydrogen. VISCOUNT ELVEDEN and ERIC SINKINSON (T., 1923, **123**, 2715—2716).

The Low Temperature Activation of Hydrogen. ALLAN ERNEST MITCHELL and ABRAHAM LINCOLN MARSHALL (T., 1923, **123**, 2448—2457).

The Catalytic Decomposition of Hydrogen Peroxide Solution by Carbons prepared from Carbohydrates. J. B. FIRTH and F. S. WATSON (*J. Soc. Chem. Ind.*, 1923, **42**, 371—372T; cf. T., 1923, **123**, 1750).—The volume of oxygen liberated

from hydrogen peroxide by carbon from various carbohydrate sources was studied. When the samples of carbon were merely dried at 100° , it was found that those from cellulose and rice starch were moderately active; those from dextrin, inulin, and wheat starch were slightly active; whilst those from dextrose, lactose, lævulose, maltose, and potato-starch were practically inactive. Heating the carbons in a vacuum for two hours at 600° increased their catalytic activity in all cases. The increase was most marked in the case of inulin carbon, and least for potato-starch and lævulose carbons. Previous sorption and removal of iodine caused a marked increase in the activity in all cases except that of wheat-starch carbon. The increase in the activity of cellulose-carbon was especially striking. The relative bulk of a carbon is not a decisive factor in determining its activity. H. H.

Vapour Pressures and Crystal Lattices of the Hydrogen Halides. F. A. HENGLEIN [with R. ROTH and P. ANDRES] (*Z. Physik*, 1923, 18, 64—69).—The following values, expressed in mm. of mercury, have been found for the vapour pressures of solid hydrochloric acid, liquid and solid hydrobromic acid, and solid hydriodic acid, at the respective temperatures (measured on the absolute scale) stated: HCl (solid): 161° , 122.2; 158.9° , 100.2; 156.7° , 82.6; 156.0° , 76.0; 149.7° , 40.2; 142.2° , 17.9; 121.0° , 0.891; 115.1° , 0.363; HBr (liquid): 208.7° , 869.9; 194.5° , 400.9; 187.3° , 255.9; (solid) 177.6° , 124.5; 161.2° , 28.2; 157.0° , 17.66; 156.0° , 16.0; 148.7° , 7.30; 144.1° , 4.03; HI (solid): 208.3° , 162.0; 194.7° , 68.0; 177.7° , 18.8. The author's results in the case of hydrobromic acid are not in agreement with those of McIntosh and Steele (A., 1904, ii, 533). The respective vapour pressures in mm. of mercury can be represented as a function of the absolute temperature by equations of the form $\log p = 7.5030 - K/T^n$, the following being the respective values of K and n : HCl (liquid), 945.7, 1.0160; (solid), 1966.3, 1.1600; HBr (liquid), 1037.2, 1.0160; (solid), 2202.0, 1.1602; HI (liquid), 1197.3, 1.0160; (solid), 1435.9, 1.0496. The results indicate that as in the case of the halogens, the hydrogen halides form molecular lattices. Moreover, the crystal form of solid hydrogen iodide is different from that of hydrogen chloride and hydrogen bromide, and it is possible that at lower temperatures a second crystalline modification occurs. The following values of vapour pressure (in mm.) at the melting point characterise the respective molecular and ionic lattices:—molecular lattices: Cl, 8.9; Br, 44.1; I, 87.0; HCl, 125.2; HBr, 224.2; HI, 369; ionic lattices: KCl, KBr, KI, about 0.4. J. S. G. T.

Irregularities in the Rate of Solution of Oxygen by Water. H. G. BECKER and E. F. PEARSON (*Sci. Proc. Roy. Dubl. Soc.*, 1923, 17, 197—200).—Measurements of the rate of absorption of oxygen at a still water surface show that, up to 60 or 70% of saturation, the absorption follows the same logarithmic law as if the water were kept continually mixed, but beyond this point wide irregularities occur. The causes determining the uniform

mixing in the early stages and its failure in the later stages of absorption have not been elucidated. E. H. R.

Recent Progress in the Production of Ozone with High Tension Discharges. FRANK E. HARTMAN (*Trans. Amer. Electrochem. Soc.* [advance copy], 1923, 295—306).—The paper deals with the production of ozone by the silent discharge methods. Data are given which show that the energy density of an ozoniser is a straight-line function of the cycles; and that the yield of ozone is a straight-line function of the energy density at atmospheric pressure. It is further shown that ozonising at high gas pressures is conducive to better cooling of the electrodes, thus making it possible to produce high concentrations of ozone with high energy densities. A relationship is also established between high gas pressures and the efficiency of an ozoniser. J. F. S.

Preparation of Ozone with a High Frequency Alternating Current. ALFRED STARKE (*Z. Electrochem.*, 1923, 29, 358—364).—The author has made experiments to ascertain whether by increasing the frequency of the alternating current up to the value 10,000 it is possible to reach the increased theoretical intake of energy in an ozone tube without decreasing the energy yield, the ozone concentration, and the safety of the tube. Experiment shows that by using a frequency of 10,000 at constant voltage, about 200 times as much ozone can be produced in the same tube as with a frequency of 50. An unfavourable effect of the high frequency could not be found in connexion with the energy yield, the concentration of the ozone, or the safety of the tube; on the other hand, a slight influence of the frequency on the work factor was found. The work factor increases up to a frequency of 3,200, and then falls slightly. A calculation shows that the very high costs of a large ozone plant are considerably reduced by employing a high frequency alternating current. J. F. S.

Amorphous Sulphur in Flowers of Sulphur and its Transformation in the Preparation of Precipitated Sulphur. R. HUERRE (*J. Pharm. Chim.*, 1923, [vii], 28, 223—232).—Amorphous sulphur insoluble in carbon disulphide, is converted into the soluble modification when heated at about 100° with an animal or vegetable oil, with a 10% solution of sodium sulphite, or with water alone. The insoluble sulphur does not dissolve in a cold 10% solution of sodium sulphite, and only a trace dissolves in the boiling solution. Amorphous sulphur is completely soluble in a cold aqueous solution of sodium sulphide, and from the solution the soluble modification is obtained by precipitation with an acid or even by extraction with carbon disulphide. W. T. K. B.

Action of Selenium Oxychloride on Various Metals and Metallic Oxides. WARD L. RAY (*J. Amer. Chem. Soc.*, 1923, 45, 2090—2094).—Selenium oxychloride reacts with metallic copper at the ordinary temperature, forming a black substance which is a mixture of cuprous and cupric selenides. On continued action, the selenides are converted into anhydrous cupric chloride:—

$3\text{Cu} + 4\text{SeOCl}_2 = 3\text{CuCl}_2 + 2\text{SeO}_2 + \text{Se}_2\text{Cl}_2$. Anhydrous cupric chloride reacts with selenium oxychloride to form a green, crystalline acid selenite, $\text{CuCl}_2 + 3\text{SeO}_2 = \text{CuSeO}_3, \text{SeO}_2 + \text{SeOCl}_2$. The selenium oxychloride acts merely as a solvent for cupric chloride and selenium dioxide formed by hydrolysis of some of the oxychloride by moist air. Silver is changed successively into the selenide and chloride by the same reagent. The oxides of copper, silver, lead, nickel, cobalt, iron, antimony, bismuth, and tin are converted into chlorides by the action of selenium oxychloride and selenium dioxide is formed. J. F. S.

Equation of State for Pure Nitrogen, Gas Phase. LEIGHTON B. SMITH and ROBERT S. TAYLOR (*J. Amer. Chem. Soc.*, 1923, **45**, 2107—2124).—The *p.v.T.* relationship of pure gaseous nitrogen has been studied by the isometric method over the temperature range 0° to 200° and the pressure range 30—300 atms. The Keyes equation expresses the data obtained within the limits of experimental error. The equation obtained is $p_{\text{atm.}} = 2.92855T/(v-\delta) - 1623.63/(v+0.2954)^2$, where $\delta = 0.18683 - 0.3113/v$. The weight of a litre of nitrogen at *N.T.P.* is calculated from the equation of state to be 1.2509 g., as compared with the generally accepted value, 1.2507 g. The compressibility coefficient at 0° is calculated and found to be 0.00061, as compared with 0.00056 from Otto and Holborn's equation and Rayleigh's work, and 0.00043 and 0.00044 from Chappius Maverick, respectively. J. F. S.

Nitrogen Fixation by Means of the Cyanide Process and Atomic Structure. L. HAMBURGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1923, **26**, 480—485).—From consideration of atomic structure, it is deduced that for reactions which occur in the gas phase, the relation, critical energy supply/reaction temperature = constant, should hold good. For reactions of the type $\text{MO} = \text{M} + \text{O}$, there then exists the relation, ionisation potential of the metal (V)/absolute temperature of reaction (T) = k . This is found to be substantially true for the alkali and alkaline-earth metals. For reactions between compounds, however, *e.g.*, $\text{MCO}_3 = \text{MO} + \text{CO}_2$, the term ionisation potential cannot strictly be employed, because the electron which is to be ionised is probably already moving in a distorted orbit, so that an amount of energy less by V' than the ionisation potential of the free metal will be required to detach the electron completely. V' is termed the dislocation potential of the compound, and is probably nearly equal to its excitation potential (V''). It is found that, in accordance with this theory, $(V - V'')/T$ is practically constant for cyanising reactions. H. H.

The Glow of Phosphorus, and its Extinction by Moist Oxygen. LORD RAYLEIGH (*Proc. Roy. Soc.*, 1923, [A], **104**, 322—332).—The author has investigated the conditions determining the possibility of detaching the luminosity from a stick of glowing phosphorus by a blast of air, a phenomenon previously described by L. and E. Bloch (*A.*, 1908, ii, 1032). It was found that the velocity of the blast necessary to effect such detachment increased

greatly with rise of temperature and decreased greatly with increase in the oxygen content of the air blast. Thus at 4° , the necessary velocity was increased 1,000 times by an increase of 1% in the oxygen content of the air blast employed. When the velocity of the blast was 100 cm. per sec. or more, the glow exhibited a tendency to cling to certain points at which depressions occurred on the phosphorus surface and from which the luminosity spread out fanwise. Extinction of the glow by an atmosphere of moist oxygen is regarded as the limiting case of slow propagation, and arises probably owing to failure of the catalytic action of the products of combustion of the phosphorus to effect propagation of the glow. Oxygen, present in excess, inhibits such catalytic action, possibly by a process of condensation analogous to that whereby the motion of ions produced in gaseous combustion is reduced.

J. S. G. T.

Change of Realgar into Orpiment and the Analogous Behaviour of Arsenic Sulphide Sols. S. S. BHATNAGAR and B. LAKSHMAN RAO (*Kolloid Z.*, 1923, **23**, 159—164).—It is shown that the hydrosulphide-ion, SH' , and not the sulphide-ion, S'' , is the active agent in the precipitation of metallic sulphides by hydrogen sulphide. The colloidal solutions of sulphides obtained in this way can be regarded as solutions of hydrosulphides. When a colloidal solution of arsenic sulphide is heated or when hydrogen is passed through it so that all the free and combined hydrogen sulphide is removed, the formula of the colloidal sulphide is not As_2S_3 , but much more nearly As_2S_2 or AsS . It is shown that the action of heat on a red colloidal solution converts it into a yellow sol with the precipitation of sulphur, according to the equation $\text{As}_2\text{S}_2 \cdot x\text{H}_2\text{S} + x\text{O} = \text{As}_2\text{S}_3 + x\text{H}_2\text{O} + (x-1)\text{S}$. When the content of combined hydrogen sulphide is small, no sulphur is precipitated. The action of light and heat consists mainly in the transformation of one variety into the other, and may be represented by the equation $\text{As}_2\text{S}_2 + \text{H}_2\text{S} + \text{O} = \text{As}_2\text{S}_2 \cdot \text{S} + \text{H}_2\text{O}$. By analysis, measurement of density, and the absorption spectrum, it is shown to be likely that the red variety is identical with realgar and the yellow precipitate with orpiment, both in colour and in other properties.

J. F. S.

Perborates. HEINRICH MENZEL (*Z. physikal. Chem.*, 1923, **105**, 402—441).—By means of freezing point and electrical conductivity measurements at 0° , it is shown that a combination between hydrogen peroxide and boric acid in aqueous solution cannot be substantiated, and in consequence the decomposition constant of perboric acid, $K = [\text{H}_2\text{O}_2][\text{H}_3\text{BO}_3]/[\text{H}_3\text{BO}_3 \cdot \text{H}_2\text{O}_2]$, must be exceedingly large. The effect of varying quantities of hydrogen peroxide on the equivalent conductivity of metaborate and borax solutions of various concentrations has been investigated. It is shown that with increasing concentration of hydrochloric acid and increasing additions of hydrogen peroxide the electrical conductivity is continuously decreased, which is to be regarded as due to the formation of many additive products with small degree of hydrolysis and small

mobility. Cryoscopic measurements with solutions of metaborates and borax in the presence of hydrogen peroxide show that the metaborate-ion and the more complicated ions from concentrated solutions of borax combine with hydrogen peroxide, and in the higher concentrations of metaborates a polymerisation of the simpler ions also takes place, since the osmotic concentration is smaller than that of the original metaborate solution. By means of partition experiments with amyl alcohol, the combination of hydrogen peroxide with the metaborate-ion is also demonstrated. These results taken together with the freezing-point measurements show that in 0.02—0.07 *M* metaborate solutions containing hydrogen peroxide the simple ion $(\text{BO}_2, \text{H}_2\text{O}_2)'$ is in equilibrium with free metaborate and free hydrogen peroxide, whilst in concentrated solutions, polymerisation takes place and more than 1 mol. of hydrogen peroxide is combined with a single boron atom. In the case of the simple acid, $\text{H}_3\text{BO}_3, \text{H}_2\text{O}_2$, and its ion, $\text{BO}_2, \text{H}_2\text{O}_2'$, it is found that the decomposition constant of perboric acid bears the same relation to the decomposition constant of its ion as the dissociation constant of perboric acid bears to the dissociation constant of boric acid. Since free perboric acid is not present to a measurable extent and its decomposition constant is very large, an apparent dissociation constant for perboric acid can be deduced from the equilibrium $\text{H}' + (\text{BO}_2, \text{H}_2\text{O}_2)' \rightleftharpoons \text{HBO}_2 + \text{H}_2\text{O}_2$, which has the form

$$\frac{[\text{H}'][\text{BO}_2, \text{H}_2\text{O}_2']}{[\text{HBO}_2][\text{H}_2\text{O}_2]} = K'_p,$$

and is equal to the quotient of the true dissociation constant of perboric acid and its decomposition constant, and therefore equal to the ratio between the dissociation constant of boric acid to the decomposition constant of the perborate-ion. From partition experiments, it is found that the decomposition constant, K_z , of the perborate-ion at 0° is 2.4×10^{-2} , and at 18°, 3.3×10^{-2} from which the apparent dissociation constant of perboric acid, K'_p , is calculated to be $> 1 \cdot 10^{-8}$ for 0° and 1.7×10^{-8} for 18°. Independently from the above, colorimetric measurements with dilute solutions give as the apparent dissociation constant of perboric acid $K'_p = 2 \times 10^{-8}$ against the boric acid constant $K_b = 5.7 \times 10^{-10}$. Further, colorimetric measurements show that in the more concentrated solutions a greater reduction of alkalinity and affinity takes place, due to the formation of complicated acids, a fact which explains the evolution of carbon dioxide from mixtures of borax and hydrogen carbonates on the addition of hydrogen peroxide.

J. F. S.

Vitreous Carbon. A Special Form of Crystalline Carbon.

K. A. HOFMANN and CURT RÖCHLING (*Ber.*, 1923, **56**, [B], 2071—2076).—By exposing a heated, chemically inert surface to the luminous flame of some aliphatic hydrocarbons or halogenated compounds, a deposit of a hard, lustrous, crystalline form of carbon is obtained. The minimum temperature of the surface is 650°, and both the nature of the surface and the kind of compound used to carburet the gas are important. A steel surface, probably owing to the intermediate formation of metallic carbides, gives

only a deposit of graphitic carbon, whilst flames of burning benzene and naphthalene gave only amorphous, sooty carbon, or, at higher temperatures, graphitic carbon.

The vitreous form of carbon now described has a high density ($d_4=2.07$), is very pure (C=99.06%, H=0.48%), and has a low electrical conductivity ($\frac{1}{8}$ — $\frac{1}{15}$ of that of Ceylon graphite, and $\frac{1}{3}$ — $\frac{1}{8}$ of that of Acheson graphite). It is also very hard, that prepared at 900° having a hardness equal to that of quartz, at 1100° having a hardness equal to that of topaz, whilst that prepared at 1300° is harder than carborundum. It is considered to be a form intermediate between graphite and diamond, and its X-ray spectrum shows characteristic lines of both these forms. H. H.

Silica. I. Loss of Water of Kaolin and its Behaviour in the Solid State towards the Carbonates and the Oxides of the Alkaline Earths. G. TAMMANN and W. PAPE (*Z. anorg. Chem.*, 1923, 127, 43—67).—Experiments were carried out with carefully washed Oschatz earth dried at 150°, and its dehydration and the behaviour of the carbonates and the oxides of the alkaline earths towards the anhydrous compound $Al_2O_3 \cdot SiO_2$ formed and towards kaolin were studied. At 550°, kaolin loses water and decomposes into alumina and silica, and at 930° the alumina undergoes a change. These conclusions are based on the following results. After heating at 550°, the alumina of kaolin is soluble in acids, further heating at 900° renders pure alumina and that of kaolin difficultly soluble in acids. Pure alumina evolves heat at 850—1060°; kaolin evolves heat at 930°, the amount being proportional to its alumina content. Both alumina and kaolin show an increase in density at still higher temperatures, and they both lower the dissociation temperature of the alkaline-earth carbonates (1 atmosphere by about 220°). W. T.

Crystal Structure of Potassium Hydrogen Fluoride. RICHARD M. BOZORTH (*J. Amer. Chem. Soc.*, 1923, 45, 2128—2132).—The positions of the potassium and fluorine atoms in tetragonal potassium hydrogen fluoride have been determined by X-ray photographs. The dimensions of the unit cell are $5.67 \times 5.67 \times 6.81$ Å. The structure may be described as an ammonium chloride arrangement of potassium atoms and fluorine “dumb-bells,” the two atoms of each “dumb-bell” lying in a plane perpendicular to the tetragonal axis. For the hydrogen atoms, there are two possible positions, one of which is in the middle of the “dumb-bell,” forming an HF_2' -ion. The distance between potassium and fluorine atoms is 2.77 Å., between two potassium atoms 3.41 and 4.01 Å., and between two fluorine atoms 2.25 Å. In the case of potassium fluoride, the distance between potassium and fluorine is 2.68 Å. and between two potassium atoms 3.79 Å. The complete unit cell contains 4 mols. of potassium hydrogen fluoride.

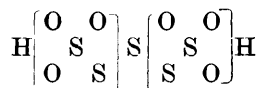
J. F. S.

Saturated Solutions of Potassium and Magnesium Sulphate. S. M. LEVI (*Z. physikal. Chem.*, 1923, 106, 93—104).—Solubility determinations of the system magnesium sulphate—

potassium magnesium sulphate have been made at a series of temperatures from 0° to 37.8° , and a further series for the system potassium sulphate–potassium magnesium sulphate for temperatures between 0° and 63.4° . The values interpolated for 25° from the present measurements agree with those determined by van Klooster (A., 1917, ii, 471). The solubility curve of magnesium sulphate for the system potassium sulphate–double salt shows a sharp break at about 52° , which is not in agreement with the dilatometric and tensimetric determinations of the transition point of the system potassium sulphate–schönite–leonite determined by van't Hoff as 47.5° . A simple process is described whereby thermometrically the transition points of the systems double salt–ice–less soluble component, and double salt–both components, may be distinguished from one another.

J. F. S.

The Energy Content and Constitution of the Potassium Polythionates. F. MARTIN and L. METZ (*Z. anorg. Chem.*, 1923, **127**, 83–100).—The heats of formation of potassium di-, tri-, tetra-, and penta-thionate, potassium sulphite, and potassium thiosulphate were determined in a Berthelot-Mahler bomb; to ensure complete combustion it was necessary to mix the salt with potassium chlorate and magnesium. The heats of formation were found to be $K_4S_2O_6$, 415 Cal.; $K_2S_3O_6$, 401 Cal.; $K_2S_4O_6$, 393 Cal.; $K_2S_5O_6$, 386 Cal.; K_2SO_3 , 273 Cal., and $K_2S_2O_3$, 283 Cal. Thus the addition of solid sulphur to the polythionates is endothermic. The constitution of these salts is discussed from the point of view of Werner's co-ordination theory. They are given a binuclear structure—the central atom sulphur being assigned a co-ordination number equal to 4 and a valency of +6, whilst the co-ordinated sulphur atoms have a valency of –2. Pentathionic acid is formulated thus:



The method of preparation of the salts is given in detail. W. T.

Mechanism of certain Catalysed Reactions. CARLO SANDONNINI (*Atti R. Accad. Lincei*, 1923, [v], **32**, ii, 84–88).—Investigation of the changes occurring in solutions of potassium and ammonium hydrogen sulphites in presence of selenium indicates that, under certain conditions, the total reaction may be expressed by the equation: $4MHSO_3 \rightarrow 2M_2SO_4 + SO_2 + S + 2H_2O$. This probably takes place in the three stages, (1) $M_2SO_3 + Se \rightarrow M_2SSeO_3$, (2) $M_2SSeO_3 + M_2SO_3 + 2H_2SO_3 \rightarrow M_2SO_4 + M_2S_3O_6 + Se + H_2O$, and (3) $M_2S_3O_6 \rightarrow M_2SO_4 + SO_2 + S$. Thus, the true catalytic action of the selenium would cease when only one-half of the total sulphuric acid is formed. It is found that, when reprecipitation of the selenium occurs in accordance with equation (2), the quantity of sulphuric acid present does not correspond exactly with one-half of the final amount, and that the latter exceeds what should be formed according to equations (1) and (2). These divergences

may be attributable to the facts that the end of the initial phase cannot be gauged exactly, that the reactions become superposed, and that the excess of sulphur dioxide undergoes partial oxidation. The quantity of sulphur which separates and that of sulphur dioxide not participating in the reaction do not, indeed, correspond exactly with those calculable from the above reactions. It is possible also that secondary reactions lead to the formation first of selenothionate and thiosulphate and afterwards of other polythionates, and that the formation and subsequent decomposition of these compounds give rise to the divergences mentioned above.

T. H. P.

Solubility of Sodium Chlorate. HUGH CHESTER BELL (T., 1923, **123**, 2713—2714).

Stability of Solutions of Alkali Chlorites. G. R. LEVI and G. NATTA (*Gazzetta*, 1923, **53**, 532—538; cf. this vol., ii, 767).—Solutions of chlorites are not altered at 100°, even when hydrogen or oxygen is passed through them. Various finely divided metals are, however, capable at even moderately high temperatures of exerting a marked catalytic effect on the decomposition of chlorites which, in presence of palladium or gold, is expressed by the equation $9\text{NaClO}_2 = 4\text{NaCl} + 5\text{NaClO}_3 + \text{O}$ (1); this reaction is modified by a current of hydrogen to $2\text{NaClO}_2 = \text{NaCl} + \text{NaClO}_3 + \text{O}$ (2). Similar decompositions are produced by platinum and nickel, but in these cases the loss of oxygen is greater, although the decomposition is less rapid; the effect of copper is negligible. Decomposition of solutions of chlorites in quartz vessels exposed to sunlight is accompanied by formation of ozone, which probably results also from reaction (1).

The decomposition of chlorite into chloride and chlorate by the agency of catalysts corresponds only partly with that effected when the solid salt is heated at 180—200°, the loss of oxygen in the latter case being very small (A., 1922, ii, 567). T. H. P.

Stability of Sodium Thiosulphate Solutions. MARTIN KILPATRICK, jun., and MARY L. KILPATRICK (*J. Amer. Chem. Soc.*, 1923, **45**, 2132—2135).—The stability of several 0.01*N*-solutions of sodium thiosulphate has been investigated over a period of eight months. It is found that freshly boiled redistilled water yields a solution of thiosulphate that is more stable than a solution made with ordinary laboratory distilled water, ordinary distilled water, or redistilled water through which carbon dioxide-free air has been bubbled. Carbon dioxide, oxygen, and dilute sodium hydroxide have very little effect on the stability of solutions of sodium thiosulphate. The decomposition in these solutions is caused by bacteria. J. F. S.

The Ammines of the Alkali Halides. WILHELM BILTZ and WERNER HANSEN (*Z. anorg. Chem.*, 1923, **127**, 1—33).—The following compounds were prepared and investigated; the heats of formation in calories and the temperature at which the dissociation pressure equals 100 mm. of mercury are given. LiCl, NH_3 , 12.4,

+70°; $\text{LiCl}, 2\text{NH}_3$, 11.5, +44°; $\text{LiCl}, 3\text{NH}_3$, 10.7, +23.5°; $\text{LiCl}, 4\text{NH}_3$, 8.8, -20.5°; $\text{LiCl}, 5\text{NH}_3$, 8.0, -44°; LiBr, NH_3 , 13.6, +102°; $\text{LiBr}, 2\text{NH}_3$, 11.7, +48°; $\text{LiBr}, 3\text{NH}_3$, 11.1, +33°; $\text{LiBr}, 4\text{NH}_3$, 10.2, +20°; $\text{LiBr}, 5\text{NH}_3$, 8.05, -44°; $\text{LiBr}, 6.5\text{NH}_3$, 6.9, -67°; LiI, NH_3 , 16.0, +169°; $\text{LiI}, 2\text{NH}_3$, 13.8, +108°; $\text{LiI}, 3\text{NH}_3$, 12.2, +64°; $\text{LiI}, 4\text{NH}_3$, 11.6, +60.5°; $\text{LiI}, 5\text{NH}_3$, 8.1, -43°; $\text{LiI}, 5.5\text{NH}_3$, 7.2, -62°; $\text{LiI}, 7\text{NH}_3$, 7.1, -65°; $\text{NaCl}, 5\text{NH}_3$, 7.8, -49°; $\text{NaBr}, 5.25\text{NH}_3$, 8.45, -31.5°; $\text{NaBr}, 5.75\text{NH}_3$, 6.95, -66°; $\text{NaI}, 4.5\text{NH}_3$, 9.4, -3°; $\text{NaI}, 6\text{NH}_3$, 7.5, -52°; $\text{KBr}, 4\text{NH}_3$, 7.15, -64°; $\text{KI}, 4\text{NH}_3$, 7.65, -46°; $\text{KI}, 6\text{NH}_3$, 7.35, -55°; $\text{RbBr}, 3\text{NH}_3$, 7.1, -62°; $\text{RbI}, 6\text{NH}_3$, 7.5, -55°. The compound $\text{NaCl}, 2.5\text{NH}_3$ described by Friedrich (A., 1921, ii, 503), could not be isolated. The capacity of the alkali halides to co-ordinate ammonia increases from caesium to lithium and from chlorides to iodides. Methods of investigation were as previously described (A., 1922, ii, 59). W. T.

The System Ammonium Nitrate-Ammonia. F. HALLA and K. HIRSCHKO (*Z. anorg. Chem.*, 1923, 127, 137—152).—Diver's liquid, which is formed by passing ammonia over ammonium nitrate, is only stable up to a temperature of 23.7° with a pressure of 1 atmosphere of ammonia. Above this temperature it exists in a metastable condition (supersaturated solution). The system ammonia-ammonium nitrate forms a simple binary system. The rate of absorption of allotropic forms of the nitrate were found to be the same. W. T.

Double Decomposition in the Absence of Solvents. IV. The Systems Formed by Metallic Nitrates, Chlorates, and Halides. A. G. BERGMANN (*J. Russ. Phys. Chem. Soc.*, 1923, 474—492).—A number of binary mixtures of salts have been investigated by the thermal method.

A.—Systems with silver nitrate. The system $\text{AgNO}_3\text{--HgBr}_2$ is complex in nature, the liquidus curve showing a maximum in the region of 50%, but this is probably not due to compound formation, as the molten mass solidifies over a large range of temperature. The mixtures after melting are hygroscopic; they are very sensitive to overheating. The system $\text{AgNO}_3\text{--HgCl}_2$ is similar in nature; the liquidus curve also shows a break in the region of 50%, but the mass solidifies even more slowly; the mixtures are also hygroscopic. The system $\text{AgNO}_3\text{--CdI}_2$ was only partly studied, because mixtures containing more than 20% of the latter constituent readily underwent decomposition. The eutectic is observed in the neighbourhood of 93° and 11% CdI_2 , the liquidus curve is very steep, doubtless owing to the formation of complex compounds, but no double decomposition occurs; the crystals separating when the melt solidifies are not like the hexagonal plates of cadmium iodide. A very similar result is obtained with cadmium chloride; the liquidus curves are also very steep. Silver chloride and iodide appear to be quite insoluble in cadmium nitrate, either in the molten state or in solution.

On melting silver nitrate with thallium chloride or iodide double

decomposition is complete, the two immiscible layers obtained consisting of silver halide and thallium nitrate; thallium thus behaves in the same way as the alkali metals. The calculated thermal effect is -11.2 and -13.57 cal., respectively, and therefore favourable to the reaction.

B.—Nitrates of alkalis and alkaline earths. The nitrates of the alkalis and the alkaline-earth group are all partly miscible with mercuric halides in the molten state; here, again, the greater the miscibility the less is the negative thermal effect of the double decomposition.

C.—Chlorates. The chlorates of sodium, potassium, and silver form two layers when melted with mercuric chloride or iodide, but they were not studied in detail; the thermal effect of double decomposition is actually positive.

The various liquidus curves for systems containing silver nitrate are tabulated; the flattest curves represent systems where double decomposition takes place, whilst the steepest denote the formation of complexes; the curves of systems containing chlorides are the flattest, those with iodides the steepest. G. A. R. K.

Changes between Metals or Metallic Oxides and Carbon. KURT NISCHK (*Z. Elektrochem.*, 1923, 29, 373—390).—A graphical method of representation is described by means of which equilibria in ternary and quaternary systems may be plotted. A number of metals have been investigated with regard to their affinity for carbon in comparison with their affinity for oxygen by melting a mixture of the oxide and carbon together. It is shown that when copper is added to the mixture a definite percentage of the metal from the oxide is found alloyed with the copper; the percentage depends on the affinity of the metal for carbon. Barium and strontium on reduction of the oxide passed completely into carbide even in the presence of metallic copper. In the case of calcium and magnesium, a small amount of these metals was found in the copper. Glucinum and aluminium can exist to the extent of several per cent., alloyed with copper, in the presence of carbon. Boron, silicon, and titanium show a still greater affinity for carbon. Chromium, molybdenum, and manganese exhibit a great affinity for carbon, but they can exist alloyed with copper in the presence of carbon. The tendency to carbide formation decreases with the change in the position of the element in the periodic system, from group I to group VIII and in the case of cobalt and nickel it is a minimum. Microscopic investigation in the case of chromium and molybdenum shows that the carbides richest in metal are Cr_2C and Mo_2C , respectively. Some experiments were made with calcium carbide as reducing agent; this substance is very useful, since with a suitable addition of fluorspar a completely molten mixture is obtained. A method is described whereby glucinum, boron, silicon, and titanium can be cheaply alloyed with copper. Photomicrographs of sections of the reaction mixtures and copper alloys are included in the paper. J. F. S.

Calcium Carbonate Hexahydrate. JOHN EDWIN MACKENZIE (*T.*, 1923, 123, 2409—2417).

The Solubility and Hydrolysis of Calcium Carbonate.

H. O. ASKEW (*Trans. New Zealand Inst.*, 1923, **54**, 791—796).—The solubility of calcite in gas-free water at 25° in a closed vessel is 13.4×10^{-5} g.-mols. per litre. The presence of traces of carbon dioxide exerts a considerable influence on the solubility, the mean value found when using ordinary distilled water being 19.6×10^{-5} g.-mols. per litre. The solubility is affected, apparently in an irregular manner, by the presence of other salts. In the measurement of hydrolysis, the velocity-constant method was not successful and some unknown factor seemed to affect electromotive force measurements, so that trustworthy values were not obtained.

H. J. E.

The Dissociation of Dolomite. CECIL S. GARNETT (*Min. Mag.*, 1923, **20**, 54—59).—The statement that dolomite [$\text{CaMg}(\text{CO}_3)_2$] when heated first breaks down with magnesium oxide and calcium carbonate ($\text{MgO} + \text{CaCO}_3$) is not confirmed. White, crystalline dolomite-rock from Steetley near Worksop (which gave on analysis CaO 30.4, MgO 21.4, CO_2 47.6, SiO_2 0.16, Al_2O_3 0.09, FeO 0.41%) was heated in a flask through which passed a current of air, and the carbon dioxide evolved was absorbed in potassium hydroxide solution. A selection of the observed values is:

Temp.	350°	550°	650°	760°	805°	830°	898°
$\text{CO}_2\%$	0.01	0.42	2.21	19.6	33.1	44.8	47.6

The presence of free calcium oxide was established after dissociation had only commenced. The rock fragments suffered no contraction in volume by the heating. Grecian magnesite (MgCO_3) heated under the same conditions lost 0.84% CO_2 at 500°; dissociation was vigorous from 540° and complete below 650°. Artificially prepared magnesium carbonate ("magnesia alba") lost 0.72% CO_2 at 250°; dissociation was appreciable at 300° and complete at about 430°.

L. J. S.

The Conversion of Calcium Phosphates into Chloro-derivatives of Phosphorus by Means of Sulphur Chloride.

P. P. BUDNIKOV and E. A. SHILOV (*J. Soc. Chem. Ind.*, 1923, **42**, 378r).—Calcium phosphates may be converted almost quantitatively into phosphorus trichloride by heating them at 1,000° with sulphur chloride and a catalyst. Suitable catalysts are silica or coal, separately or together. It is advisable to convert calcium orthophosphate into the metaphosphate before heating with sulphur chloride.

H. H.

Allotropy of Zinc. L. LOSANA (*Gazzetta*, 1923, **53**, 539—

545).—Measurements of the variation with temperature of the cubical expansion of zinc indicate the existence at 176° and 320° of singular points which indicate with certainty the occurrence of allotropic transformations. When the temperature variations are measured, in comparison with those of a substance exhibiting no allotropic changes, by means of highly sensitive thermo-electric couples, small but distinct divergences are observed at 173° and 323°. The mean values found for these transformation points are 174° and

322° for the α - to β - and β - to γ -changes, respectively. If the zinc contains traces of iron or tin, the former of these points is not observed, whereas when cadmium is present the distance between the two points is considerably diminished. Between -150° and the ordinary temperature, no anomaly occurs except a change in the direction of the thermal curve at about -80° which is too slight to justify the assumption of an allotropic transformation. T. H. P.

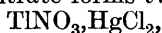
Use of Mercury in the Purification of Zinc Sulphate Solutions. SAMUEL FIELD and WILLIAM E. HARRIS (*Trans. Amer. Electrochem. Soc.* [advance copy], 1923, 269—293).—The need for zinc sulphate solutions of a high degree of purity in the electrolytic zinc industry is explained and the advantages of a pure salt are pointed out. The use of mercury as a purification agent is based on the overvoltage of mercury against hydrogen; this is discussed in detail. By amalgamating finely divided negative metals, such as zinc and aluminium, complete purification can be readily and economically effected even in strongly acid solutions. The mercury is added to the zinc liquors as mercuric sulphate, followed by zinc powder or zinc blue. The impurities are eliminated in preference to the hydrogen of the acid added. Economy of zinc is thus effected, and the method becomes applicable also for cases in which high acid content would prohibit purification owing to high consumption of zinc. J. F. S.

Attempted Separation of the Isotopes of Lead. The Atomic Weight of Lead. O. HÖNIGSCHMID and M. STEINHEIL (*Ber.*, 1923, 56, [B], 1831—1837).—Lead chloride was fractionally distilled in a high vacuum by Brönstedt and von Hevesy, and the end fractions were submitted to the authors for atomic-weight determinations. The samples were fused and distilled in quartz apparatus in a current of hydrogen chloride before analysis, which was carried out nephelometrically against pure silver dissolved in nitric acid in order to determine the ratios $\text{PbCl}_2 : 2\text{Ag}$ and $\text{PbCl}_2 : 2\text{AgCl}$. The result for the more volatile fraction (mean of ten) was $\text{Pb} = 207.229 \pm 0.003$, and for the less volatile fraction (mean of ten) $\text{Pb} = 207.236 \pm 0.003$. This difference is too small, in the authors' opinion, to warrant any claim for separation, and they suggest the value $\text{Pb} = 207.23$ for ordinary lead. H. H.

Atomic Weight of Uranium-lead. O. HÖNIGSCHMID and L. BIRCKENBACH (*Ber.*, 1923, 56, [B], 1837—1839; cf. preceding abstract).—The atomic weight of lead from Upper Katanga in the Belgian Congo was determined by the method described in the preceding abstract. The mean of three determinations gave $\text{Pb} = 206.048$, whence the authors conclude this to be pure uranium-lead. H. H.

Double Decomposition in the Absence of Solvents. III. The Systems Thallium Nitrate:Mercuric Chloride and Bromide. A. G. BERGMANN, T. A. HENKE, and F. M. ISAÏKIN (*J. Russ. Phys. Chem. Soc.*, 1923, 54, 466—473; cf. this vol., ii, 568).—In continuation of previous work, the above systems have

now been examined and the results were found to confirm the theoretical conclusions already expressed; no double decomposition is observed. Thallium nitrate forms an equimolecular compound with mercuric bromide, melting at 152° ; there is, in addition, an eutectic at 146° and 30% of mercuric bromide; the cooling curves are, otherwise, of simple type. With mercuric chloride (m. p. 282° , rhombic), thallium nitrate forms two compounds,



and $2\text{TlNO}_3, \text{HgCl}_2$. The transition points observed in this system are the eutectic of the latter compound and thallium nitrate, corresponding with 12.8% of mercuric chloride and 176° ; the melting point of the compound $2\text{TlNO}_3, \text{HgCl}_2$ at 195° ; another eutectic at 192° and 37% of mercuric chloride; the melting point of the equimolecular compound at 202.5° and the eutectic formed by this compound and mercuric chloride at 197° . No solid solutions appear to be formed. The equimolecular compound crystallises not unlike thallium nitrate, but the crystals are better defined, whilst the compound $2\text{TlNO}_3, \text{HgCl}_2$ forms distinctive long needles.

G. A. R. K.

Reduction of Copper Oxide by Carbon Monoxide and the Catalytic Oxidation of Carbon Monoxide in the Presence of Copper and Copper Oxide.

HOWARD ALGERNON JONES and HUGH STOTT TAYLOR (*J. Physical Chem.*, 1923, **27**, 623—651).—The reduction of copper oxide by carbon monoxide has been investigated under varying conditions. It is shown that the process is autocatalytic, copper being the auto-catalyst, the reduction occurring at the copper-copper oxide interface. The retarding effects of carbon dioxide and oxygen on the primary reaction of the reduction process, that is, the formation of copper nuclei, are pointed out. The mechanism for the combination of carbon monoxide-oxygen mixtures over copper oxide is shown to be alternate reduction and oxidation of the copper oxide. The mechanism for the combination of carbon monoxide-oxygen mixtures over copper is shown to be the oxidation of an adsorbed layer of carbon monoxide. It is shown that oxygen is a "permanent poison" in the combination of carbon monoxide with oxygen over copper.

J. F. S.

Cupric Oxide Jellies. HARRY B. WEISER (*J. Physical Chem.*, 1923, **27**, 685—691).—Hydrated cupric oxide jellies are formed when a suitable concentration of colloidal oxide is precipitated at a suitable rate. The desired conditions may be realised by adding ammonia to cupric acetate in the presence of a small amount of sulphate and allowing the colloidal solution to precipitate spontaneously. Jellies are not formed by adding ammonia to cupric acetate alone, since a colloid of suitable concentration cannot be prepared in this way.

J. F. S.

Baskerville and Catlett's Lanthanates. FERRUCCIO ZAMBONINI and GUIDO CAROBBI (*Atti R. Accad. Lincei*, 1923, [v], **32**, ii, 53—59).—In criticising the work of Baskerville and Catlett

(A., 1904, ii, 260), the authors point out that the resemblance between lanthanum and aluminium is slight and quite insufficient to suggest the existence of lanthanum compounds corresponding with the aluminates; unlike aluminium, which is markedly amphoteric, lanthanum shows very distinct basic properties. The supposed compound, $\text{Na}_2\text{La}_4\text{O}_7$, is shown to be a mixture of lanthanum oxide, various indefinite substances, and the double carbonate, $\text{La}_2(\text{CO}_3)_3 \cdot \text{Na}_2\text{CO}_3 \cdot 12\text{H}_2\text{O}$, the last being formed by the action of water on the product obtained when lanthanum oxide is fused with sodium carbonate. The other compounds obtained by Baskerville and Catlett by heating lanthanum oxide with metallic hydroxides on a water-bath, namely, $\text{NaH}_9\text{La}_5\text{O}_{15} \cdot 4\text{H}_2\text{O}$, $\text{LiH}_9\text{La}_5\text{O}_{15} \cdot 2\text{H}_2\text{O}$, $\text{KH}_9\text{La}_{10}\text{O}_{15} \cdot 15\text{H}_2\text{O}$, and $\text{Ba}(\text{H}_9\text{La}_5\text{O}_{15})_2$, are composed of lanthanum oxide and hydroxide, together with the hydroxide and carbonate of the alkali or alkaline-earth metal; the first two of these compounds may contain also lanthanum carbonate, and double carbonates likewise may be present, although the protracted digestion on the water-bath would probably completely destroy them.

T. H. P.

Ternary Alloys of Aluminium, Zinc, and Tin. L. LOSANA and E. CAROZZI (*Gazzetta*, 1923, 53, 546—554).—This work was completed before the publication of that of Crepaz (this vol., ii, 641).

The metals employed contained, respectively, 99.83% of aluminium, 99.92% of zinc, and 99.92% of tin. For the system aluminium-tin, a few melting-point estimations were made in the region between 0 and 10% of aluminium, the results obtained differing only slightly from those of Heycock and Neville (T., 1890, 57, 376) and of Gwyer (A., 1906, ii, 544). Similarly for the system aluminium-zinc, the few values found agree well with Rosenhain and Archbutt's complete investigation (A., 1911, ii, 895).

In the ternary system, the eutectic contains 1.46% of aluminium, 10.37% of zinc, and 88.17% of tin, melts at 194° , and is characterised clearly by the maximum time of crystallisation with respect to the other alloys. Aluminium and zinc form solid solutions over a moderately wide region of the diagram, the mixed crystals exhibiting distinct transformations at temperatures varying with the proportion of aluminium present; the same happens when a little tin is present. Alloys containing high percentages of zinc show a transformation point corresponding with the passage from the third to the second form of this metal, but the thermal change is very slight and difficult to detect. Of greater magnitude, although not very distinct, is the variation due to the change from the third to the second modification of the tin. In no case is the point of transformation of β - to α -zinc detectable.

T. H. P.

An Example of Polymorphism in an Intermetallic Compound. DAVID STOCKDALE (*Trans. Faraday Soc.*, 1923, 19, 135—139).—Evidence is given, from an examination of the equilibrium curves and of the microstructure of aluminium-copper alloys, for the existence of the compound Cu_2Al containing 17.5% Al and melting at 1016° , but unstable above 1015° . On cooling

alloys containing 14 to 21% of aluminium an arrest point occurs between 875° and 770° and is at the maximum in the alloy containing 17.8% of aluminium, corresponding with Cu_2Al . Addition of copper lowers this point considerably, and addition of aluminium slightly. No micrographical change takes place on cooling through the arrest point; it is therefore probable that the heat evolution or absorption is due to a change in the arrangement of the atoms or molecules in the compound Cu_2Al itself, i.e., to a polymorphic transformation [cf. *J.S.C.I.*, 1923, 556A]. A. R. P.

Iron Carbide. FRANZ WEVER (*Mitt. Kaiser Wilh.-Inst. Eisenforsch.*, 1922, 4, 67—80; from *Chem. Zentr.*, 1923, iii, 187).—By X-ray analysis it is shown that the forms of cementite shown in the iron-carbon thermal diagram are not distinguishable by their lattice structure. Iron carbide, Fe_3C , crystallises in a rhombic lattice denoted by the quadratic form $\sin^2\theta/2 = 0.0464x^2 + 0.0367y^2 + 0.0208z^2$. The edge lengths are $a = 4.481 \text{ \AA.}$, $b = 5.034 \text{ \AA.}$; $c = 6.708 \text{ \AA.}$ The density is calculated therefrom as 7.82. Data by the Debye-Scherrer method above 210° show that the magnetic transformation is not associated with a change in the type of lattice. The quadratic form is expressed by $\sin^2\theta/2 = 0.0456x^2 + 0.0362y^2 + 0.0203z^2$. The edge lengths are $a = 4.52 \text{ \AA.}$; $b = 5.08 \text{ \AA.}$; $c = 6.77 \text{ \AA.}$ G. W. R.

The Acid Decomposition of Metallographically Defined Iron and Manganese Carbide Alloys. R. SCHENCK, J. GIESEN, and FR. WALTER (*Z. anorg. Chem.*, 1923, 127, 101—122).—The alloys (iron-carbon and iron-manganese-carbon) were dissolved in hydrochloric acid, and the hydrocarbons evolved identified by (1) bromination, (2) condensation by liquid air, and (3) absorption by charcoal. In the case of the iron-carbon alloys and those of low manganese content, the chief gaseous products are propylene, Δ^3 -butylene, ethylene, the higher olefines, methane, and ethane. In the case of the iron-manganese carbon alloys rich in manganese, the chief product is octene; some still higher olefines were also found, but ethane and ethylene could not be detected. Quantitative results are given. W. T.

Chlorites of certain Cobaltamines. G. R. LEVI (*Atti R. Accad. Lincei*, 1923, [v], 32, i, 623—626).—*Hexamminecobalt chlorite*, $[\text{Co}(\text{NH}_3)_6](\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$, prepared from the luteo-chlorite and silver chlorite, forms slender, orange-yellow needles, explodes on percussion and, when treated in solution with cupric chloride, yields the double salt, $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3 \cdot \text{CuCl}_2$.

Chloropentamminecobalt chlorite, $[\text{Co}(\text{NH}_3)_5\text{Cl}](\text{ClO}_2)_2$, obtained similarly, gradually emits chlorous vapours, and is exploded when struck, but gives no double compound with cupric chloride. Aquo-pentamminecobalt chlorite, obtainable in solution, cannot be isolated in the solid form.

A table is given showing all the chlorites, numbering 34, now known. According to the results as yet obtained, there exists but little analogy between chlorites and nitrites.

The solubilities of barium, lead, and silver chlorites have been measured. At 0°, 100 g. of solution contain 30.5, 0.035, and 0.17 g. respectively, and at 100°, 44.7, 0.41, and 2.11 g., respectively, of these salts.

T. H. P.

Nickel Sulphide. FRITZ EPHRAIM (*Ber.*, 1923, 56, [B], 1885—1886; cf. this vol., ii, 423).—Nickel sulphide is readily soluble in yellow ammonium polysulphide solution, but much less soluble in colourless ammonium sulphide. By analogy with copper sulphide, of which the same is true, which forms the red ammonium copper tetrasulphide, it was thought that a similar compound might exist in the case of nickel. Nickel sulphate was added to a solution of ammonium polysulphides in an air-tight flask, and after some days a considerable quantity of a black, crystalline substance of composition intermediate between $(\text{NH}_4)_2\text{NiS}_4$ and $(\text{NH}_4)_3\text{NiS}_5$ was deposited. Salts of cobalt, iron, zinc, manganese, and cadmium did not give similar compounds.

H. H.

Density Measurements of some Simple and Complex Salts of Nickel and Cobalt. WILHELM BILTZ and ERWIN BIRK (*Z. anorg. Chem.*, 1923, 127, 34—42).—The lattice structure of hexamminenickelous chloride has been measured by Scherrer (*A.*, 1922, ii, 514); the lattice constants of the hexammines of the nickel group can be calculated from their densities, assuming that their structures are the same. The following values for the densities were obtained, high boiling fractions of petroleum ($d=0.7975$ — 0.7998) being used as the pycnometer liquid. NiCl_2 sublimed 3.521, NiCl_2 (prepared from the hexammine) 3.508. NiBr_2 sublimed 5.098, BiBr_2 (prepared from the hexammine) 5.042. NiI_2 (prepared from the hexammine) 5.834. CoCl_2 3.367. CoBr_2 4.849. CoI_2 5.584. $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$ 1.468. $[\text{Ni}(\text{NH}_3)_6]\text{Br}_2$ 1.889. $[\text{Ni}(\text{NH}_3)_6]\text{I}_2$ 2.113. $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2$ 1.479. $[\text{Co}(\text{NH}_3)_6]\text{Br}_2$ (prepared by the wet method) 1.871, (prepared by the dry method) 1.879. $[\text{Co}(\text{NH}_3)_6]\text{I}_2$ 2.096. $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ 1.710. $[\text{Co}(\text{NH}_3)_6]\text{Br}_3$ 2.340. $[\text{Co}(\text{NH}_3)_6]\text{I}_3$ 2.746. Agreements with previous determinations are not good. The method of preparation of the salts is given in detail. W. T.

The Lattice Structure, Directions of Slip, and Slip Planes of White Tin. H. MARK and M. POLANYI (*Z. Physik*, 1923, 18, 75—96).—The authors find that the phenomena associated with the extension of a single crystal of tin are analogous to those exhibited under similar conditions, by a single crystal of zinc (*ibid.*, 1922, 12, 58). White tin crystallises in the ditetragonal-bipyramidal system, space group D_{4h}^{19} . The lengths of the axes of the crystal structure are respectively a 5.84 Å., c 3.15 Å., and the elementary cell contains four atoms. Slipping occurred in the directions [100], [101], and [111]. Of these directions, [100] occurred most frequently, and [111] only at a high temperature. The slip planes were represented by (110) and (100), the former occurring more frequently (8:3) than the latter.

J. S. G. T.

Preparation of Coarsely Crystalline, Anhydrous Titanium Trichloride, and the Mechanism of the Reduction of Titanium Tetrachloride by Means of Hydrogen. FRIEDRICH MEYER, ALFRED BAUER, and RICHARD SCHMIDT (*Ber.*, 1923, **56**, [B], 1908—1914; cf. A., 1912, ii, 1051).—The two requirements for the successful preparation of coarsely crystalline titanium trichloride by reduction of the tetrachloride are, first, a steep temperature gradient to ensure rapid cooling, and secondly, the depression of the hydrogen chloride concentration. The first condition is best secured by using a non-conducting (quartz) tube of narrow bore, with air cooling at the receiver end. The second is attained most easily by the addition of metallic titanium to the reaction mixture. It is shown that the reduction is not direct, but that three reactions, $\text{TiCl}_4 + \text{H}_2 = \text{TiCl}_2 + 2\text{HCl}$; $\text{TiCl}_2 + \text{TiCl}_4 = 2\text{TiCl}_3$; $2\text{TiCl}_3 + 2\text{HCl} = 2\text{TiCl}_4 + \text{H}_2$, may proceed simultaneously. H. H.

The Chemistry of Hafnium. G. VON HEVESY (*Chemistry and Industry*, 1923, **42**, 929—930).—The natural oxides of zirconium, such as baddeleyite, contain only 1% or 2% of the new element No. 72, hafnium, whilst the common zirconium minerals, such as zircon, contain up to 7%. The minerals richest in hafnium are the secondary zirconium minerals alvite, cyrtolith, naegeite, and malakon, which may yield zirconium containing up to 30% of hafnium. The hafnium content of a specimen or preparation is determined by comparing the intensity of X-ray lines due to hafnium with the intensity of the line due to a known quantity of the neighbouring element No. 73 (tantalum) added to the specimen. Separation of hafnium from zirconium is accomplished through the different solubilities of their corresponding salts and the different basicity of their oxides. Zirconium potassium fluoride has a solubility of 2.6% at 20°, hafnium potassium fluoride nearly 3.0%. Hafnium ammonium fluoride forms prismatic, pseudo-hexagonal crystals. Hafnium ammonium oxalate and hafnium ammonium sulphate are more soluble than the corresponding zirconium salts, whilst, of the oxychlorides, that of hafnium is the less soluble. Hafnium is more basic than zirconium, and consequently when the latter is precipitated as a basic salt hafnium accumulates in solution. Concentrated preparations of hafnium are purified from zirconium by dissolving the oxychloride in alcohol and adding ether, when the basic salt, $\text{Zr}_2\text{O}_3\text{Cl}_2 \cdot 5\text{H}_2\text{O}$, is precipitated; this is less soluble than the corresponding hafnium compound. The properties of hafnium are in every way much closer to those of zirconium than to those of thorium. In several cases, the solubility of a hafnium compound is greater than that of the corresponding zirconium or thorium compound. E. H. R.

Germanium. VI. Metallic Germanium. Reduction of Germanium Oxide. Preparation of Fused Germanium. Physical and Chemical Properties. P. M. DENNIS, KATHARINA M. TRESSLER, and F. E. HANCE (*J. Amer. Chem. Soc.*, 1923, **45**, 2033—2047; cf. this vol., ii, 570).—Germanium dioxide may be dehydrated by heating at 950° for three hours; the product is not volatile at 1,250° and is not hygroscopic. Germanium dioxide may

be reduced to the metal by the alumino-thermic method, but the metal obtained constitutes a yield of only 61%, and there is a big loss of germanium dioxide by volatilisation. Small quantities of germanium dioxide (2 g.) may be reduced completely to the metal, in the form of a grey powder, by heating for two hours at 540° in a current of hydrogen, and there is no loss of material as hydride. But if larger quantities (10—14 g.) are employed, the yield is always below the theoretical quantity, and a black deposit shading off to brown and yellow appears in the colder parts of the tube. Coherent germanium is best prepared from the powder by fusion with sodium chloride at 980—1,000° for thirty minutes. In this way, about 96% of the powder is recovered as a single, lustrous button; the residue remains with the flux as sodium germanate. Fusion with sodium sulphate gave only a 73·8% yield, the residue of the germanium being present as sulphide, due to reduction of the sodium sulphate. Borax also proved to be an unsuitable flux. Metallic germanium which is quite free from oxide does not lose weight when heated in highly purified hydrogen to temperatures not exceeding 800°, but volatilisation of germanium does take place when hydrogen is passed over the molten metal. Pure germanium melts at 958·5°. Germanium expands on solidification and gives rise to protuberances on the buttons as it cools. It has d_{20}^{20} 5·35, which compares favourably with the value 5·36 calculated from X-ray analysis. Germanium is extremely brittle, and has a hardness between that of adularia and that of epidote, about 6·25. Germanium crystallises in elongated crystals bounded in some cases by octahedral faces and often covered with dendritic branches. Some of the crystals obtained were 3 cm. long. The thermo-electric power of germanium is a linear function of the temperature, and the electrical resistance is an exponential function of the form $\log R = \log A + \alpha T + Q/kT$, except over the range 100° to 600°, where an inversion takes place. More exact examination shows that germanium passes through a gradual molecular inversion with two or more modifications between 117° and 560°. When heated at 730° in oxygen, germanium is incompletely oxidised to a mixture of germanous oxide and germanium dioxide; at higher temperatures the lower oxide volatilises, so that it is impossible to oxidise germanium completely in oxygen. Germanium is not attacked by hydrogen sulphide at temperatures below 200°, and the action of the gas is comparatively slight until the hydrogen sulphide commences to dissociate. The reaction then becomes one between germanium and sulphur, with the formation of germanous sulphide. Sulphur dioxide acts on crystallised germanium at temperatures a little below 500°; the reaction becomes rapid between 510° and 530°, with the formation of the dioxide and disulphide of germanium. At the ordinary temperature and at 90°, germanium is not attacked by water, 50% sodium hydroxide solution, 1:1-hydrochloric acid, concentrated hydrochloric acid, or 1:1-sulphuric acid. It is slightly tarnished by 10% sodium hydroxide, both cold and warm. Dilute nitric acid oxidises it superficially to the dioxide, but the concentrated acid, beyond darkening the surface slightly, had no other action. Concentrated

sulphuric acid has no action at the ordinary temperature, and only a very slight action at 90°. Hydrofluoric acid, 19*N*, has only slight action, but 3% hydrogen peroxide slowly converts the metal into the dioxide and dissolves it. Metallic germanium dissolves rapidly in molten potassium hydroxide, sodium hydroxide, sodium carbonate, potassium nitrate, and sodium peroxide; it dissolves slowly in molten potassium hydrogen sulphate and potassium chlorate, and is not attacked by molten potassium cyanide. Attempts to prepare germanium carbide were without success.

J. F. S.

Hydrosol of Vanadium Pentoxide. A. DUMANSKI (*Kolloid Z.*, 1923, 23, 147—159).—The methods of preparation and the properties of vanadium pentoxide hydrosol have been investigated. It is shown that the hydrosol as well as solutions of vanadium pentoxide yield the ions of hexavanadic acid. Electrical conductivity measurements indicate a gradual hydrolysis of the pentoxide hydrosols on dilution with water. This hydrolysis is confirmed by measurements on the absorption of light. The colloidal particles of vanadium pentoxide are negatively charged and are very small, so small as to be indistinguishable in the ultramicroscope. The sol is coagulated by electrolytes and the positive ion of the electrolyte is adsorbed. The adsorption compounds thus obtained pass, on keeping, into ordinary chemical compounds. Determinations of the depression of the freezing point indicate that the colloidal particles are not very large, and from these measurements the equivalent of the colloidal particle is deduced as approximately 1,000. The colloidal particles are given a formula of the type $[H_3V_6O_{17}(V_2O_5)_n]'$ or $[H_2V_6O_{17}(V_2O_5)_n]''$. Starting from the value of the equivalent as 1,000, the second of these formulæ in which $n=5$ is obtained, namely, $[H_2V_6O_{17}(V_2O_5)_5]''$. The double refraction of the sol increases with its age and with the formation of a turbidity in the sol. The gels of this colloid consist of orientated particles, which exhibit double refraction when they are still. Vanadium pentoxide sol on reduction furnishes the sols of lower oxides of vanadium. These sols are all charged negatively. J. F. S.

Atomic Weight of Antimony from Different Sources. I. SHEIKH D. MUZAFFAR (*J. Amer. Chem. Soc.*, 1923, 45, 2009—2013).—An account of preliminary determinations of the atomic weight of antimony obtained from stibnite from various sources. The experiments cover material obtained from Peru, Bolivia, Borneo, and Hungary. The antimony from all samples was purified by the same method and converted into the trichloride and the ratio between antimony trichloride and potassium bromate determined by titration. The reaction between the two substances is given by the equation $3SbCl_3 + KBrO_3 + 6HCl = 3SbCl_5 + KBr + 3H_2O$. The following results were obtained: Hungarian material, $Sb=121.144$ (7 expts.), Borneo material $Sb=121.563$ (7 expts.), Peruvian material, $Sb=121.720$ (7 expts.), and Bolivian material, $Sb=122.374$ (11 expts.). Each set of results is remarkably concordant. The author is of the opinion that the present results point

to the occurrence of a different distribution of the isotopes of antimony in the different stibnites. J. F. S.

The Hydrates of Antimony Pentoxide. GERHARDT JANDER and ARTHUR SIMON (*Z. anorg. Chem.*, 1923, **127**, 68—82).—Hydrates of antimony pentoxide were prepared by three methods, (1) the hydrolysis of the pentachloride at 0—1°, (2) hydrolysis at 100°, (3) oxidation of the trichloride by concentrated nitric acid and hydrolysis of the product at 60°. The products were dried on porous plates in the air, and were found to contain (1) 30.57, (2) 9.97, (3) 7.91 mols. of water to 1 mol. of the pentoxide. After drying over sulphuric acid, the water contents were (1) 3.68, (2) 2.17, (3) 0.60 mols. per mol. Sb_2O_5 . Drying at 105° reduced the molecules of water per mol. of the pentoxide to (1) 2.43, (2) 1.02, (3) 0.45. The behaviour of the three hydrates towards alkali and phosphoric acid was investigated, and their vapour tension isotherms were measured. Results indicate that no definite hydrates were formed, but that gels were present, the behaviour of which depend on grain size, which varies with the method of preparation (cf. stannic acid, Mecklenburgh, A., 1914, ii, 529). Alkogels of the pentoxide were also prepared, and these were de-alcoholated by placing them over glycerol; the curves of de-alcoholation were similar to those of dehydration. The pentoxide was also able to take up benzene when kept in an atmosphere of the latter. W. T.

Bismuth Reduced by Dextrose. H. COUSIN (*J. Pharm. Chim.*, 1923, [vii], **28**, 179—181).—The black precipitate produced by the action of dextrose on a bismuth salt in presence of alkali was found on analysis to contain different amounts of bismuth, the percentage of the metal present increasing with the proportion of dextrose and sodium hydroxide used in the reaction. By adding a large excess of dextrose, the reaction may be utilised as a means of estimating bismuth, but the author does not recommend the method. H. J. E.

Electrical Conductivity and the Chemical Constitution of Alloys. II. The System Bismuth-Thallium. W. GUERTLER and A. SCHULZE (*Z. physikal. Chem.*, 1923, **106**, 1—17; cf. this vol., ii, 418).—The electrical conductivity of alloys of thallium and bismuth has been determined at 80° and 180°. The results confirm the condition diagram of this system obtained by other methods and make additions to the diagram. J. F. S.

Heterogeneous Equilibrium Produced by the Hydrolysis of Bismuth Chloride. KARL JELLINEK and WALTHER KÜHN (*Z. physikal. Chem.*, 1923, **105**, 337—355).—The equilibrium set up when various quantities of water are added to solutions of bismuth sesquioxide in hydrochloric acid has been examined by estimating the quantity of bismuth and hydrochloric acid left in solution after the addition of definite amounts of water. The solubility curve of the ternary system bismuth sesquioxide—hydrochloric acid—water has been determined, and it is shown that in certain concentrations the oxychloride, BiOCl , constitutes the solid phase, whilst in others

the hydroxide, $\text{Bi}(\text{OH})_3$, is the solid phase. In alkaline solution, the oxychloride passes quantitatively into the hydroxide. The bismuth normal potential has been measured and the value $+0.266$ volt found in terms of the normal hydrogen electrode. The hydrogen-, chlorine-, and bismuth-ion concentrations have been determined for solutions of hydrochloric acid saturated with the oxychloride and by means of these results the law of mass action has been shown to be true for the reaction $\text{Bi}^{+++} + \text{H}_2\text{O} + \text{Cl}' \rightleftharpoons \text{BiOCl} + 2\text{H}'$. The results make it probable that complex chloro-bismuthic acids exist. Modified analytical methods have been deduced for the estimation of bismuth and chlorine in solutions of bismuth chloride. In the case of the estimation of bismuth the modification consists in precipitating as sulphide, filtering on a Gooch crucible, washing with acidified water, and drying at 110° . The free sulphur is then removed by placing the crucible in a furnace at 260 – 300° and heating for thirty minutes in a current of carbon dioxide. The results are accurate to 0.2% . J. F. S.

The Supposed Volatility of Tantalalic Acid with Hydrofluoric Acid. Some Tantalum Compounds. OTTO HAHN and KARL F. PUETTER (*Z. anorg. Chem.*, 1923, **127**, 153–168).—Pure tantalalic acid was prepared by the oxidation of the element in a stream of oxygen, and it was found to be non-volatile. Hydrofluoric acid solutions of pure tantalalic acid on evaporation undergo hydrolysis; the residue shows no volatility on heating. Commercial tantalalic acid loses weight on heating; this is due to the alkali which it contains. The higher the alkali content the greater is the volatility. The following new crystalline compounds were prepared: *tantalum hydrogen fluoride*, $\text{HF} \cdot \text{TaF}_5 \cdot 6\text{H}_2\text{O}$; *barium tantalum fluoride*, $3\text{BaF}_2 \cdot 2\text{TaF}_5$; *monammonium tantalum fluoride*, $\text{NH}_4\text{F}_2 \cdot \text{TaF}_5$. Heating barium tantalum fluoride is a convenient method for the preparation of pure tantalum pentafluoride. W. T.

Platinum Oxide as a Catalyst in the Reduction of Organic Compounds. III. Preparation and Properties of the Oxide of Platinum obtained by the Fusion of Chloroplatinic Acid with Sodium Nitrate. ROGER ADAMS and R. L. SHRINER (*J. Amer. Chem. Soc.*, 1923, **45**, 2171–2179; cf. Voorhees and Adams, A., 1922, ii, 558; Carothers and Adams, this vol., ii, 310).—The fusion of sodium nitrate and chloroplatinic acid has been carried out at temperatures between 310° and 700° . The various samples of platinum oxide are tested as catalysts as follows. Maleic acid (20 g.) or benzaldehyde (20 g.) is dissolved in 150 c.c. of 95% alcohol. To the benzaldehyde solution, 1 c.c. of $0.0001M$ -ferrous chloride solution is added (Carothers and Adams, *loc. cit.*). The solutions are then reduced as previously described, using 0.25 g. of catalyst, and the time elapsing before reduction commences and the time taken for complete reduction are noted. The period of reduction is least when the catalyst has been prepared at about 500° , according to the benzaldehyde test, 400 – 500° , as shown by the reduction of maleic acid. The best temperature is certainly about 500° .

Analyses of the oxide agree with the formula $\text{PtO}_2 \cdot \text{H}_2\text{O}$. The

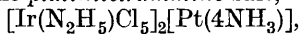
compound is amorphous; if produced at comparatively low temperatures, it is a very light brown, but this colour deepens as the fusion temperature is increased. The oxide dissolves only slightly in hot aqua regia, or in boiling, concentrated hydrochloric acid. It is insoluble in boiling, concentrated nitric acid. Nevertheless, boiling hydrobromic acid (10%), or cold hydrobromic acid of constant b. p., readily dissolves the oxide, with evolution of bromine, and formation of bromoplatinic acid. The oxide is rapidly dissolved when warmed with a mixture of hydrochloric and sulphurous acids. It causes the immediate decomposition of hydrogen peroxide, being itself apparently unchanged. It is gradually reduced when boiled with ethyl alcohol in the absence of air, acetaldehyde being produced.

It is shown that, for the production of the catalyst, the nitrates of lithium, potassium, calcium, barium, and strontium, are much less efficient than sodium nitrate. The oxide produced by this method is far more active as a catalyst than the other oxides of platinum described in the literature. Moreover, it is much more readily prepared.

W. S. N.

A New Series of Complex Iridium Salts containing Hydrazine. L. TSCHUGAEV (*Ber.*, 1923, 56, [B], 2067—2068).

—If potassium chloroiridiate be warmed in solution on the water-bath with excess of hydrazine hydrochloride, the solution assumes a reddish-brown colour and then contains the *complex acid*, $[\text{Ir}(\text{N}_2\text{H}_5)\text{Cl}_5]\text{H}$. The *platinitetrammine* salt,



forms flesh-coloured platelets, and the *cæsium* salt, $[\text{Ir}(\text{N}_2\text{H}_5)\text{Cl}_5]\text{Cs}$, is also crystalline, and slightly more soluble in water than the former. The platinitetrammine salt is quantitatively converted into green Magnus's salt by treatment with excess of potassium chloroplatinite.

H. H.

Mineralogical Chemistry.

New Lead-Copper Minerals from the Mendip Hills (Somerset). L. J. SPENCER, with Analyses by E. D. MOUNTAIN (*Min. Mag.*, 1923, **20**, 67—92).—The only published analysis of Mendip minerals is that of mendipite by Berzelius (1823). A new analysis of this gave I, confirming the accepted formula $2\text{PbO}, \text{PbCl}_2$. Embedded in the mendipite from Higher Pitts, but in sparing amounts, are the two new minerals *chloroxiphite* (anal. II and III; $2\text{PbO}, \text{PbCl}_2, \text{Cu}[\text{OH}]_2$) and *diaboleite* (anal. IV; $\text{Pb}[\text{OH}]_2, \text{PbCl}_2, \text{Cu}[\text{OH}]_2$).

Chloroxiphite, named from $\chi\lambda\omega\rho\acute{o}s$, green, and $\xi\acute{\iota}\phi\omicron s$, a sword, is monoclinic ($ac=62.75^\circ$) with a bladed habit and dull olive-green colour; the streak is a characteristic pale greenish-yellow; $H. 2\frac{1}{2}$. Parallel to c is a perfect cleavage and parallel to a a poorer cleavage. The pleochroism is strong (emerald-green and yellowish-brown); optically negative with axial plane perpendicular to the plane of

symmetry. The mineral is readily soluble in nitric acid. When heated it decrepitates, giving off water and lead chloride, and it melts to a brown liquid, which solidifies to a bright-green glass. All the water is lost below 250° . Diaboleite, named from $\delta\acute{\alpha}$, apart or distinct from boleite, is tetragonal ($a:c=1:0.95$), with bright sky-blue colour and pearly lustre on the basal cleavage. It is optically uniaxial and negative with marked pleochroism (dark-blue to almost colourless); $n_{1.98}$, $H. 2\frac{1}{2}$. The mineral is soluble in nitric acid and behaves like chloroxiphite when heated.

By alteration, mendipite passes into hydrocerussite. This has hitherto been regarded as a rare mineral found only as films of minute pearly scales. The text-book formula is based on an analysis of the artificial crystalline material, which is identical with "white-lead" (*cerussa*). Large (5 cm.) rhombohedral crystals ($a:c=1:0.61$) from the Mendips have, however, been found in some old collections (*e.g.*, the Woodwardian collection, 1728, at Cambridge). There is a good cleavage with pearly lustre and snow-white colour parallel to the base, and the crystals are optically uniaxial and negative. When heated, the material decrepitates violently, breaking up into pearly scales and changing to orange yellow in colour. All the water is lost at 250° , and all the carbon dioxide on ignition (at 200° loss 0.87%, at 250° 2.76%). Analyses V and VI give the formula $2\text{PbCO}_3, \text{Pb}(\text{OH})_2$. The presence of a little chlorine suggests an end-member $2\text{PbCO}_3, \text{PbCl}_2$ (distinct from phosgenite). By further alteration, hydrocerussite changes to cerussite (PbCO_3), and good pseudomorphs of cerussite after hydrocerussite have been found. Chloroxiphite alters to a mixture of hydrocerussite and malachite ($\text{CuCO}_3, \text{Cu}(\text{OH})_2$), and in contact with the surrounding manganese-ore in which the nodules of lead-ore are embedded, has by further alteration given rise to crednerite (CuMn_2O_4 or $\text{CuO}, \text{Mn}_2\text{O}_3$).

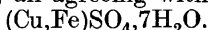
Crednerite, hitherto regarded as a rare or doubtful mineral, has been found at Higher Pitts as radiating fan-like groups or hemispherical masses of thin plates with an iron-black colour and bright metallic lustre. It is perhaps monoclinic, but pseudo-hexagonal by twinning, and with perfect cleavages; opaque; streak, sooty black; $H. 4$. It is not attacked by nitric acid, but dissolves in strong hydrochloric acid with evolution of chlorine (oxygen equivalent in anal. VII 6.22%). Deducting from anal. VII 6.10% of malachite and 1.05% of cerussite, seen in micro-sections to be intimately intermixed with the crednerite, the figures under VIII give the above formula.

	PbO.	CuO.	Mn ₂ O ₃ .	Cl.	CO ₂ .	H ₂ O. less	Total O for Cl.	Sp. gr.
I.	92.51	—	—	9.35	—	—	99.75	7.240
II.	81.15	10.90	—	7.19	—	2.56	100.18	6.763
III.	79.82	10.47	—	8.97	—	2.52	99.75	—
IV.	72.09	12.90	—	10.89	—	6.14	99.56	6.412
V.	86.52	—	—	0.27	11.21	2.23	100.17	6.80
VI.	86.43	—	—	0.32	11.32	2.00	100.00	6.786
VII.	0.88	36.57	60.62	—	1.88	—	99.95	4.972
VIII.	—	34.68	65.32	—	—	—	100.00	5.03

Other minerals described from Higher Pitts are wulfenite (PbMoO_4) and mimetite ($3\text{Pb}_3\text{As}_2\text{O}_8, \text{PbCl}_2$). The "green ore" mined in the Mendips centuries ago, apparently in some quantity, is shown from specimens preserved in the Woodwardian collection (1728) to be pyromorphite.

L. J. S.

Crystallised Sulphates from Huelva, Spain. HENRY F. COLLINS (*Min. Mag.*, 1923, 20, 32—38).—Pisanite resulting from the oxidation of cupriferous pyrites in the Rio Tinto mines gave analyses I—V, I—IV of well-developed monoclinic crystals and V of a stalagmitic mass, all agreeing with the formula



Crystals with less than 7 or 9% CuO are light green, whilst those with more copper are blue in colour. Solutions containing more copper than the proportion 14% Cu to 8% Fe deposit chalcantite together with the highly cupriferous pisanite. Chalcantite is, however, less common than pisanite, owing to the usual excess of iron in the mine waters. Chalcantite from the La Mimbrera mine near Zalamea gave VI.

In ancient (? Roman) workings in the Concepcion mine near Zalamea was found a cavity filled with mixed sulphates and fragments of partly sulphatised pyrites. Coquimbite as pinkish-violet crystalline masses, rarely as large, hexagonal prisms; anal. VII on material that had been dried over sulphuric acid, and the water consequently low for the formula $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$. Copiapite (VIII) as a friable aggregate of bright yellow, pearly scales. Voltaite (IX) as brilliant black or greenish-black octahedra, with $\text{RO} : \text{R}_2\text{O}_3 : \text{SO}_3 : \text{H}_2\text{O} = 3.5 : 1 : 6.5 : 10$. Pink tufts of an undetermined mineral resembling halotrichite gave X, with $\text{RO} : \text{R}_2\text{O}_3 : \text{SO}_3 : \text{H}_2\text{O} = 1 : 5 : 18 : 33$.

Roemerite (?) as white or yellowish silky tufts of acicular crystals on stalactites of pisanite from the Sotiel mine near Calañas gave XI, corresponding with $3(\text{RO}, \text{SO}_3) + \text{R}_2\text{O}_3 \cdot 3\text{SO}_3 + 19\text{H}_2\text{O}$. Bloedite (?) as greenish, transparent crusts on old timbers in the abandoned Monte Romero mine gave XII. Goslarite as long, silky fibres hanging in bunches from the roof in the Almagrera mine at Tharsis gave XIII.

	Al_2O_3	Fe_2O_3	FeO	CuO	ZnO	CaO	MgO	SO_3	H_2O	Insol.	Total.
I.	—	—	19.67	4.82	1.13	—	—	28.98	44.76	—	99.77*
II.	—	—	18.10	7.70	—	—	—	28.72	44.94	—	99.46
III.	—	—	15.40	10.58	—	—	—	28.82	44.52	—	99.32
IV.	—	—	15.08	11.51	0.35	—	—	28.66	44.70	—	100.30
V.	—	—	10.28	17.54	—	—	—	—	—	—	—
VI.	—	—	0.80	30.42	0.51	0.50	0.22	35.56	31.24	—	99.25
VII.	2.25	25.84	—	—	—	0.15	0.16	44.19	27.25	—	99.84
VIII.	†	30.65	0.72	—	—	0.50	0.50	47.97	18.72	0.10	99.16
IX.	2.14	11.38	14.47	0.22	—	0.90	3.00	47.02	16.44	—	99.22‡
X.	—	27.08	0.98	—	—	0.91	0.20	48.48	20.19	0.71	98.55
XI.	—	13.10	8.60	2.12	0.65	1.30	3.80	41.49	28.80	—	99.86
XII.	—	—	2.90	1.63	—	—	14.83	44.63	25.62	1.80	98.82§
XIII.	—	2.78	trace	0.96	24.78	0.30	0.55	28.12	41.32	—	99.47¶

* I, also MnO 0.31, $\text{NiO} + \text{CoO}$ 0.10.

† VIII, a little Al_2O_3 included with Fe_2O_3 .

§ XII, also Na_2O 7.41.

‡ IX, also alkalis 3.65.

¶ XIII, also NiO 0.66.

A large number of experiments are recorded on the crystallisation of mixed solutions of copper and ferrous sulphates in various proportions. In the monoclinic series of mixed crystals,

(Fe,Cu)SO₄.7H₂O (pisanite), the maximum amount of copper that can be taken up is 14.65% Cu(=65.95% CuSO₄.7H₂O); and in the triclinic series, (Cu,Fe)SO₄.5H₂O the maximum amount of iron is 0.84% Fe(=3.65% FeSO₄.5H₂O). L. J. S.

Scheelite of Traversella. G. CAROBBI (*Atti R. Accad. Lincei*, 1923, [v], 32, ii, 79—83).—No complete analytical data for the scheelite of Traversella have yet been published. A brownish-yellow to honey-yellow crystal, carefully freed from impurities, gave on analysis:

H ₂ O.	WO ₃ .	MoO ₃ .	Nb ₂ O ₅ .	Ta ₂ O ₅ .	CaO.	BaO.	SrO.	MgO.
0.01	79.51	0.58	0.08	0.02	19.57	trace	trace	0.05
Yttria earths		Ce ₂ O ₃ .	La ₂ O ₃ ,Nd ₂ O ₃ ,Pr ₄ O ₇ .			Total.		
0.06		0.03	0.05			99.96		

T. H. P.

Oligoclase from North Carolina. SEITARÔ TSUBOI (*Min. Mag.*, 1923, 20, 93—107).—A cleavage mass of oligoclase from Hawke mine, Bakersville, gave:

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ (+FeO).	MgO.	CaO.	Na ₂ O.	K ₂ O.	Total.
61.70	23.99	0.43	0.40	5.09	8.81	0.17	100.59

This corresponds with orthoclase 0.9, albite 75.1, anorthite 24.0 mol.%. Detailed determinations are given of the optical constants of this and of some other intermediate plagioclases; and the results are applied (pp. 108—122) to a dispersion method of determining the chemical composition of small cleavage flakes of plagioclases by immersion in a mixture of cassia oil and clove oil. L. J. S.

A Peculiar Chlorite-rock from Derbyshire. CECIL S. GARNETT (*Min. Mag.*, 1923, 20, 60—64).—An intrusive sill of olivine-dolerite ("toadstone") at Ible shows along one stratum an alteration into a chlorite-rock. This is soft and friable with a dark olive-green colour, and consists of a confused mass of lamellar and foliated aggregates. The foliated mineral has *d* 2.52, and gave analysis I. The surrounding dolerite is penetrated by numerous small veins filled with a fibrous mineral resembling chrysotile in appearance. This is dark olive-green with *d* 2.37 and gave anal. II. These minerals are compared with epichlorite, and they evidently owe their origin to hydrothermal action following the solidification of the dolerite.

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MgO.	CaO.	H ₂ O.	Total.
I.	37.5	10.4	8.8	10.8	20.8	nil	12.0	100.3
II.	42.7	8.2	13.6	2.8	20.7	nil	11.7	99.7

L. J. S.

The Dartmoor Granite. ALFRED BRAMMALL and H. F. HARWOOD (*Min. Mag.*, 1923, 20, 20—26, 39—53).—Minute crystals

of brookite and anatase, and rarely of rutile, are found in the sands of several streams and in the red pneumatolysed granite, but were not detected in the fresh grey granite of Dartmoor. They have presumably resulted from the decomposition by pneumatolytic processes of the original titanium-bearing minerals present in the grey granite, namely, ilmenite and sphene, and the more abundant biotite which contains up to 2.04% TiO_2 . Biotite from the Haytor granite gave analysis I; after prolonged boiling in strong hydrochloric acid it gave II (partly bleached) and III (completely bleached). The residue is silvery-white and flaky (cf. "bauerite," A., 1913, ii, 868). From it the whole of the titania is readily extracted by a 2% solution of salicylic acid, and much of the silica by sodium carbonate solution.

Nine detailed analyses (TiO_2 0.04—1.11) are given of the different types of granite, which belong to sheets intruded at different periods (IV of the typical "blue granite" of Haytor), two of the associated slates ("killas"), and nine of the porphyritic crystals of felspar (V from Haytor). A red garnet isolated from the granite of Clinkwell Tor gave VI, corresponding with 20.9% of the spessartine molecule.

	SiO_2 .	TiO_2 .	Al_2O_3 .	Fe_2O_3 .	FeO .	CaO .	MgO .	K_2O .	Na_2O .	H_2O (at 110°).	H_2O ($> 110^\circ$).	Total.
I.	34.65	1.77	20.37	3.49	18.48	0.76	5.25	8.31	0.53	1.00	4.52	100.65 *
II.	76.37	1.23	6.19	0.86	nil	0.87	0.30	3.24	2.53	0.86	7.07	99.52
III.	80.69	0.61	3.62	0.49	nil	0.51	nil	1.40	0.64	6.96	5.10	100.02
IV.	73.66	0.16	13.81	0.21	1.51	0.67	0.45	5.02	2.89	0.41	1.25	100.35 †
V.	65.16	tr.	19.17	0.06	—	0.46	0.14	11.68	3.07	0.10	0.33	100.35 ‡
VI.	37.60	nil	17.78 ?	1.33	29.67	1.31	2.00	—	—	0.13	0.57	99.40 §

* I, also Li_2O 0.32, MnO 0.48, V_2O_5 0.04, F 0.68; BaO , Cr_2O_3 , ZrO_2 (?), traces.

† IV, also P_2O_5 0.24, Cl 0.01, MnO 0.06; ZrO_2 , BaO , Li_2O , traces; CO_2 , S , SrO , nil.

‡ V, also BaO 0.18.

§ VI, also MnO 9.01.

Some account is given of the heavy minerals (monazite, zircon, spinel, corundum, sillimanite, andalusite, cordierite, etc.) isolated from the normal granites and from the dark patches, the latter probably representing altered fragments of foreign rocks enclosed by the granite.

L. J. S.

Meteorite of St. Sauveur, France. A. LACROIX (*Compt. rend.*, 1923, 177, 561—565).—The material of this stone, which fell on July 10, 1914, at St. Sauveur in Haute-Garonne, is black, dull, and very fine-grained with but few chondrules; d 3.66. It closely resembles the Pillistfer, Daniel's Kuil, Khairpur, and Hvittis falls. Polished surfaces show grains of nickeliferous iron and of troilite; and thin sections show that the bulk of the stony material consists of an enstatite poor in iron, with small amounts of clino-enstatite, oldhamite (CaS), maskelynite (a fused felspar, optically isotropic, and with the composition of andesine, An 31%), and very little apatite (as crystals) and graphite. Analyses by Raoult of the portions soluble and insoluble in acid give the following bulk composition:

SiO_2 .	Al_2O_3 .	FeO .	MgO .	CaO .	Na_2O .	K_2O .	P_2O_5 .	Loss at 105° .	
33.40	3.29	0.21	17.00	1.12	0.96	0.21	0.17	0.09	
Fe.	Ni.	Co.	Mn.	Cr.	Ca.	S.	C.	Total.	
34.86	1.62	0.12	0.05	0.08	0.64	5.82	0.10	99.74	

This corresponds with the mineralogical composition : pyroxenes 41·25, feldspars 13·38, olivine 1·40, nickel-iron 27·49, troilite 14·26, oldhamite 1·15, daubreelite 0·22, apatite 0·34, graphite 0·10%. The metallic portion is present in unusually large amount and is very poor in nickel ($\text{Fe} : \text{Ni} = 16 : 1$), whilst the enstatite is very poor in iron.

L. J. S.

Analytical Chemistry.

A Quantitative Buchner Filter. R. J. CROSS (*Ind. Eng. Chem.*, 1923, **15**, 910).—An ordinary Buchner funnel is provided with a glass or porcelain cylinder, which is held by a clamp into which the whole funnel fits, in such a way as to hold the filter firmly down on the perforated plate. The joint between this retaining cylinder and the perforated plate is made to fit accurately, by grinding an annular channel in the surface of the plate, slightly wider than the thickness of the retaining cylinder, the end of which is ground true. On the completion of the filtration, the clamp is loosened and slid back, a watch glass is placed over the cylinder, and the whole filter inverted, the filter and its contents being loosened by blowing through the stem of the funnel. A flat joint with a rubber gasket is used for connexion with the suction flask. [Cf. *J.S.C.I.*, 1923, 1104A.]

H. C. R.

An Improved Methyl-orange. JAMES MOIR (*J. S. African Chem. Inst.*, 1923, **6**, 69—70).—The indicator proposed is *p*-sulpho-*o*-methoxybenzeneazodimethyl- α -naphthylamine; it changes from orange in alkaline solution to bluish-violet in acid solution, the range of p_H over the change being 4.9 to 3.5. The indicator is slightly sensitive to carbon dioxide by daylight, but not by artificial light.

W. P. S.

Bromoxyleneol-blue. A True-neutrality Point Indicator. ABRAHAM COHEN (*Biochem. J.*, 1923, **17**, 535).—Bromoxyleneol-blue (dibromoxyleneolsulphonophthalein), $C_{23}H_{20}O_5Br_2S$, is prepared by adding bromine under constant shaking in the cold to xylenol-blue suspended in glacial acetic acid and keeping over-night. The filtered crystals are recrystallised from dry boiling toluene. It covers the same p_H ranges as bromothymol-blue but possesses the advantage that it is easy to prepare. Bromoxyleneol-blue can have its working range halved by the addition of bromo-cresol-purple. The resulting mixed indicator can be used where a blue end-point of Sørensen value about 6.8 is desired in a titration. S. S. Z.

Apparatus for Electrometric Titrations. A. J. PELLING (*J. S. African Chem. Inst.*, 1923, **6**, 40—48).—In the apparatus described and illustrated oxygen is excluded completely from the electrodes during the titration, and the hydrogen is washed before entering the electrode vessel by first passing it through the bulk

of the solution. The apparatus also permits the titration of substances which are decomposed by contact with platinum black saturated with hydrogen. W. P. S.

A Convenient Form of Burette for Exact Gas Analysis.

HENRY JERMAIN MAUDE CREIGHTON (*Trans. Nova Scotian Inst. Sci.*, 1919—20, **15**, [2], 115—117).—The burette consists of two parallel limbs connected by a capillary tube through a T-piece with a stop-cock at the top. The larger limb is composed of bulbs connected by constricted portions on each of which there is a graduation mark. The capacity of the upper bulb and of that portion of the parallel limb which is above the top graduation mark is 70 c.c., that of each of the other bulbs is 5 c.c. The parallel limb is a straight tube of 5 c.c. capacity graduated to read each 0.01 c.c. At the base of each limb there is a stop-cock below which are connexions to a common reservoir and pair of levelling tubes. By alternate operation of the lower stop-cocks the major portion of the gas is measured in the large limb and the fraction of 5 c.c. in the small limb. [Cf. diagram, *J.S.C.I.*, 1923, 1045A.]

H. HG.

Spectroscopic Methods in Analytical Chemistry. C. AUER-

WELSBACH (*Sitzungsber. Akad. Wiss. Wien*, 1922, **131**, IIb, 339—355; from *Chem. Zentr.*, 1923, iv, 75—76).—An apparatus for the study of spark spectra is described. All elements under normal pressures, with the exception of oxygen, nitrogen, the inert gases, the halogens, arsenic, and the elements of the sulphur group give such spectra with characteristic lines. The limitations of the method are discussed. G. W. R.

Systematic Scheme for the Detection and Separation of the Acids. Z. KARAOGLANOV and M. DIMITROV (*Z. anal. Chem.*, 1923, **63**, 1—10).—The acids are divided into eight groups, the first consisting of those volatile by distillation with acetic acid, viz. carbonic, hydrocyanic, sulphurous, thiosulphuric, hyposulphurous, nitrous, and hypochlorous acids. The vapours are passed through a nitric acid solution of silver nitrate which gives a precipitate with hydrocyanic, hypochlorous, and hydrosulphuric acids; another portion is passed through barium hydroxide solution, which is rendered turbid by carbonic or sulphurous acids, and a third portion through iodide-starch solution, which is turned blue by nitrous or hypochlorous acid. Further portions of the gases from the distillation are then subjected to specific tests for each member of the sub-groups found to be present. The solution in the distilling flask is tested for group II acids (nitric and boric) by means of diphenylamine and turmeric, respectively. A second portion of the same solution is treated with barium and calcium acetates, which precipitate group III acids (sulphuric, hydrofluosilicic, chromic, hydrofluoric, oxalic, iodic, and tartaric). The precipitate is extracted with dilute nitric acid and the precipitate is tested for sulphate (charcoal test), iodate (blue colour with hydrochloric acid, zinc, and starch), and fluosilicate (sulphuric acid and water-drop test). The solution is treated with ammonium acetate

and calcium and barium acetates and the precipitate is heated with sulphuric acid, the gases being passed through barium chloride, then through barium hydroxide solution; a cloudiness in the former indicates hydrofluoric, and in the latter, oxalic acid. If tartaric acid is present, the hydrofluoric and oxalic acids must be removed by means of calcium sulphate in acetic acid solution; the filtrate is then tested for chromic and tartaric acids as usual. The filtrate from the third group is made slightly alkaline with ammonia, and barium acetate is added to precipitate group IV acids (phosphoric, arsenic, and silicic) which are tested for as usual. The group V acids (hydriodic, arsenious, and hydroferrocyanic) are separated from the neutral, diluted filtrate by the addition of lead acetate; hydriodic acid is detected in the precipitate by boiling it with dilute acetic acid and adding chlorine water and starch to the solution after filtration; arsenious acid by separating the lead from this solution and passing hydrogen sulphide through it, and hydroferrocyanic acid by treating the material insoluble in dilute acetic acid with ferric chloride. The filtrate from group VI is made strongly ammoniacal and boiled with a large excess of lead acetate, which precipitates hydroferrocyanic acid and the remainder of the arsenious acid. Group VII, consisting of hydrochloric, hydrobromic, and thiocyanic acids, is separated from the filtrate from group VI by addition of nitric acid and silver nitrate. The final filtrate contains only perchloric, chloric, and bromic acids; it is treated with sulphuric acid to separate lead, then with zinc and silver nitrate, which reduces the latter two acids to silver chloride and bromide. The filtrate is boiled with potassium hydroxide and filtered, and the alkaline liquid is boiled with ferrous sulphate, acidified with nitric acid, and treated with silver nitrate; a white turbidity indicates perchlorate.

A. R. P.

New Gravimetric Method of Estimating the Relative Humidity of Air with the Help of a Flow Meter. JULIUS OBERMILLER and MARTHA GOERTZ (*Z. physikal. Chem.*, 1923, **106**, 178—190).—A method for estimating the relative humidity of air is described which consists in passing a current of air through a meter to determine the velocity and then dividing the stream into two exactly equal parts, one of which is sent through a phosphoric oxide drying tube and the other is saturated with moisture and passed through a similar drying tube. Both tubes are weighed, and the fraction: increase of weight of the first drier/that of the second drier gives the relative humidity.

J. F. S.

Electrometric Titration of Iodate, Bromate, Chlorate, and Ferricyanide with Titanous Sulphate. W. S. HENDRIXSON (*J. Amer. Chem. Soc.*, 1923, **45**, 2013—2017).—Iodate, bromate, and chlorate may be titrated electrometrically with titanous sulphate at the ordinary temperature to an accurate end-point. There is no necessity to titrate back an excess of the reducing agent. The iodate is titrated best in sulphuric acid solution. There is a rise in potential of about 0.25 volt at the commencement of the titration, after which the *E.M.F.* remains steady until the end-

point is reached, when the voltage drops sharply by about 0.3 volt. The change is represented by the equation $5\text{Ti}_2(\text{SO}_4)_3 + 2\text{HIO}_3 + 5\text{H}_2\text{SO}_4 = 10\text{Ti}(\text{SO}_4)_2 + 6\text{H}_2\text{O} + \text{I}_2$. If more titanous sulphate is added after the end-point is reached, the *E.M.F.* falls slowly to about 0.1 volt lower, and then there is a sudden drop of a further 0.1 volt, which indicates the completion of the reaction $\text{Ti}_2(\text{SO}_4)_3 + \text{I}_2 + \text{H}_2\text{SO}_4 = 2\text{HI} + 2\text{Ti}(\text{SO}_4)_2$. Bromate may be titrated in sulphuric or hydrochloric acid solution. There is a sharp rise of about 0.3 volt on starting the titration, after which the voltage remains practically steady for some time; it then falls about 0.1 volt rapidly, followed by 0.05 volt slowly. After this there is a sudden drop of about 0.7 volt, which occurs at the end-point. In the case of chlorate, either sulphuric acid or hydrochloric acid may be used. The voltage rises rapidly about 0.5 volt with the first few drops of titanous sulphate, and remains practically constant until the reaction is complete, when it falls suddenly about 0.8 volt. Ferricyanide is titrated in the presence of sulphuric acid, and gives a sharp end-point. It may be estimated as accurately as any other form of iron. In all cases, the results by these methods are extremely accurate.

J. F. S.

Estimation of Chlorine, Bromine, and Iodine in Organic Compounds. J. HESLINGA (*Diss. Delft*, 1923, 1—72).—Hydrogenation of organic compounds in presence of various catalysts does not yield a quantitative formation of the halogen acids. Combustion in a stream of ammonia is satisfactory for all classes of organic halogen derivatives except aromatic compounds containing chlorine; the latter are completely decomposed by a mixture of ammonia and hydrogen at combustion temperatures. The decomposition is carried out in an empty quartz tube, of which one part is heated to redness; a plug of cotton wool inserted in the cool end is sufficient to retain all the ammonium halide. Cyanide is usually formed, and is destroyed before estimation of the ammonium halide in solution by boiling with acetic acid.

Very good results are also obtained by combustion in a stream of air containing ammonia, in presence of glowing ferric oxide. The resultant gases are passed through an alkaline sulphite solution, and the halogen is titrated after removal or oxidation of the sulphite.

Both methods are suitable for micro-determinations.

The removal of halogen by means of potassium hydroxide in presence of acetone may be used for estimations in some cases. Aliphatic halogen compounds also are decomposed by potassium hydroxide in alcoholic solution in sunlight in presence of *p*-benzophenone and other aromatic ketones; this method is quantitative for some aliphatic bromine and iodine compounds.

S. I. L.

Estimation of Fluorine in Zinc Blende. L. DA ROCHA-SCHMIDT and K. KRÜGER (*Z. anal. Chem.*, 1923, 63, 29—32).—One g. of finely powdered ore is mixed with 2 g. of freshly ignited and finely powdered quartz powder and 2 g. of carefully washed and ignited silver sand. The mixture is placed in the decomposition

flask and covered with 10 g. of anhydrous chromium trioxide. The flask is connected to a Peligot tube containing 15 c.c. of 50% alcohol saturated with potassium chloride, and a current of perfectly dry air free from carbon dioxide is passed slowly through the apparatus. By means of a dropping funnel, 20 c.c. of anhydrous sulphuric acid (made by evaporating the concentrated acid to two-thirds its bulk and cooling in a desiccator) is allowed to flow into the flask, which is then heated on a paraffin-bath slowly to 130—140°, and maintained at that temperature for three hours. The contents of the Peligot tube are then titrated with *N*/10-sodium hydroxide solution, using cochineal as indicator; 1 c.c. of the standard solution = 0.0057 g. of fluorine. For accurate results, absolute dryness of reagents and apparatus is necessary.

A. R. P.

Titration of Hydrofluoric and Hydrofluosilicic Acids in Mixtures containing Small Amounts of Hydrofluosilicic Acid.

PAUL H. M. P. BRINTON, LANDON A. SARVER, and ARTHUR E. STOPPEL (*Ind. Eng. Chem.*, 1923, **15**, 1080—1081).—The results of the analyses of the same samples of commercial hydrofluoric acid by Scott's method in three different laboratories showed a wide divergence. This was traced to the effect of the silica in the standard alkali used. The use of sodium hydroxide made from sodium by the action of water vapour, the sodium hydroxide being caught in platinum and stored in bottles lined with ceresin, caused all discrepancies to disappear. The rapidly fading end-points of the cold titration were no longer in evidence, and sharp end-points in which the pink colour persisted for from one to four minutes were obtained. Electrometric titrations showed that in the absence of silica in the standard alkali solution the hydrolysis of the potassium fluosilicate in ice-cold solution was sufficiently slow to allow a ready reading of the cold end-point, whereas in the presence of appreciable amounts of silica in the alkali the change in the hydrogen-ion concentration on keeping was much more rapid, and the end-point colour correspondingly fleeting. If accurate results are desired by this method, estimations of silica must be made in even freshly prepared standard alkali solutions and corrections applied to the figures found for the two acids. The weight of silica added during the titration up to the cold end-point should be multiplied by 2.393 to find the weight of hydrofluosilicic acid to be deducted from that found in the mixture. To find the weight of hydrofluoric acid to be added to that found by analysis, the weight of silica added should be multiplied by 1.991.

H. C. R.

A Simple, Sensitive Process for the Detection of Oxygen by a Biochemical Method. HANS SCHMALFUSS (*Ber.*, 1923, **56**, [B], 1855—1856).—The process is based on the observation that a piece of filter-paper impregnated with worm blood and *l*-β-3 : 4-dihydroxyphenyl-α-alanine becomes blackened as the result of melanin formation when exposed to oxygen. The reaction is not influenced by the presence of nitrogen, hydrogen, carbon

monoxide, or carbon dioxide, but bromine, chlorine, hydrogen sulphide, hydrocyanic acid, and sulphur dioxide must be removed. In the presence of 0.9% of oxygen, the paper becomes darkened within three minutes. H. W.

Colorimetric Estimation of Small Amounts of Oxygen.
PERCY GEORGE TERRY HAND (T., 1923, 123, 2573—2576).

Micro-sampling for the Determination of Dissolved Oxygen.
R. V. ALLISON and J. W. SHIVE (*Soil Sci.*, 1923, 15, 489—491).—A modified Winkler apparatus is described for the sampling of liquid media in which dissolved oxygen is to be estimated. G. W. R.

A Rapid Gasometric Method of Estimating Dissolved Oxygen and Nitrogen in Water. H. G. BECKER and W. E. ABBOTT (*Sci. Proc. Roy. Dubl. Soc.*, 1923, 17, 249—253).—Air dissolved in water is set free by dissolving in the water some highly soluble substances, of which potassium hydroxide has been found the most effective. An apparatus is described in which this fact is applied to the determination of the quantity of air dissolved in water. The water to be examined is saturated in a bulb with potassium hydroxide and the air liberated is measured. The oxygen is then absorbed in alkaline pyrogallol and the residual nitrogen is measured. The total air found by this method is slightly greater than by other methods, due to air in the potassium hydroxide, whilst the oxygen is slightly lower, through incomplete absorption. E. H. R.

A New Method of Estimating Sulphur, Arsenic, and Antimony in Organic and Inorganic Compounds by "Sinter-Oxidation." FRITZ FEIGL and REGINA SCHORR (*Z. anal. Chem.*, 1923, 63, 10—29).—Sulphur, arsenic, and antimony are quantitatively converted into sulphate, arsenate, and antimonate by heating any organic or inorganic compound containing these elements with twice its weight of a mixture of equal parts of sodium carbonate and potassium permanganate under a layer of the same mixture in an iron crucible for one hour at a low red heat. The residue from this "sinter-oxidation" is boiled with water, the solution cooled and treated with one-half its volume of alcohol, and the insoluble material collected and washed with 30% alcohol. The solution is used for the estimation of sulphur as barium sulphate and of arsenic, either iodometrically or as magnesium ammonium arsenate. The residue is dissolved in hydrochloric acid and a little oxalic acid, and the antimony is estimated iodometrically in strong hydrochloric acid solution. The process is applicable to the estimation of these elements in sulphide, sulpharsenide, and sulphantimonide ores as well as in such organic substances such as phenylthiocarbamide, salvarsan, and arsenic acids. A. R. P.

Estimation of "Sulphonitric" and "Sulphonitrous" Acids.
ANDRÉ GRAIRE (*Compt. rend.*, 1923, 177, 821—823).—The author

discusses the disadvantages of the common methods of analysing sulphuric acid containing nitrous and nitric acids, etc. Nitrometer estimations may give low results owing to the presence of iron and copper salts, which hold back nitric oxide. This fact is demonstrated by oxidising with permanganate the acid remaining in the nitrometer (after displacing the usual nitric oxide formed), then treating with ferrous chloride, and measuring the second volume of nitric oxide formed. This supplementary method may be used to obtain accurate analyses of the acids in question. E. E. T.

The Influence of the Nature and Position of Substituents on the Kjeldahlisation of Aromatic Nitro-compounds. B. M. MARGOSCHES and WILHELM KRISTEN [with ERWIN SCHEINOST] (*Ber.*, 1923, 56, [B], 1943—1950; cf. Margosches and Vogel, A., 1920, ii, 50; 1922, ii, 522).—The authors have greatly extended the scope of their examination of the kjeldahlisation of aromatic nitro-compounds which now includes nitro-phenols, -benzoic acids, -benzyl alcohols, -benzaldehydes, -anisoles, -phenetoles, -benzyl chlorides, nitroanilines, nitroacetanilides, and nitrotoluidines. The substance is treated with sulphuric acid alone or in the presence of potassium sulphate, copper oxide, or mercuric oxide.

Accurate results are obtained in the estimation of nitrogen with *o*-nitrophenol, *o*-nitrobenzoic acid, *o*-nitrobenzaldehyde, *m*-nitroaniline, *m*-nitroacetanilide, *m*-nitrodimethylaniline, and 2:6-dinitrophenol by treatment with sulphuric acid alone or in the presence of catalysts or substances which raise the boiling point of the acid.

The substituents may be arranged with regard to their behaviour on kjeldahlisation by sulphuric acid alone in the following classes: (a) the substituents, $\cdot\text{OH}$, $\cdot\text{OMe}$, $\cdot\text{CO}_2\text{H}$, and $\cdot\text{CHO}$, favour the accuracy of the process mainly when they are in the ortho-position to the nitro-group; (b) the residues, $\cdot\text{NH}_2$, $\cdot\text{NHAc}$, and $\cdot\text{NMe}_2$, have a similar action when in the meta-position; (c) the substituents $\cdot\text{Me}$, $\cdot\text{CH}_2\cdot\text{OH}$, and $\cdot\text{CH}_2\text{Cl}$ appear generally to be without influence. The effect of a nitro-group on a second nitro-group could not be established with certainty.

The effect of a substituent on the kjeldahlisation of the nitro-group appears to be explicable by the increase or diminution of the reactivity of the nitro-group induced by the presence of the substituent. H. W.

The Sulphate-Molybdate Method of Estimating Phosphoric Acid. V. A. BECKLEY and A. MARAIS (*J. S. African Chem. Inst.*, 1923, 6, 35—39).—When this method is used, it is recommended that the phosphomolybdate precipitate be washed with 3% sodium nitrate solution, using 20 c.c. each time; the precipitate should be disturbed as little as possible. After the fifth washing, each quantity of filtrate should be tested and as soon as it yields a red coloration on the addition of 0.05 c.c. of *N*/10-sodium hydroxide solution, using phenolphthalein as indicator, the precipitate may be considered to be washed completely. W. P. S.

[Estimation of Phosphoric Acid and Potassium in Soils, etc.] H. F. L. BISCHOFF and B. DE C. MARCHAND (*J. S. African Chem. Inst.*, 1923, 6, 53—60).—The authors have investigated the effect of certain conditions, etc., on the accuracy of the estimation of potassium and phosphoric acid in soils and fertilisers. In the estimation of available potash in soils, ignition of the soil extract does not cause loss of potassium and the quantity of citric acid-soluble phosphoric acid found in basic slag is not affected appreciably when considerable variations are made in the time of shaking or in the volume of citric acid solution used. The solubility of bonemeal and rock phosphate in citric acid solution increases with the fineness of the material; samples of these substances should be analysed in the state in which they are received, and should not be ground previously to analysis. W. P. S.

Estimation of Minute Quantities of Arsenic. III. O. BILLETER and E. MARFURT (*Helv. Chim. Acta*, 1923, 6, 771—779).—Previous work on the detection of minute quantities of arsenic (cf. A., 1919, ii, 32; this vol., ii, 335) left two points still in an unsatisfactory state. The destruction of organic matter is not absolutely complete and the quantitative estimation of the arsenic by comparison of the mirrors is imperfect. The first difficulty may be overcome as follows. The organic matter to be tested is treated with fuming nitric acid and sulphuric acid as before, the nitric acid driven off, the sulphuric acid solution neutralised with sodium carbonate, and evaporated to dryness. There are then added, for 20 g. of organic matter, 2 g. of potassium perchlorate and 0.3 g. of potassium bromide and the mixture is transferred little by little to a platinum crucible heated to redness, finishing with a gentle fusion. The distillation with sulphuric acid is then carried out as before. The sensitivity of the Marsh apparatus is increased by forming the mirror in a capillary tube at a point which will just prevent the passage of a platinum wire 0.3 mm. thick.

For the estimation of the arsenic in the mirror, the portion of tube containing the mirror is treated with five to ten times the theoretical quantity of iodine solution and a little sodium hydrogen carbonate in a stoppered test-tube. After two or three hours the arsenic has all dissolved and the excess of iodine is titrated with thiosulphate, using starch as indicator. The solutions used are 0.005 to 0.01*N*, and the necessary degree of refinement is obtained by using special burettes, one of 0.5 c.c. capacity graduated to 0.002 c.c. and one of 2 c.c. graduated to 0.01 c.c. for larger quantities. Accuracy to 0.03 m.mg. of arsenic is claimed by this method. Experiments to determine the proportion of the original arsenic recovered in the mirror showed that the yield is greater the smaller the quantity of arsenic being dealt with. Starting with 100 m.mg. of arsenic, 92.5% was found in the mirror, whilst with 1 m.mg. or less, 99% was found. E. H. R.

Simple Method of Estimating Arsenic. POUSSIGUES (*Ann. Chim. Analyt.*, 1923, 5, 263—267).—Copaux's method of estimating phosphates by measuring the volume of the oily yellow

liquid formed by their interaction with sodium molybdate solution in the presence of sulphuric acid and ether is slightly modified and extended to arsenic. Nitric acid (d 1.20) is used instead of sulphuric acid and the ether must be free from alcohol. A special graduated tube similar to a Gerber milk tube but larger in size is used for the estimation, and the liquid is deposited in the graduated end by centrifuging. The apparatus is calibrated by testing a solution of known arsenic content and a correction is applied for the solubility—which is considerable—of the oily liquid in the acid layer. If 100 c.c. of liquid, corresponding with 1 g. of the mineral, are taken, minerals containing less than 1.16% of arsenic give no oily deposit owing to the solubility of the latter, but this difficulty can be overcome by suitably concentrating the solution before testing. The density of the aqueous phase must be kept low or the yellow liquid will not sink. The presence of metals does not affect the results, but in the presence of antimony the mineral should be dissolved in hydrochloric and tartaric acids. Citric acid, alcohol, and too great excess of sulphuric acid are harmful, and phosphoric acid must be absent. Specimen analyses given agree well with gravimetric analyses of the same samples.

H. C. R.

The Estimation of Arsenic as Silver Arsenate. W. ESCHWEILER and W. RÖHRS (*Z. angew. Chem.*, 1923, **36**, 464—466).—The arsenate solution, obtained either by fusion of the material with sodium hydroxide and nitrate or by oxidation of an ammoniacal arsenic sulphide solution by means of hydrogen peroxide, is acidified with nitric acid and carefully neutralised to methyl-orange with ammonia. Two g. of ammonium nitrate and 1 g. of ammonium acetate are added, and the solution is heated to boiling. Silver nitrate solution is added drop by drop until the precipitate coagulates and settles, leaving the supernatant liquid quite clear. The precipitate is collected, washed with cold water, and either heated at 500° and weighed as Ag_3AsO_4 or dissolved in nitric acid and its silver content estimated by titration with potassium thiocyanate. If chlorides are present, the precipitate is dissolved in nitric acid and, after filtering off the silver chloride, reprecipitated as before. Large quantities of sulphates cause the results to be too high; addition of several g. of potassium nitrate prevents this interference. [Cf. *J.S.C.I.*, 1923, 1046A.]

A. R. P.

Estimation of Arsenic in Foods. R. M. HANN (*J. Assoc. Off. Agric. Chem.*, 1923, **7**, 48—54).—The addition of potassium iodide is recommended in the estimation of arsenic by the Gutzeit method in order to ensure complete evolution of the arsenic. Hydrochloric acid may be used in place of sulphuric acid. W. P. S.

Direct Estimation of Arsenic in Toxicology. J. LEWIS (*J. S. African Chem. Inst.*, 1923, **6**, 65—68).—In the estimation of arsenic in toxicological specimens by Green's method (A., 1920, ii, 634) equally trustworthy results are obtained whether the organic matter is destroyed by evaporation with sulphuric acid and nitric

acid or the material simply disintegrated by boiling with dilute sulphuric acid without oxidation. In both cases, the loss amounts to about 0.1 mg. when dealing with 1 mg. quantities of arsenic trioxide.

W. P. S.

The Separation of Arsenic from Antimony and Tin.

LUDWIG MOSER (*Z. anal. Chem.*, 1923, **63**, 40—41).—A criticism of Järvinen's paper (this vol., ii, 254) in which attention is directed to the earlier work of Moser and Ehrlich (this vol., ii, 315) showing that arsenic trichloride is removed completely from a solution saturated with hydrogen chloride by heating on a water-bath whilst passing a current of air through the liquid. The reduction of arsenic acid to arsenious acid by ferrous sulphate is complete only in strong hydrochloric acid solutions. Järvinen's statement that arsenic acid is volatile from hydrochloric acid solutions is incorrect; potassium chlorate does not oxidise arsenious to arsenic acid completely in these solutions, and it is the unoxidised portion of the arsenic that is volatilised.

A. R. P.

Microanalytical Estimation of Carbon and Hydrogen by Pregl's Method.

A. FRIEDRICH (*Z. angew. Chem.*, 1923, **36**, 481—482).—Too large an increase in weight in the absorption vessels may be traced to impurities given off by the rubber connexions or contained in the oxygen used. The rubber connexions should be reduced to a minimum, and should be previously washed for two hours in hot sodium hydroxide (40—50%), then washed free from alkali, and finally steamed out for two hours. Impurities in the oxygen may be removed by passing the gas over red-hot copper oxide and absorbing any carbon dioxide formed with 50% sodium hydroxide. New absorption vessels tend to lose slightly in weight when wiped with a moist cloth and should be boiled out before being used for the first time. Using lead peroxide asbestos, as described by Pregl, the combustion tube and contents require to be heated to redness for only two to three hours before use, and not for several weeks, as commonly supposed.

W. T. K. B.

Analysis of Combustible Gases.

ENRIQUE HAUSER (*Bull. Soc. chim.*, 1923, [iv], **33**, 1141—1232).—A lecture delivered, 23rd May, 1922, before the Société chimique de France.

H. J. E.

The Application of Micro-analysis to the Elementary Analysis of Fuels.

H. GAULT and MAURICE NICLOUX [with G. PFERSCH and R. GUILLEMET] (*Bull. Soc. chim.*, 1923, [iv], **33**, 1299—1304).—In carrying out estimations of the carbon and hydrogen content of a series of bituminous schists by the ordinary methods, inconsistent results were obtained. The method of micro-analysis was therefore tried, the quantities of material used being from 3—5 mg., and this gave concordant results; moreover, a considerable saving of time was effected. The authors are of opinion that these advantages would be gained by using the method in other cases of fuel analysis.

H. J. E.

The "Pyro-Tannic Acid" Method for Estimating Carbon Monoxide in Blood and Air. R. R. SAYERS, W. P. YANT, and G. W. JONES (*U.S. Bur. Mines Repts. Investigations*, 1923, No. 2486; cf. Sayers and Yant, A., 1922, ii, 868).—Blood-standards not being permanent, standards are prepared from pigments for use in the method of estimation of carbon monoxide in blood whereby normal blood forms a grey suspension but blood containing carbon monoxide a light carmine precipitate when treated in aqueous dilution with a mixture of tannic acid and pyrogallol. Estimations with blood are accurate to $\pm 5\%$; calculations therefrom of the carbon monoxide content of air are accurate to 0.005% of the total volume when not more than 0.05% is present, or 0.03% when 0.18% is present.

CHEMICAL ABSTRACTS.

The Residue from Silica in Rock Analysis. M. AUROUSSEAU (*J. Washington Acad. Sci.*, 1923, 13, 330—332).—The residue which remains after silica (obtained in the usual course of analysis) has been treated with hydrofluoric acid is usually quite small in quantity. The author has examined such a residue obtained during the analysis of a silicic andesite; it amounted to 0.52% of the mineral and contained Al_2O_3 12.7% , Fe_2O_3 24.7% , MgO 15.8% , TiO_2 30.0% , and SO_3 8.0% , together with small quantities of calcium, phosphoric acid, and manganese.

W. P. S.

Separation and Estimation of Potassium and Sodium. A Perchlorate Precipitation Process using Normal Butyl Alcohol. G. FREDERICK SMITH (*J. Amer. Chem. Soc.*, 1923, 45, 2072—2080).—A method has been developed for the separation and estimation of sodium and potassium, which depends on the precipitation of potassium perchlorate from aqueous solution by the addition of a comparatively large volume of *n*-butyl alcohol. The method of procedure is as follows. The mixed chlorides of sodium and potassium, which must be free from sulphate, are evaporated to dryness with an excess of perchloric acid. Two or three c.c. of water are added and the perchlorate dissolved by heating; then 65 or 100 c.c. of *n*-butyl alcohol containing 0.5 — 1% of perchloric acid, the larger volume being taken when 3 c.c. of water are required to dissolve the perchlorates, are heated to boiling and added slowly with vigorous stirring to the perchlorate solution. This effects the precipitation of the potassium perchlorate, and after all has been precipitated the whole is gently boiled for half a minute and cooled to room temperature. The precipitate is collected on a Gooch crucible, washed with 10 portions of 1 — 2 c.c. of the precipitating solution, dried at 125 — 250° , cooled, and weighed. The filtrate and washings are evaporated to dryness and the sodium is estimated as sulphate. This process is rapid and gives excellent results. The solubility of potassium chlorate in anhydrous *n*-butyl alcohol, and in that containing various quantities of water and perchloric acid, has been determined at 25° . The amount dissolved is very small; the quantity dissolved in the solution used for precipitation is only 1 mg. per 100 c.c.

J. F. S.

Estimation of the Titratable Alkali of the Blood with Dinitrosalicylic Acid. JAMES B. SUMNER and ROGER S. HUBBARD [with LUCY L. FINNER] (*J. Biol. Chem.*, 1923, **56**, 701—709).—Greenwald and Lewman's method (this vol., ii, 87) has been modified, dinitrosalicylic acid being used in place of picric acid. This has the advantage that the total dinitrosalicylic acid in the filtrate may be readily estimated colorimetrically by means of the coloration produced with ferric chloride. E. S.

Comparative Tests of Various Volumetric Methods for the Estimation of Sodium Sulphide. ANON (*Chem. Ztg.*, 1923, **47**, 752—753).—Results obtained by the gravimetric method (oxidation with bromine water followed by precipitation of the liquid with barium chloride) of estimating sodium sulphide in various preparations of the salt were compared with those obtained by the following five volumetric methods: (1) Direct titration with iodine of the slightly acidified solution, (2) addition of excess of iodine to the acid solution followed by titration of the excess with thiosulphate, (3) direct titration without acidifying, (4) addition of excess of iodine without acidifying, followed by titration with thiosulphate, (5) direct titration with iodine in the presence of 0.5—2.0 g. of sodium hydrogen carbonate. Method (1) gave the most satisfactory results, methods (3) and (4) were quite good, but not so exact as (1), method (2) gave low and method (5) high results. The presence of carbonate up to 4% has practically no influence on the results obtained without acidifying, whereas 10% increases the sulphide figures by 1.2%. A. R. P.

The Micro-estimation of Magnesium. ST. GADIENT (*Helv. Chim. Acta*, 1923, **6**, 729—733).—The method is essentially that of Hammett and Adams (*A.*, 1922, ii, 587), modified in some of its details. Exact directions for carrying out the estimation are given. When estimating magnesium in serum by this method, it is unnecessary first to remove the albumin. [Cf. *J.S.C.I.*, 1923, Nov.] E. H. R.

The Conductometric Titration of Alkaloids. W. D. TREADWELL and S. JANETT (*Helv. Chim. Acta*, 1923, **6**, 734—743).—The alkaloids brucine, quinine, narcotine, and morphine can be titrated accurately with hydrochloric acid by the conductometric method; caffeine is too weak a base to give a distinct break in the titration curve. To avoid the formation of non-conducting layers at the electrodes of the titration cell, when using direct current, a commutator was used giving alternations of 4—8 per second, and the solution was kept stirred with a current of nitrogen. The indicator was a high-resistance millivolt meter shunted between the battery and the commutator. The current used is a few milliamperes with an *E.M.F.* of eight volts. During titration, the titration curve, representing the change of current strength, rises gradually, flattening somewhat as the end-point is approached, and rises sharply as soon as free acid is present in solution. The break in the curve is quite sharp. E. H. R.

The Estimation of Zinc by Schaffner's Method with Repeated Precipitation of the Iron. C. BOY (*Chem. Ztg.*, 1923, **47**, 758).—In Schaffner's method for titrating zinc with sodium sulphide, the proportions of free ammonia in assay and standard must be the same. If the iron is precipitated several times with ammonia to remove the zinc completely, the amounts of free ammonia in a series of assays will vary. To rectify this, the solutions should be boiled until all free ammonia is expelled and a cloudiness due to precipitated basic zinc chloride is produced; 5 c.c. of 1:1-hydrochloric acid are added, followed by 15 c.c. of ammonia, and the whole is set aside over-night uncovered. Approximately equal quantities of ammonia will be contained in all the trials in the morning.
A. R. P.

The Quantitative Treatment of Metals of the Ammonium Sulphide Group. G. LUFF (*Z. anal. Chem.*, 1923, **63**, 32—39).—Manganese may be separated from iron and aluminium by one precipitation with ammonia, zinc and nickel by two, and cobalt by three precipitations by operating as follows: Ten grams of ammonium chloride are added for every 100 c.c. of solution, followed by ammonia until neutral; the solution is boiled for fifteen minutes, then treated with ammonia drop by drop until it reacts just alkaline to litmus, and filtered. The precipitate is washed with a hot, dilute, faintly ammoniacal solution of ammonium nitrate, and, if necessary, redissolved in hydrochloric acid and the process repeated. A single precipitation of iron and aluminium by means of pyridine serves to separate these elements from manganese satisfactorily; in the presence of zinc, nickel, and, especially, cobalt, the precipitate contains appreciable quantities of these elements and should be redissolved in acid and reprecipitated with ammonia. The pyridine precipitation is carried out in the same manner as that by means of ammonia, 5 c.c. of pyridine being added to each 100 c.c. of solution containing 10 g. of ammonium chloride.
A. R. P.

[Estimation of Manganese and of Zinc as Sulphates.] W. F. HILLEBRAND (*Z. anal. Chem.*, 1923, **63**, 41—42).—It is pointed out that contrary to Huber's statement (*A.*, 1922, ii, 398) manganese sulphate is slowly decomposed at 600° and that the heating should be conducted at 450—500° (cf. Blum, *A.*, 1912, ii, 1214). Gutbier and Staib's observation (*A.*, 1922, ii, 396), that zinc sulphate, heated with an excess of sulphuric acid, tenaciously retains traces of free acid, is confirmed.
A. R. P.

Volumetric Estimation of Iron. A*New Method of Reduction. P. F. THOMPSON (*Proc. Australasian Inst. Mining Met.*, 1922, N.S., No. **47**, 343—346).—Zinc sulphide emulsion is prepared by passing hydrogen sulphide, with occasional additions of ammonia solution, into a solution of 100 g. of zinc sulphate in 2 litres of water until precipitation is complete, decanting, washing the precipitate a few times with very dilute sulphuric acid, and diluting to 2 litres. To a hot solution of ferric iron in dilute sulphuric acid, the emulsion is slowly added until a decided turbidity is obtained; the liquid

is boiled until a drop, tested with thiocyanate, indicates complete reduction. If a brown sulphide is formed, the solution is filtered. After being boiled with dilute sulphuric acid and a little marble until the sulphur has become granular and hydrogen sulphide removed, the ferrous iron is estimated in the usual way.

CHEMICAL ABSTRACTS.

Quantitative Separation of Uranium from Thorium and the Rare Earths in Pitchblende by Means of Sodium Thiosulphate. W. RISS (*Chem. Ztg.*, 1923, 47, 765—766).—The pitchblende is dissolved in nitric acid, the insoluble matter separated, and the filtrate evaporated to dryness several times to remove the acid. The residue is dissolved in water, exactly neutralised with dilute ammonia, and sodium thiosulphate added in excess. The solution is boiled for ten minutes, and left for twenty-four hours. If sufficient thiosulphate has been used, the supernatant liquid is almost colourless, and the precipitate contains all the thorium, the greater part of the uranium, and small quantities of rare earths (chiefly cerium). To separate the rare earths completely, the precipitate is redissolved in hydrochloric acid and reprecipitated. The precipitate is then dissolved in hydrochloric acid and the thorium precipitated with oxalic acid, ignited, and weighed as thorium oxide, which should be pure white. To determine uranium, the oxalic acid in the filtrate is destroyed by evaporating to dryness and heating the residue with concentrated sulphuric acid. The uranium can then be precipitated with ammonia. The filtrate, after the separation of the thiosulphate precipitate, is tested for thorium, and if this is absent, precipitated with oxalic acid, which removes the rare earths. Iron is precipitated with ammonium carbonate, and the rest of the uranium with ammonia, the two uranium precipitates being ignited and weighed together.

H. C. R.

Colorimetric Estimation of Small Quantities of Bismuth.

L. CUNY and G. POIROT (*J. Pharm. Chim.*, 1923, 28, [vii], 215—223).—The orange-coloured colloidal solutions of quinine iodobismuthate given by a standard bismuth solution and the solution to be estimated are compared colorimetrically. For the standard solution, 2.23 g. of bismuth oxide are dissolved in, and made up to 1 litre with, 10% nitric acid, and 25 c.c. of this solution are added to 175 c.c. of 10% nitric acid and made up to 1 litre with distilled water. To 5 c.c. of this solution are added 3 c.c. of a clear, 10% solution of gum arabic, then 1 c.c. of a solution containing 1 g. of quinine hydrate and 5 c.c. of 10% nitric acid per 100 c.c., and finally 1 c.c. of a 5% solution of potassium iodide. The solution under estimation, with additions as above, is compared with a thickness of 5 mm. of the standard, and the thickness required for matching the colour is arranged, by suitable dilution, to be between 4 and 7 mm. In a series of test estimations the maximum error was 3.5%. The presence of various substances, *e.g.*, hydrochloric, sulphuric, and acetic acids, and various metallic salts, vitiates the results. Coloured precipitates or colloidal solutions are given by salts of the following

metals: silver (yellow), mercurous (dirty green, changing to red), mercuric (yellow), lead (light yellow), stannous (orange; but no reaction in presence of gum arabic), antimony (dark yellow), copper (brown), ferric (liberation of iodine and formation of quinine periodide), cadmium (white). Salts may also cause flocculation of the colloidal quinine iodobismuthate. W. T. K. B.

Tests of Official Vaseline, Liquid Vaseline, Paraffin, and Light Petroleum: Action of Cold Concentrated Sulphuric Acid. F. RICHARD (*J. Pharm. Chim.*, 1923, [vii], 28, 209—214).—The author suggests the abolition from the French "Codex" of the vague directions for testing pharmaceutical vaselines, etc., with 60% sulphuric acid. It is preferable to triturate or agitate the material with twice its weight of cold concentrated sulphuric acid, after an hour's contact, with which no more than a pale yellow coloration should be obtained. The material should also have a neutral reaction to litmus and leave no ponderable ash or residue when calcined or evaporated on the boiling water-bath. W. T. K. B.

Use of the Salts of the Arylsulphonhalogenoamides in the Estimation of Phenols. ELWYN ROBERTS (*T.*, 1923, 123, 2707—2712).

The Effect of Phenol in the Estimation of Reducing Sugars by the Picramic Acid Methods. H. C. SWEANY (*J. Lab. Clin. Med.*, 1923, 8, 572—578).—Phenol, present at a concentration of 1 in 4,000, causes a two- to three-fold increase of colour in the estimation of sugar by Lewis and Benedict's or Benedict's method. The phenols present in normal blood cause a 10% error in the estimation of blood-sugar by the former, but not by the latter, method. It is likewise essential to eliminate phenols from urine before estimating the sugar by picramic acid methods which are also inapplicable in the case of sugar solutions preserved by phenols and many related substances. The phenol may possibly react with the decomposition products of dextrose to give a product which either is coloured or becomes reduced to picric or picramic acid.

CHEMICAL ABSTRACTS.

The Chemical Analysis of Cotton. I. The Absorption of Methylene-blue by Cotton. CONSTANCE BIRTWELL, DOUGLAS ARTHUR CLIBBENS, and BERT P. RIDGE (*J. Text. Inst.*, 1923, 14, T, 297—313).—An examination has been made of the relations between the absorption of methylene-blue by bleached cotton and (1) the ash content of the cotton, in view of the work by Rona and Michaelis (*A.*, 1920, ii, 475), (2) the origin of the raw cotton, and (3) the nature of the bleaching process. Two analytical methods are described. The first, a colorimetric method, employs solutions of methylene-blue hydrochloride about 0.05 to 0.25 millimole per litre, made by diluting a solution containing 10 millimoles per litre, which is standardised by titration with titanous chloride. The cotton is shaken with the dye solution (usually 0.4 millimole per l.) for eighteen hours in a stoppered bottle and then the free liquid is compared in a Kober-Klett colorimeter with a standard about half

as strong as the original (0.2 millimole per l.). The weight of cotton is so chosen that the colorimeter reading is nearly the same for the test as for the control, say, 17—23 as against 20, since the depths of colour of methylene-blue solutions are not strictly proportional to their concentrations. For normally-bleached American cotton, the quantity required, under the above conditions, is about 1.5—2 g. for 50 c.c. of dye; of bleached Egyptian cotton, 0.8—1 g. is sufficient.

The second analytical method is for more concentrated solutions of dye, about 2.5 to 3.5 millimoles per litre. The methylene-blue solutions are titrated with a solution of naphthol-yellow-S, which gives a reddish-brown precipitate, the supernatant liquid changing ultimately from blue to yellow. The yellow solution can be standardised against methylene-blue, or the dye itself, $C_{10}H_4O_8N_2SNa_2$, can be recrystallised from dilute alcohol and accurately weighed out. In order to use a high proportion of cotton relatively to the volume of methylene-blue, and to recover most of the liquid for titration, the cotton is placed in the bottom of a wide tube constricted in the middle, left immersed in the dye for eighteen hours, and then the tube is inverted into a wider tube and centrifuged for fifteen to thirty seconds at 1,500 r.p.m. Using about 2.5 g. of cotton and 15 c.c. of dye, it is possible to recover 12—13 c.c. of clear liquid for titration. The approach of the end-point when adding naphthol-yellow-S is detected by observing the colour of a drop of the liquid on a glass rod, and thereafter the tube is centrifuged after each addition until the blue gives place to yellow.

The first important result obtained is the proof that an increase in the ash content of the cotton, or, more strictly, in the alkalinity of the ash, causes an increased adsorption of methylene-blue, other factors being constant. In order to study other effects, it is necessary, therefore, to wash the cotton submitted for examination under controlled conditions before further tests. Agitation with 0.1*N*-acid for two or three hours, followed by washing with distilled water, finally on a centrifuge, until the washings are indifferent to an iodide-iodate-starch mixture, is recommended. A second result of general importance is the proof that Egyptian cotton, although bleached and washed by the same process, absorbs distinctly more methylene-blue than American cotton, even if the Egyptian cotton is grown in America. The other results have significance in the practice of bleaching, but it may be said that, from cotton material of known origin, the methylene-blue absorption offers a method of quantitatively following the progressive purification of cotton cellulose during bleaching, and ultimately of measuring the success of the bleaching operation, that is, of determining whether "over-bleaching" or inefficient scouring have occurred. J. C. W.

Titrimetric Estimation of Formic Acid. BROR HOLMBERG and SVEN LINDBERG (*Ber.*, 1923, 56, [B], 2048—2052).—The authors take advantage of the fact that when a formate reduces mercuric chloride to the mercurous form, one equivalent of hydrogen chloride is liberated. The solution to be tested is neutralised, excess of standard baryta added, and boiled for about an hour to

complete the oxidation of the formate. Then sodium or potassium bromide solution is added to ensure the precipitation of the calomel, the solution is made acid with a known amount of hydrochloric acid, and boiled to expel the carbon dioxide. Finally, the solution is again neutralised with baryta. The difference between the acid added and the sum of the two portions of baryta obviously gives the amount of acid formed and is equivalent to the formate reduced. The method gives good results and can be used in the presence of acetates. H. H.

Estimation of Amino-acids by Electrometric Titration.

ERIK M. P. WIDMARK and ERIK L. LARSSON (*Biochem. Z.*, 1923, **140**, 284—294).—Amino-acids behave during electrometric titration with strong alkali as weak acids devoid of amphoteric character. By measuring the increasing conductivity of amino-acid solutions during the gradual addition of small volumes of 1.0*N*-sodium hydroxide and plotting the results, it was found that the increase was linear up to a point corresponding with complete neutralisation, beyond which a much more rapid increase was noted. The amount of alkali used up to the point of break in continuity serves as a means of estimation. Dibasic acids show two such points, one corresponding with each carboxyl group. The method is applicable to dipeptides and to all the amino-acids examined with the sole exception of arginine. J. P.

Estimation of Small Quantities of Oxalic Acid. Application to Urine. J. KHOURI (*Ann. Chim. Analyt.*, 1923, [ii], **5**, 205—207).—The solution containing oxalic acid is evaporated, the residue obtained is treated with a known volume of alcoholic carbamide solution and again evaporated; the excess of carbamide is then extracted with ethyl alcohol or amyl alcohol, and, after the alcoholic solution has been evaporated, estimated by the hypobromite method. The difference between this quantity and that present originally (as estimated in another portion of the carbamide solution) gives the amount of carbamide combined with the oxalic acid as carbamide oxalate, $2\text{CO}(\text{NH}_2)_2 \cdot \text{C}_2\text{H}_2\text{O}_4$. In the case of urine, the oxalic acid which may be present is extracted with ether, the solvent is evaporated, and the residue obtained treated as described. W. P. S.

Estimation of *p*-Sulphamidobenzoic Acid in "Saccharin." O. BEYER (*Chem. Ztg.*, 1923, **47**, 744).—An investigation into the degree of accuracy of methods of estimating *p*-sulphamido-benzoic acid in commercial "saccharin" showed that the German official method (A., 1920, ii, 518) is capable of showing quantities of 1% and upwards when 10 g. of the sample are taken for analysis and may be considered sufficiently accurate for practical purposes. Hefelmann's method does not give such good results, and is not so convenient, because saccharin does not dissolve so readily in the 73% sulphuric acid prescribed as in the 25% hydrochloric acid prescribed in the official method. H. C. R.

Detection of Ethyl Phthalate in Brandy. S. ELLES (*Z. Unters. Nahr. Genussm.*, 1923, **45**, 379—381).—In the presence of concentrated sulphuric acid, pyrogallol gives a violet coloration with ethyl phthalate. In testing plain brandies, 20—50 c.c. of the sample are treated with 5 drops of 15% sodium hydroxide and evaporated to dryness before the test is applied. In the case of products containing sugar and extract matter such as formic acid, 20—50 c.c. of the sample diluted with an equal volume of water are extracted with 25 c.c. of light petroleum (b. p. 30—50°). Tinctures should be treated with the minimum necessary quantity of lead acetate and filtered before dilution and extraction with light petroleum. The light petroleum extract is evaporated to dryness without the addition of sodium hydroxide and the test applied to the residue. The test is sensitive to 0.01% of ethyl phthalate in straight brandies and to 0.1—0.4% in cases in which extraction with light petroleum is necessary. H. C. R.

Estimation of Phenolphthalein. S. PALKIN (*J. Assoc. Off. Agric. Chem.*, 1923, **7**, 14—17).—The iodine method described previously by the author yields fairly trustworthy results, but there is a tendency for the figures obtained to be too low. An alternative method, in which the phenolphthalein is precipitated from its alkaline solution by the addition of hydrochloric acid and then extracted with ether and weighed, gives results which are slightly too high. W. P. S.

Estimation of Phenylcinchoninic Acid (Cinchophen, Atophan). WILLIAM RABAK (*J. Assoc. Off. Agric. Chem.*, 1923, **7**, 32—34).—To estimate phenyleinchoninic acid in tablets or powders, 1 g. of the sample is extracted repeatedly with hot alcohol, the alcoholic extracts are filtered, the filtrate is treated with an excess of *N*/10-sodium hydroxide solution, and then titrated with *N*/10-hydrochloric acid, using phenolphthalein as indicator. Each c.c. of *N*/10-alkali solution is equivalent to 0.02491 g. of phenylcinchoninic acid. W. P. S.

Gravimetric Method for Estimating the Hydroxyl Value and the Acetyl Value [of Oils]. E. B. ELSBACH (*Chem. Umschau*, 1923, **30**, 235—237).—The oil is heated at 100° in a flask provided with a tube sealed through the side of the neck and bent at right angles inside the flask, so that it passes downwards and terminates in a constriction close to the bottom of the flask. Dry carbon dioxide or nitrogen is passed through this tube into the oil, which is heated until constant in weight, 4—6 c.c. of acetic anhydride are then added, and the flask is again heated, a reflux condenser being used. When the acetylation is complete, the reflux condenser is removed and dry carbon dioxide again passed through the heated liquid until the excess of acetic anhydride is removed. If *p* denotes the percentage increase in weight, based on the original weight of the oil, the hydroxyl value is $p \times 13.354$ and the acetyl value $p \times 13.354 / 1 + p/100$. The latter, being based on the weight of acetylated oil, is always less than the former. The determination takes two and a half to four hours. H. C. R.

Estimation of Formaldehyde in Presence of Substances Found in Formalin. P. BORGSTROM (*J. Amer. Chem. Soc.*, 1923, 45, 2150—2155).—The iodometric method (this vol., ii, 590) can be used for the estimation of formaldehyde in the presence of methyl alcohol, formic acid, or pure methylal, but not in the presence of acetone or ethyl alcohol. The hydrogen peroxide method (*loc. cit.*) can be used if methyl alcohol, ethyl alcohol, formic acid, or methylal is present; if acetone is present in concentration equal to that of the formaldehyde, the figure obtained for the latter will be about 2% high. Methyl alcohol, ethyl alcohol, formic acid, or methylal does not affect the estimation of formaldehyde by the neutral sulphite method (*loc. cit.*), but acetone introduces an error which cannot readily be corrected. W. S. N.

Estimation of the Purity of Vanillin. S. B. PHILLIPS (*Analyst*, 1923, 48, 367—373).—A volumetric method of estimating vanillin is described depending on the formation of an anhydro-derivative by the interaction of vanillin and *p*-toluidine dissolved in 80% alcohol. This compound contains the original hydroxyl group of the vanillin, and is therefore soluble in alkali, giving a yellow solution. A measured excess of standard alkali is added, followed by a comparatively large volume of cold water. The addition of standard acid first neutralises the excess of alkali, and then liberates the anhydro-derivative from its sodium salt. The first drop of acid which liberates the derivative gives a yellow turbidity, the free derivative being practically insoluble in the liquid phase. The volume of alkali required for the titration of the vanillin is thus obtained. Accurate results are obtained when benzoic acid is present as an adulterant in quantities up to 10%, but with higher percentages of acid it is advisable to use a gravimetric method. No sample of first class vanillin was found to contain more than 1% of acid (as vanillic acid) although some of the samples had been kept in cardboard containers for ten years. The gravimetric method suggested comprises the precipitation of vanillin as the semicarbazone from dilute acetic acid solution. The precipitate is easy to wash and filter, and may be dried in a water oven for six to eight hours without losing a weighable quantity by volatilisation. The vanillin may be separated from impurities such as piperonal by dissolving the semicarbazone in ammonium hydroxide solution. Vanillinsemicarbazone, by virtue of its hydroxyl group, forms a soluble ammonium salt giving a yellow solution, whilst piperonalsemicarbazone is insoluble. Test analyses in which piperonal was added to vanillin gave results agreeing with the actual percentage present to within 1 part in 450 parts. Details of the purification of the vanillin used in this work and of the *p*-toluidine used in the volumetric method are given. The oxidation of samples of purified vanillin exposed to air, moisture, and light was practically negligible. With vanillin in solution, however, oxidation proceeds much more rapidly, whilst solutions of vanillin in alkali behave similarly to alkaline pyrogallate solution. The following corrected melting points are

given : vanillinsemicarbazone, 232°; piperonalsemicarbazone, 218°; vanillin *p*-nitrophenylhydrazone, 223°; vanillin-*p*-bromophenylhydrazone, 148°.
H. C. R.

"Permutite" as a Reagent for Amines. JOHN C. WHITEHOEN (*J. Biol. Chem.*, 1923, **56**, 751—764).—Bases with a dissociation constant of not less than 5×10^{-9} (for example, alkylamines, basic amino-acids, histamine, tyramine) may be removed almost completely from neutral, and less completely from acid or alkaline, solution in water by shaking with, or preferably by filtration through, permutite. Other solvents (ethyl alcohol, amyl alcohol, ether) may also be employed, but the same bases are not necessarily removed as from water. Recovery of the bases is best effected by treatment of the permutite with a saturated solution of potassium chloride. A study of the reaction with ammonium chloride has shown that the mass law is obeyed; in the expression $[\text{NH}_4\text{Cl}][\text{Na permutite}] = K[\text{NH}_4 \text{ permutite}][\text{NaCl}]$, K has a value of 0.75. The temperature coefficient of the reaction between 0° and 17° is 1.6.

A colorimetric method for the estimation of adrenaline, based on its removal from interfering substances by means of permutite, is being worked out.
E. S.

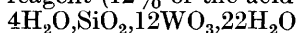
Determination of the Benzoylcegonine, Tropacocaine, and Ecgonine Yields of the Coca Leaf. A. W. K. DE JONG (*Indische Mercur*, 1923, **46**, 305).—The benzene extract of the leaves is evaporated, treated with 1% acetic acid, then with alcohol, and the residue redissolved in benzene from which the benzoylcegonine crystallises. Ecgonine is estimated in the remaining benzene solution by polarimetry. For the estimation of tropacocaine, the benzene extract is shaken with 0.1*N*-hydrochloric acid, which is titrated with 0.1*N*-sodium hydroxide. CHEMICAL ABSTRACTS.

Estimation of Procaine (Novocaine). ALFRED W. HANSON (*J. Assoc. Off. Agric. Chem.*, 1923, **7**, 17—20).—The bromide-bromate method described previously (A., 1922, ii, 405) is trustworthy, and the presence of small amounts of nitrates does not interfere. When the substance is extracted from its ammoniacal solution and titrated, the results obtained tend to be too low.
W. P. S.

Detection of apoMorphine. L. VON ITALLIE (*Pharm. Weekblad*, 1923, **60**, 1046—1049).—The method of Feinberg (*Z. physiol. Chem.*, 1913, **84**, 363) is not always trustworthy. In a neutral solution, in presence of oxidising agents, red, violet, or blue colorations are imparted to organic solvents by traces of apo-morphine after keeping. Ammonium persulphate, after addition of pure sodium hydrogen carbonate, gives a strong reaction with one part of apomorphine in 100,000 parts.
S. I. L.

Improved Method for the Estimation of Nicotine in Tobacco and Tobacco Extracts. O. M. SHEDD (*J. Agric. Res.*, 1923, **24**, 961—970).—One g. of tobacco extract (more if much

lower than 40% grade) or 5 g. of dried and powdered tobacco are moistened with 2.5 c.c. of alcoholic sodium hydroxide solution (NaOH, 6 g.; water, 40 c.c.; 90% alcohol, 60 c.c.) For extracts twice this quantity is used, and enough calcium carbonate is added to make the whole into a moist mass. The mixture is extracted for five hours in a Soxhlet extractor with ether. The cooling water of the condenser should not be above 20° and the volume of solvent in the extraction flask should not be allowed to become less than 25 c.c. After extraction, excess of ether is removed, but the residual volume must not go below the minimum necessary to keep all extracted matter in solution. The ether extract is transferred to a separating funnel (washing out the flask first with ether and then with dilute hydrochloric acid) and washed with 4—6 portions (10 c.c. each) of cold dilute hydrochloric acid (1 : 4). A tendency to the formation of emulsions can be prevented by the addition of 1 c.c. of alcohol. Successive washings are filtered through glass wool into a 100 c.c. graduated flask. Washing with acid should be continued until no precipitate with the silicotungstic reagent is produced. The accumulated washings are made up to a standard volume, and an aliquot portion corresponding with about 0.25 g. of extract or 1—2 g. of tobacco, removed and diluted with water to 400—500 c.c. Sufficient hydrochloric acid (1 : 4) is added to ensure the presence of at least 3 c.c. per 100 c.c. of liquid. One c.c. of silicotungstic acid reagent (12% of the acid



—others are useless) is added for each 0.01 g. of nicotine presumed to be present. The mixture is stirred thoroughly until the crystalline precipitate will settle rapidly. A few drops of the supernatant liquid are tested to ensure that excess of the reagent has been added. After eighteen to twenty-four hours the precipitate is filtered, preferably through a Hirsch or Buchner funnel, and washed with dilute hydrochloric acid (1 : 1000), dried, and transferred without removal from the filter-paper to a platinum crucible. The latter is heated until all carbon is eliminated and finally ignited over a Teclu or Meker burner for not more than ten minutes. The weight of precipitate $\times 0.114$ gives the weight of nicotine.

A. G. P.

[Analysis of] Potatoes with a High Content of Solanine.

A. BÖMER and H. MATTIS (*Z. Unters. Nahr. Genussm.*, 1923, **45**, 288—291).—Solanine was estimated in potatoes by a variation of von Morgenstern's method, in which the extracted juice was made alkaline with ammonia, evaporated to dryness with 10 g. of kieselguhr, and extracted for five hours in Soxhlet's apparatus with 95% alcohol. The alcohol was evaporated off and the residue twice precipitated from warm dilute acetic acid solution with ammonia. The colourless product was weighed. The results obtained by this method were in some cases even higher than those given for the impure product of Schmiedeberg and Meyer's method, and were nearly twice those given by von Morgenstern's method for the same samples. They varied from 25.3 to 58.8 mg. per

100 g. for some samples of potatoes which were inedible, the values for normal potatoes being 2.0—7.5 mg. per 100 g. H. C. R.

Estimation of Pyramidone. ALFRED W. HANSON (*J. Assoc. Off. Agric. Chem.*, 1923, 7, 29—32).—Pyramidone may be extracted from its alkaline solution by chloroform, the extract then evaporated, the residue dried, and weighed. If desired, this residue may be converted into the hydrochloride, by evaporation with hydrochloric acid, and weighed as such, or the solution of the hydrochloride may be treated with silver nitrate solution and the silver chloride collected and weighed. The weight of silver chloride found is multiplied by 1.6131 to obtain the amount of pyramidone present.

W. P. S.

The Estimation of Santonin in Flores Cinae (Tansy). L. M. VAN DEN BERG (*Pharm. Weekblad*, 1923, 60, 858—870).—After close examination of the methods of Katz (*Arch. Pharm.*, 1899, [B], 237) and others, a procedure was worked out, based on treatment of the hot aqueous suspension with dilute hydrochloric acid, extraction with chloroform, and recrystallisation from hot dilute alcohol. The santonin separated is not always pure, resin being usually present, especially when the santonin content of the powder is low.

S. I. L.

Estimation of Methylene-blue. H. O. MORAW (*J. Assoc. Off. Agric. Chem.*, 1923, 7, 20—29).—In the iodometric method described, 0.1 g. of the methylene-blue is dissolved in 100 c.c. of water, the solution is treated with 30 c.c. of glacial acetic acid, and 30 c.c. of *N*/5-iodine solution are added. After fifty minutes, the mixture is diluted with water to 200 c.c., filtered, and the excess of iodine is titrated in an aliquot portion of the filtrate. Each c.c. of *N*/10-iodine solution is equivalent to 0.007475 g. of methylene-blue.

W. P. S.

Fluorescent Oxidation Products of Bilirubin and their Importance as Sources of Error in the Detection of Urobilin. H. K. BARRENSCHEEN and O. WELTMANN (*Biochem. Z.*, 1923, 140, 273—278).—The commonly employed method of detecting urobilin by oxidation to a green fluorescent substance with iodine in the presence of zinc acetate does not give trustworthy results when applied to body fluids other than urine. The complications are ascribed to the presence of bilirubin.

J. P.

Arsphenamine [Salvarsan]. I. A Colorimetric Method for the Estimation of Salvarsan in Blood and Tissues. A. C. KOLLS and J. B. YOUMANS (*Bull. Johns Hopkins Hosp.*, 1923, 34, 149—151).—A colorimetric method for the estimation of salvarsan is based on the diazotisation of the amino-groups, and the coupling of the diazotised product with orcin to produce a bright red substance. Details are given for the application of the method to whole blood, tissues, spinal fluid, blood plasma, and urine.

CHEMICAL ABSTRACTS.

General and Physical Chemistry.

Improved Temperature Control for the Pulfrich Refractometer. T. M. LOWRY and R. G. PARKER (*J. Sci. Instrum.*, 1923, **1**, 16—21).—Particulars are given of tests of a Pulfrich refractometer in which the temperature control is improved by the provision of water passages of greater bore than usual, the avoidance of unnecessary lengths of tube of small bore in the flow system, and the use of an additional water-jacket surrounding on three sides the liquid under examination.
J. S. G. T.

Volume of the Molecule and Refractive Index. RICHARD LORENZ and W. HERZ (*Z. anorg. Chem.*, 1923, **127**, 205—208, 369—371; cf. A., 1922, ii, 821).—The quotient, ψ , of molecular refractive power, $[R_L]$, by molecular volume for all substances should be $\psi_s=0.331$ at the boiling point, and $\psi_0=0.4668$ at absolute zero (calculated according to the law of corresponding states). These values are quoted for some thirty compounds, and are found to deviate more or less from the theoretical. If $(n^2-1)/(n^2+2)$ really represents the volume of the molecules of a medium of refractive index n , then there should be some correspondence between $[R_L]$ observed and that calculated from the known radius of the molecule and the Avogadro number. Satisfactory agreement between these values is obtained in the case of carbon dioxide, hydrogen, methyl chloride, and ethylene.

ψ_s should be calculable not only from n_s , the refractive index at the boiling point, but also from D_s , the dielectric constant at the boiling point. Calculated in this way, ψ_s approaches more nearly to 0.331, the theoretical value, except in the case of dipolar molecules, which must show anomalous dispersion.
H. H.

Contraction of Volume and Refractive Index of Liquid Mixtures. L. COUNSON (*Arch. Sci. phys. nat.*, 1923, **128**, 361—369).—The author has determined the respective densities and refractive indices, at about 20°, of aqueous solutions of tartaric acid and ammonium heptamolybdate containing either 10 or 25 g. per litre, and of mixtures of these solutions. The results indicate that q and c in Pulfrich's relation $(R-R_v)/R=q(D-D_v)/D=qc$, in which D and R are, respectively, the actual values of the density and refractive index of the mixture, whilst D_v and R_v are the corresponding values calculated on the assumption that these properties are additive in nature (Pulfrich, *Z. physikal. Chem.*, 1889, **4**, 561), are of the same sign (positive).
J. S. G. T.

Disposition of an Arc in a Vacuum permitting the Obtaining of Spectra of Metals using Very Small Quantities of Material. (Mlle.) BERTHE PERRETTE (*Compt. rend.*, 1923, **177**, 876—879).—The original paper should be consulted for details (including a diagram of the apparatus used). The cathode, of tungsten (or tungsten-thorium),

is maintained at a high temperature by an auxiliary current. The anode, a small disk of tungsten, contains a minute cavity in which the experimental material is placed.

E. E. T.

Röntgen Spectrograph for Analytical Chemical Purposes.

PAUL GÜNTHER and IWAN STRANSKI (*Z. physikal. Chem.*, 1923, **106**, 433—441).—A description is given of an X-ray spectrograph, and its use for chemical purposes is illustrated by measurements with a mixture of the rare earths from monazite from which cerium and thorium have been removed.

J. F. S.

The Dependence of the Intensity of Spectral Lines on Gas Pressure. L. STRUM (*Z. Physik*, 1923, **18**, 372—378).—By application of the theory of probability to electronic orbits in their relation to the fields due to neighbouring atoms, an expression for the energy, E , emitted in the form of radiation of wave-length λ , by a gas at pressure p , through which a discharge passes, is deduced in the form $E = \delta p e^{-\gamma n^4 p^{2/3}} / \lambda$, where n is the appropriate quantum number associated with the line in the series formula, and δ and γ are factors of proportionality. The formula is in accord with experimental results, more especially with the results obtained by Beatty (*Phil. Mag.*, 1917, [vi], **33**, 49; 1923, **45**, 1080) which indicate a maximum intensity of the line H α when the gas pressure is 1.4 mm.

J. S. G. T.

The Multilinear Spectrum of Hydrogen. II. With an Addendum on the Continuous Spectrum. E. GEHRCKE and E. LAU (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1923, **24**, 242—252).—In continuation of previous work (this vol., ii, 197), the authors describe an arrangement suitable for the excitation of the red and green Fulcher bands of the hydrogen spectrum. They find that, in contradistinction to other lines in the multilinear spectrum, these bands are more strongly excited by slow cathode rays than by fast rays. Wave-lengths of lines constituting the red, green, and blue bands are detailed, and the potentials necessary for their excitation and the relative intensities of lines in the respective bands discussed. Residual lines in the bands are classified in three groups, one of which forms an approximately symmetrical series having its centre at λ 9799.25, whilst the remaining two groups exhibit an approximately constant difference between corresponding members of the respective groups. The conditions of excitation of the continuous spectrum between λ 360 and $230\mu\mu$ resemble those for the excitation of the multilinear spectra. The possible origins of both these spectra are briefly discussed.

J. S. G. T.

Excitation of the Spectra of Hydrogen and of Nitrogen in Low Voltage Arcs. O. S. DUFFENDACK (*Physical Rev.*, 1922, **20**, 100).—The fact that in a two-element tube the lines and bands of hydrogen appeared with the arc, whereas the bands did not appear when the gas was dissociated in the tungsten furnace, is additional evidence that the lines are due to the atom and the bands to the molecule. In the case of nitrogen, both the first and second positive bands appeared with the arc; the former increased, and

the latter decreased in intensity with increased voltage. The negative bands appeared one or two volts above the ionising potential, and increased markedly in intensity. Three new bands were observed at 5075, 5018, and 4961 Å. Four lines were observed at 5003, 5006, 5667, and 5680 Å., but never below 70 volts; at potentials above this, the arc became a "flare" with greatly increased conductivity. It is concluded that the positive bands are due to the neutral molecule, the negative bands to the ionised molecule, and the lines to the atom, and that the molecule is ionised without dissociation.

A. A. E.

The Distribution of Intensity in the Broadened Balmer Lines of Hydrogen. E. O. HULBERT (*Physical Rev.*, 1923, 22, 24—36).—The broadening of the Balmer lines of hydrogen by condensed discharges was examined at various pressures, and the effect is ascribed to the large proportion of ionised atoms produced by the momentarily high current density.

A. A. E.

The Effect of Crossed Electric and Magnetic Fields on the Hydrogen Spectrum. OTTO HALPERN (*Z. Physik*, 1923, 18, 287—303).—The author develops a mathematical analysis showing how, by appropriate choice of variables, the Hamilton function associated with a hydrogen or singly-ionised helium atom in crossed electric and magnetic fields (combined Stark and Zeeman effects) may be expressed in the form of a convergent series capable of being quantised. It follows that, under such conditions, the hydrogen lines are split into a number of sharply defined lines and are not merely widened.

J. S. G. T.

The Electron-affinity Spectrum of the Iodine Atom. WALTER GERLACH and FRITZ GROMANN (*Z. Physik*, 1923, 18, 239—248).—According to Franck (*ibid.*, 1921, 5, 428), the combination of an electron with an electrically neutral, electronegative atom should give rise to the emission of a continuous spectrum having a limiting frequency, ν_0 , towards the red end equal to E/h , where E denotes the electron-affinity of the atom and h is Planck's constant. The authors suggest the identification of the continuous spectrum λ 3460—3340 Å. emitted by dissociated iodine vapour with this electron-affinity spectrum. The value of the electron affinity of the iodine atom, calculated from this result is $81.8 + 0.2$ cal. per g.-mol., in close agreement with the mean value of about 82, calculated from the lattice energy of sodium iodide and potassium iodide by Born's lattice theory and with the same result deduced from the ionisation potential of hydrogen iodide. Evidence was obtained that the spectrum in the region λ 4800 Å., observed by Steubing (A., 1921, ii, 361), could not be identified with the electron-affinity spectrum of iodine vapour.

J. S. G. T.

The Spectrum of Fluorine. HENRY G. GALE (*Physical Rev.*, 1922, 19, 530).—Fluorine was prepared by Smythe's method (A., 1922, ii, 99), and its spectrum observed through a fluorite window at atmospheric or reduced pressure, using copper electrodes tipped

with gold. Of fifty-two lines between λ 3470 and λ 7800, all except seven on the red side of λ 7400 are included in the tables of Exner and Haschek, Porlezza, Lunt, or Moissan. With a powerful spark, fifteen additional lines appear in the red and orange regions.

A. A. E.

New Spectra of Oxygen and Nitrogen in the Extreme Ultra-violet. J. J. HOPFIELD (*Physical Rev.*, 1922, **19**, 548).—By the use of a disruptive discharge at low pressure, the spectrum of oxygen has been extended to include lines between λ 508 and λ 1335. Nitrogen, examined in a discharge tube of the internal capillary type, gave a spectrum extending from λ 825 to λ 1400, lines at λ 307 and λ 362 being also photographed. The spectrum of air was obtained with the same tube at a pressure of 3 mm., with two minutes' exposure, to λ 1050.

A. A. E.

The Vacuum Spark Spectrum of Silicon. R. A. SAWYER and R. F. PATON (*Physical Rev.*, 1922, **19**, 256—257).—Previous investigations on the spark spectrum of silicon have exhibited but little agreement, largely on account of the rapid oxidation of the element. Application of the vacuum spark method has resulted in the observation of fifty-five lines between λ 4085.25 and λ 6372.2 to an accuracy of ± 0.3 Å., those in the range 4100—5202 being probably correct to ± 0.1 Å. Several groups of pairs of constant frequency difference have been noticed and tabulated.

A. A. E.

Intensities in the Helium Spectrum. A. LL. HUGHES and P. LOWE (*Proc. Roy. Soc.*, 1923, [A], **104**, 480—498).—The authors have investigated the dependence of the distribution of intensities in the helium spectrum, excited by impacts between electrons and atoms, on the energy of impact of the electrons, which ranged from 34 volts to 210 volts, whilst all other factors were maintained constant. The results indicate that the curve expressing the relation of the intensity of any spectrum line to the corresponding energy of impact is characteristic of the series to which the line belongs. In the doublet system, intensities decrease rapidly as the energy of impact is increased above 34 volts. The rate of decrease is greatest for the sharp series $1\pi - m\sigma$, and least for the diffuse series $1\pi - m\delta$. The principal series $1S - mP$ of the singlet system is characterised by a very great increase of intensity as the energy of impact is increased from 34 volts up to about 80 volts, beyond which little change occurs. Maximum intensity of the lines of the diffuse series $1P - mD$ corresponds with an energy of impact of about 75 volts, the rise to the maximum being progressively greater the higher the term number associated with the line. Lines of the sharp series $1P - mS$ exhibit a small initial increase of intensity as the energy of impact is increased to 60 volts, and thereafter show a slight decrease. The results are discussed in the light of the quantum theory, and the authors conclude that the transitions from one energy level to another within an atom struck by an electron, are to some extent affected by the presence of other atoms, ions, or electrons.

J. S. G. T.

The Spectrum of Neutral Helium. C. V. RAMAN and A. S. GANESAN (*Astrophys. J.*, 1923, 57, 243—247).—The ionising potential computed from Silberstein's formula $\nu = 4N(1/n_1^2 - 1/m_1^2 + 1/n_2^2 - 1/m_2^2)$ is not in agreement with the experimental value. Moreover, there is no arrangement of lines as regards series relationship, division into singlet and doublet systems, or of intensities. A. A. E.

The Spectrum of Helium. LUDWIK SILBERSTEIN (*Astrophys. J.*, 1923, 57, 248—250; cf. preceding abstract).—The author's formula covers twenty-three of the thirty so-called combination lines; the probability that the coincidences of the computed with the experimental values is fortuitous is stated to be of the order 10^{-13} . A. A. E.

Measurements of Wave-lengths in the Visible Spectrum of Helium, and the Interference Phenomena Employed in the Measurements. (MLLE) H. C. OFFERHAUS (*Arch. Néerland.*, 1923, 7, 60—94).—Details are given of the application of an étalon spectrograph, calibrated by means of the cadmium line λ 6438.4696 Å., to determine the wave-lengths of nineteen lines in the helium spectrum between λ 3888.650 and 7281.348 Å. Results are recorded to 0.001 Å., and agree very closely with corresponding results obtained by Merrill (A., 1917, ii, 434). J. S. G. T.

Positive Ray Analysis of Lithium, Zinc, and Calcium. A. J. DEMPSTER (*Physical Rev.*, 1922, 19, 271, 431; cf. A., 1922, ii, 417).—Positively charged atoms are formed by vaporising the metal in an electrically heated capsule, and bombarding the vapour with electrons from a hot cathode. After falling through a definite potential, the particles are deflected through 180° by a magnetic field, the semicircular path being smaller for the lighter than for the heavier particles. The different atoms are observed by means of their charge. The components of lithium have atomic weights 6 and 7 present in varying proportions. Zinc isotopes of atomic weights 64, 66, 68, and 70 exhibit large variations in their relative proportions. The zinc lines were compared directly with those of calcium, of which the strong line at 40 was compared with a potassium line at 39 and a magnesium line at 24; a weak calcium component has atomic weight 44. A. A. E.

Vacuum Grating Spectrograph and the Zinc Spectrum. R. W. WOOD (*Phil. Mag.*, 1923, [vi], 46, 741—750).—The construction and operation of a vacuum grating spectrograph, with which lines of short wave-length may be photographed with extreme sharpness, are briefly described. The grating employed is of 1 metre radius and is ruled with 15,000 lines to the inch, the ruled surface measuring 1×4 inches. The source of light used is the electron-arc (*Physical Rev.*, 1897), and a full exposure of the Schumann plates employed requires about twenty minutes. The sharpness of lines in the zinc spectrum photographed with this instrument is compared with that of corresponding lines given by Sawyer (A., 1921, ii, 363). Wave-lengths and intensities of twenty-one lines in the zinc spectrum between

$\lambda\lambda$ 1601.15 and 1918.67 Å. and of forty lines between $\lambda\lambda$ 832.73 and 1307.32 Å. are tabulated and compared with values given by Sawyer. The values of wave-length determined are considered to be correct to 0.1 Å. Between $\lambda\lambda$ 1283 and 1500 Å., the author records 96 lines, compared with 14 given by Sawyer. No trace is found of ten lines recorded by the latter observer between $\lambda\lambda$ 1066 and 1165 Å. The carbon line 1036.1 Å. given by Sawyer is resolved into a clearly separated doublet $\lambda\lambda$ 1037.14 and 1037.50 Å. The carbon triplet, $\lambda\lambda$ 1561.32, 1560.67, 1560.16, resolved by Simeon (this vol., ii, 45), is considered to be a doublet with components of equal intensities and a separation of one Ångström unit.

J. S. G. T.

Stages in the Excitation of the Spectra of Thallium. F. L. MOHLER and ARTHUR E. RUARK (*J. Opt. Soc. Amer.*, 1923, 7, 819—829).—In continuation of previous work (A., 1919, ii, 42; this vol., ii, 605), determinations have been made of the critical potentials, and the development of the spectrum with increasing voltage, in the case of thallium vapour. The first resonance potential has the value 0.9 volt, and the first ionisation potential the value 6.04 volts. The agreement between the latter value and the value, 6.082 volts, calculated for the level of greatest negative energy, confirms the view that $2p_2$ is a normal orbit of the atom. A higher critical potential, detectable by the photoelectric effect of the radiation, has the value 12.4 volts. With increasing voltage below the ionisation potential, successive lines of the two subordinate series in the thallium spectrum appear. Above 12 volts another line system, with strong lines in the ultra-violet, appears. It is suggested that this second spectrum is an arc spectrum resulting from a second type of single ionisation consisting in the removal of one of the two 6_1 electrons. Comparison of the critical potentials with the doublet series system of thallium indicates that the first ionisation potential is determined by the limit $2p_2$ and the first resonance potential by the difference $2p_2 - 2p_1$. The orbit $2p_1$ is meta-stable. Resonance potentials corresponding with frequencies $2p_2 - ms$ and $2p_2 - md$ give rise to the observed low voltage spectra. Corresponding critical potentials are calculated for aluminium, gallium, and indium.

J. S. G. T.

Two New Lines in the Aluminium Spectrum and their possible Series Relations. G. D. SHALLENBERGER (*Physical Rev.*, 1922, 19, 398—399).—The application to aluminium electrodes of a high potential vacuum spark yields strong, well-defined lines at λ 4150.6 and λ 2907.4 (± 0.3 —0.4 Å.), respectively. Equations are given representing the frequencies of the lines, which can scarcely be due to impurities; certain numerical relations are also mentioned.

A. A. E.

Pole Effects, Pressure Shifts, and Measurements of Wave-lengths in the Spectrum of Manganese. GEORGE SPENCER MONK (*Astrophys. J.*, 1923, 57, 222—233).—Pole effects, pressure shifts, and wave-lengths for the stronger lines of manganese between λ 4470 and λ 6021 have been measured. The evidence indicates a

correspondence between unsymmetrical broadening of the lines under pressure and pole effect. The use of a carbon pole bored and filled with manganese dioxide or of manganese poles gave moderate pole effects which were practically absent when manganese chloride was used. The wave-lengths of forty-one lines have been measured with an estimated accuracy of 0.002 \AA. , and tabulated.

A. A. E.

The Intensity of Röntgen Spectral Lines Excited by High Voltages. GUSTAV KETTMANN (*Z. Physik*, 1923, **18**, 359—371).—A method for determining photographically the intensities of Röntgen spectral lines is described, and measurements of the relative intensities of lines, excited at various voltages, in the *K*-series of chromium, copper, and silver, and in the *L*-series of lanthanum and lead, are detailed. At high voltages, the intensities of the lines attain a maximum value, owing to absorption of the rays by the anti-cathode. When absorption of the rays by the anti-cathode is very small, the respective intensities of the lines increase proportionally to the square of the voltage. The results are found to be in agreement with the theory proposed by Davis (*Physical Rev.*, 1918, **11**, 433).

J. S. G. T.

Spectra of Isotopes. A. L. NARAYAN (*Nature*, 1923, **112**, 651).—The structure of the tin lines 5631 and 4524 was carefully examined with a Lummer plate. Even when the pressure was of the order of 1 mm., both lines were simple in structure, the latter being especially sharp. McLennan's view (*A.*, 1922, ii, 541, 728) that the spectral displacement for isotopes should be given by the atomic number multiplied by the displacement calculated on Bohr's theory, requiring in this case a difference for isotopes 116 and 124 of 0.07614 , is therefore not supported.

A. A. E.

The Optical Spectrum of Hafnium. H. M. HANSEN and S. WERNER (*Nature*, 1923, **112**, 618—619).—Both the arc and the spark spectra of hafnium have been investigated, using a preparation of hafnium containing (according to *X*-ray analysis) not more than about 1% of zirconium. The previous results (this vol., ii, 200) in the case of the arc spectrum have been confirmed and extended. Comparison of the results with those of Bardet (this vol., ii, 449) appears to indicate that the hafnium spectrum, like that of zirconium, differs according to the conditions of excitation. The wave-lengths between $\lambda_{2497.0}$ and 3505.2 and the intensities are tabulated.

A. A. E.

X-Ray Spectra of Hafnium and Thulium. D. COSTER (*Phil. Mag.*, 1923, [vi], **46**, 956—963).—Particulars are given of physical methods employed in the discovery and investigation of the properties of the element of atomic number 72. The following wave-lengths (measured in *X*-units) have been determined in the *L*-series of the emission spectrum of hafnium: 1777.4, 1577.04, 1566.07, 1519.7, 1389.3, 1371.1, 1349.7, 1323.5, 1303.5, 1212.1, 1176.5, 1141.3, 1135.6, 1100.1. The estimated error is in all cases less than 0.4 X-unit . In addition, the following lines in the *L*-series of the

absorption spectrum of hafnium were determined: 1097, 1151.5, 1293.0, and the following lines in the *M*-series: 7521, 7286. Values of the wave-lengths in the *L*-series of the spectrum of the element of atomic number 69 (thulium) have been determined as follows: 1951.1, 1733.9, 1722.8, 1692.3, 1541.2, 1526.8, 1511.5, 1502.3, 1460.2, 1352.3, 1312.7, 1271.2, 1265.3, 1226.4 X-units. The author discusses the identification of two X-ray lines found by Dauvillier in the spectrum of a preparation of rare-earth metals and ascribed to cerium, the presence of which was suspected by Urbain (A., 1922, ii, 463).

J. S. G. T.

Critical Potentials of the Thorium *M*-Series Lines. P. A. ROSS (*Physical Rev.*, 1923, [ii], 22, 221—225).—The lines, α to ϵ , of Stenström, and a new line, ϵ_2 , of wave-length 2.85 Å., were observed. The critical potentials were found to agree with the predicted values.

A. A. E.

Trithiocarbonic Acid and Perthiocarbonic Acid. H. VON HALBAN, A. MACKERT, and W. OTT (*Z. Elektrochem.*, 1923, 29, 445—457).—The absorption spectra of solutions of trithiocarbonic acid (H_2CS_3) and its ethyl ester have been obtained for solutions in chloroform, ethyl alcohol, light petroleum, ether, and toluene, and that of the barium salt in water. Similar measurements have been made with solutions of perthiocarbonic acid (H_2CS_4) in chloroform, toluene, and light petroleum, and the sodium salt has been measured in aqueous solution. Very large differences are found between the spectra of the acids and those of the salts. These differences are shown by changes in the colour, which are similar to those observed with indicators. The actual existence of the free acid is amply proved by the similarity of the absorption spectrum of a solution of the sodium salt with that obtained for a solution prepared by shaking an organic solution of the acid with sodium hydroxide. The absorption curves of the acids in various solvents differ relatively little from one another, and in no case are they similar to those of the salts. The curve for the ester is similar to that of the acid, but shows a considerable displacement, and in no case can the curve for the acid be made up from the curves for the salt and ester. The absorption spectra of ethyl-thiocarbonic acid in organic solvents and its potassium salt in water and alcohol solution have also been obtained. In this case also, a marked optical effect is observed on the formation of the salt. The introduction of the first and second ethyl groups into the trithiocarbonic acid molecule produces similar displacements of the absorption spectrum. *p*-Chloro- and *p*-bromobenzyl-trithiocarbonic acids have been prepared. These substances are solid and fairly stable. The absorption spectra of the chlorobenzyl acid and of its potassium salt have been obtained and show the same differences as those found in the case of the ethyl acid and its potassium salt. The chlorobenzyl acid has a normal molecular weight in benzene solution. The velocity of decomposition of trithiocarbonic acid, perthiocarbonic acid, ethyl-trithiocarbonic acid, and *p*-chlorobenzyl-trithiocarbonic acid has been determined in several organic solvents, and it is shown that the influence of the solvent

on the decomposition is generally the same as in the case of the xanthic acids (A., 1913, ii, 312; 1918, ii, 222). The behaviour of the *p*-chloro- and *p*-bromo-benzyl acids towards the diazo-esters depends on the solvent in a way which is entirely different from that found by Hantzsch for oxygen acids (this vol., ii, 475). J. F. S.

Colour of Inorganic Compounds. W. BILTZ (*Z. anorg. Chem.*, 1923, 127, 169—186, 372; cf. Meisenheimer, A., 1921, ii, 364).—An attempt to provide a theory of the colour and constitution of inorganic compounds. Unsaturation is shown to be the chief factor in determining such colour. "Mixed" compounds formed by the union of compounds of elements in different states of oxidation show a deeper colour than either of the parent compounds, whether the components contain the same element or not. Thus AuCl is bright yellow, and AuCl_2 is orange, whilst Au_2Cl_4 is nearly black. Similarly, ZnO and Al_2O_3 are both colourless, but $\text{ZnO} \cdot \text{Al}_2\text{O}_3$ is violet. Magnetic power is also associated with colour—iron, cobalt, nickel, manganese, vanadium, copper, and chromium are all chromophores. Again, both "sub-" and "super-" compounds are coloured, and may be regarded as unsaturated. In the case of substances which contain elements of variable valency, it is found that the colour deepens as the valency decreases, if the normal valency is the highest, and conversely. Dissociation deepens colour because it increases unsaturation; and, in general, the stronger the linking between elements, the less the colour of the resulting compound. H. H.

Determination of Coefficients of Absorption. H. A. C. DENIER VAN DER GON (*Arch. Néerland.*, 1923, 7, 140—155).—Employing a thermopile and galvanometer to indicate the respective intensities of the incident and transmitted radiation, the author has determined the coefficients of absorption, at about 20° , of aqueous solutions of cupric chloride containing from 0.310 to 4.50 g.-mols. per litre, and of aqueous solutions of copper sulphate containing, respectively, 0.190 and 1.15 g.-mols. per litre, for radiation of wave-length from $411 \mu\mu$ to $810 \mu\mu$. The results indicate that in the case of the solutions of copper sulphate, Beer's law is approximately obeyed in the case of radiation of wave-length greater than $550 \mu\mu$. A like result holds in the case of the solutions of cupric chloride for wave-lengths in the neighbourhood of $565 \mu\mu$. In this region, the respective absorption curves, drawn by plotting the logarithm of the respective coefficients of absorption as ordinates against the corresponding wave-lengths as abscissæ, are coincident, whilst for radiation of greater wave-lengths, the curves differ only slightly. Absorption in these cases is attributable to the copper contained in the solutions. Each curve exhibits a well-marked minimum at a point corresponding with a shorter wave-length than that referred to. J. S. G. T.

Colour and Chemical Constitution. XVIII. Colourless Substances in Sulphuric Acid (Halochromy). JAMES MOIR (*Trans. Roy. Soc. S. Africa*, 1923, 11, 91—93; cf. this vol., ii, 108).—A method has been discovered for predicting the colour produced

when certain colourless substances are dissolved in concentrated sulphuric acid (halochromy). The laws are apparently simpler than for aqueous solution, a single set of colour factors applying to all substances. The absorption is generally above λ 360. The absorption can be calculated from that of a parent substance (*p*-hydroxybenzyl alcohol) by multiplying by colour factors depending on the difference of the compound from the parent substance. The absorption of *p*-hydroxybenzyl alcohol is λ 488. The substitution factors are : phenyl for hydrogen 0.96; phthalein or $C_6H_4 \cdot CO_2H$ for hydrogen, 1.01; hydroxyphenyl for hydrogen, 1.02; hydroxyphenyl for phenyl, 1.06; bridge oxygen, 0.87; hapton oxidation, e.g., benzhydrol to benzophenone, 0.89 or 0.70. E. H. R.

The Colour of Monocyclic Substances Calculated by Assigning an Absorption Band to Each Possible Tautomeric Form. JAMES MOIR (T., 1923, 123, 2792—2803.)

The Absorption Spectrum of Chloroform in the Near Ultra-red. J. W. ELLIS (*Physical Rev.*, 1922, 19, 546).—Five distinct bands were observed with maxima at 1.140μ , 1.385μ , 1.660μ , 1.835μ , and 2.425μ , the percentage of absorption being, respectively, 10, 16, 56, 35, and 88. The error may be $\pm 100 \text{ \AA}$. A. A. E.

The Ultra-violet Absorption of Anthracene and Benzene. J. M. HYATT (*Physical Rev.*, 1922, 19, 391—393; cf. Howe, *ibid.*, 1916, 8).—For a solution of anthracene in ethyl alcohol, fourteen bands having frequency numbers 2650, 2700, 2800, 2840, 2945, 2990, 3095, 3130, 3240, 3410, 3540, 3688, 3975, and 4115, respectively, were observed. The numbers fall into two series with mean frequency intervals of 147 and 142, respectively. For a solution of benzene in ethyl alcohol, ten bands were observed, as follows : 3720, 3780, 3830, 3920, 4015, 4120, 4210, 4295, 4365, 4465. A. A. E.

Radiochemistry and Fluorescence. JEAN PERRIN (*Compt. rend.*, 1923, 177, 665—666; cf. this vol., ii, 714).—The thermal coefficient of the disappearance of new-methylene-blue in glycerol solution, in absence of air and under the influence of light, is 1.6 for temperatures between 19° and 81° , giving 9×10^{13} for the frequency of the infra-red rays which produce critical glycerol molecules. With constant illumination, for concentrations below 5%, the disappearance obeys the law of mass action at the above temperatures. That is, the concentration of critical mols. of dye is always proportional to the concentration of unactivated dye. New-methylene-blue disappears 1,200 times as rapidly as fluorescent-blue, the thermal coefficients, however, being the same. The second blue therefore reacts with the same kind of critical glycerol molecules, produced either by absorption of infra-red radiation or by equivalent intermolecular shocks. A previous deduction, that the direct action of a critical molecule (produced using external radiation) on a non-critical molecule should be unaffected by variations of temperature, is now proved for uranine and eosin (sodium salt), the disappearance-velocities of which are unaffected by temperature elevations of 60° and 90° , respectively. E. E. T.

The Luminescence of Solidifying Antimony. E. KARRER (*Physical Rev.*, 1922, 19, 437—438).—When heated at a temperature above its melting point, antimony becomes bright red; on cooling, the brightness decreases with the temperature until solidification commences, when a sudden increase in brightness occurs, accompanied by an increase in temperature. Moreover, the brightness after the flash appears greater for a given temperature than the brightness at the same temperature before the flash. It thus appears to be a case of crystal-luminescence; the phenomenon is not due to oxidation of the antimony, since it takes place in hydrogen or in a vacuum.

A. A. E.

Determinations of Structure in Conformity with the Electron Theory. C. J. ENKLAAR (*Rec. trav. chim.*, 1923, 42, 1000—1016).—The author treats refractive dispersion from the point of view of valency electrons and considers that every atom in a saturated open-chain compound has the same number of dispersion electrons as it has valencies. Satisfactory agreement is found in many cases quoted. In benzenoid compounds, however, he finds that each carbon atom possesses twelve, instead of four, dispersion electrons, if it occurs in the nucleus, and, further, that the same is true of unsaturated carbon atoms in open-chain compounds. Determinations of the refractive dispersion of cyanogen lead to the adoption of the formula $N\equiv C\cdot C\equiv N$ for this compound. The theory is also applied to the determination of the structure of 1 : 3 : 5-trienes.

H. H.

Mutarotation. II. C. N. RIEBER (*Ber.*, 1923, 56, [B], 2185—2194).—In continuation of previous work (A., 1922, ii, 807), it is shown that the change in refractive index of aqueous solutions of dextrose when preserved takes place exactly parallel to the alteration in specific rotation and in accordance with the equation for a uni-molecular reaction. The velocity constant and the half period is the same as that deduced from measurement of specific rotation or change in volume of the solution, and the three phenomena are therefore attributable to the same cause.

The equilibrium between α -glucose, β -glucose, and glucose hydrate in aqueous solution has been fully examined; solutions of any modification containing 10% of anhydrous substance are identical after twenty-four hours as judged by density (d_4^{20} 1.037881), specific rotation ($[\alpha]_D^{25} + 52.1^\circ$), or refractive index (n_D^{20} 1.34778). If α - and β -glucose are actually in equilibrium in solution, it follows that the opposite physical changes must be observed on solution of the two varieties. This has been shown previously to be the case with the specific rotation, and is now found to be true for density, index of refraction, and heat of reaction. The actual establishment of an equilibrium is more firmly established by the observation that the half period of α -glucose is the same as that of β -glucose as determined by dilatometric, refractive, or polarimetric methods. Further, it is found that a solution of α -glucose (3.61 g.), and β -glucose (6.39 g.) in water (90 g.) does not change in density, refractive index, or specific rotation when preserved.

Glucose hydrate has frequently been considered to be an ortho-form of the true aldehyde, and not a hydrate in the usual sense. Trey's observation that solutions of glucose hydrate undergo contraction when preserved appears, however, to be erroneous, since a dilation takes place which is of the same magnitude as that observed with anhydrous glucose. Examination by the three methods has failed to disclose any difference between solutions of glucose and the hydrate which contain the same amount of anhydrous material and are of the same age. The author therefore draws the conclusion that there is no evidence of the existence of an appreciable amount of glucose hydrate or the ortho-form of glucose in aqueous solution, although the possibility is not excluded that it may be present in an amount too small to be detected by the physical methods employed, as is indicated by the behaviour of the solutions towards hydroxylamine and phenylhydrazine.

The opinion has been frequently expressed that mutarotation is impossible in the absence of a solvent. It is shown, however, that if dehydrated α -glucose is melted and cooled rapidly to the atmospheric temperature it has then an initial specific rotation of about 50° in water; the same result is observed when β -glucose is employed. Apparently, therefore, the fused masses are identical and consist (mainly) of an equilibrium mixture of the α - and β -forms. This is supported by the observation that the seeding of the under-cooled melt with α - or β -glucose induces the complete crystallisation of it as the α - or β -form, respectively, whereas a mixture of the two varieties is formed when a mixed seed is used.

Mutarotation, therefore, may be induced by melting an optically active substance, by bringing such a substance into solution, or by alteration in the concentration or temperature of the solution of the substance.

H. W.

Magnetic and Natural Rotatory Dispersion in Absorbing Media. E. O. HULBERT (*Physical Rev.*, 1923, 22, 180—187).—By a consideration of absorption of the radiation in a transparent medium, more complete formulæ for rotatory dispersion than those hitherto put forward have been derived. Certain approximations have been made, and simplified formulæ obtained which give the rotation for wave-lengths sufficiently removed from the critical wave-length, provided the refractive index and extinction coefficient conform to the Lorentz dispersion equations with one resonance frequency. In the case of carbon disulphide and 1-bromonaphthalene, the equation of magnetic rotation in isotropic media agrees closely with the experimental results.

A. A. E.

Action of Red and Infra-red Radiations on Photo-luminescent Substances. MAURICE CURIE (*J. Chim. Phys.*, 1923, 20, 292—307).—The action of red and infra-red radiation on photo-luminescent substances has been investigated in the case of zinc sulphide and calcium sulphide. In the case of zinc sulphide, it is shown that a black spot is formed on a background of brilliant luminescence at the point where the infra-red rays are concentrated. This fact indicates that these rays not only excite luminescence, but also

destroy it. When the sulphide is removed from the rays, a very brilliant luminescence is seen at one spot followed by a very dark band. This reinforcement of the luminescence varies in intensity and in the time of its duration with the nature of the phosphorescent substance. With zinc sulphide containing copper, the colour is green, and it is maintained for a much shorter time than with zinc sulphide containing manganese, in which case the colour is yellow. There are no resonance phenomena observable in the present experiments.

J. F. S.

Darkening of Zinc Sulphide by Light. ARTHUR SCHLEEDE [with M. HERTER and W. KORDATZKI] (*Z. physikal. Chem.*, 1923, **106**, 386—398).—Zinc sulphide prepared in various ways has been examined in connexion with its darkening under the influence of light. It is shown that precipitated and non-ignited zinc sulphide does not darken under any conditions of illumination. Ignited zinc sulphide which is free from materials with which it has been heated, shows a sensitiveness towards light from a quartz mercury lamp when the temperature of ignition is so high that measurable quantities of wurzite are formed. The zinc blende form of zinc sulphide is not affected by ultra-violet light from a mercury lamp. The presence of small quantities of heavy metals makes no change in the action of light in these cases. Crystallised zinc sulphide containing halogen compounds is sensitive to the long wave-length ultra-violet light, and the presence of small quantities of heavy metals intensifies the action. The sensitiveness of halogen containing zinc sulphide can be removed by washing the material, so far as the long wave-length ultra-violet light is concerned, but this has no effect on short wave-length ultra-violet light effect or on the phosphorescence. Sensitiveness to long wave-length ultra-violet light is apparently induced by fusing zinc sulphide (wurzite) with a halogen salt.

J. F. S.

Temperature Coefficient of Photochemical Reaction Rate. RICHARD C. TOLMAN (*J. Amer. Chem. Soc.*, 1923, **45**, 2285—2296).—A theoretical paper in which, on the basis of the quantum hypothesis, a simple equation for the temperature coefficient of photochemical reaction velocities has been derived. The equation agrees with that previously obtained (A., 1921, ii, 99) by the author using the methods of statistical mechanics. The existing data on temperature coefficients of photochemical reactions have been successfully interpreted with the help of the equation. It has been shown that Plotnikov's division of photochemical temperature coefficients into three distinct classes is apparently not tenable. An equation for change in temperature coefficient with frequency has been derived and used successfully in interpreting existing data. The causes of apparent deviations from Einstein's law of photochemical equivalence have been discussed.

J. F. S.

Theory of Radiation Transformation. II. Photochemical Chlorine Reaction. FRITZ WEIGERT (*Z. physikal. Chem.*, 1923, **106**, 407—432; cf. this vol., ii, 3).—A theoretical paper in which

as an example of a photochemical chlorine reaction the decomposition of ozone in the presence of illuminated chlorine is discussed. The facts, that the velocity of the reaction is independent of the ozone concentration and that, according to Bodenstein and Bonhoeffer (*Z. Physik*, 1923, **13**, 94), it takes place in accordance with the quanta of light energy absorbed by the chlorine, show that an upper limit of the concentration of ozone exists at which the whole of the light energy absorbed by the chlorine is converted into chemical energy. The same case is found in the sensitisation of the hydrogen dissociation for the resonance lines of mercury by dilute mercury vapour. In this case, with a limiting pressure of hydrogen, practically the whole of the absorbed resonance energy is converted into chemical energy. The limiting pressures of the reacting molecular species, ozone 0.5 mm. and hydrogen 10 mm. of mercury, and their relationship to the pressure of the sensitising molecules (chlorine $\frac{1}{2}$ atm., mercury 0.009 mm.) are widely different. The quantity relationship n_r/n_s in the case of the chlorine-ozone reaction is 1.3×10^{-3} , and for the hydrogen-mercury reaction 1.1×10^3 . If, on the other hand, the number of molecules is calculated in layers which produce the same amount of weakening of the radiation, they will be found to be the same in the two reactions. It is therefore likely that in both processes the initial stage is the same. The hypothesis is advanced that the radiation absorbed by the excited molecules is at first re-emitted as resonance radiation in the normal manner, and that this absorption and emission process is repeated so often that at last the absorption leads, in a binary absorption system, to an internal photoelectric effect, whereon a chemical process or a translatory displacement of the particles follows. Whereas the resonance radiation with mercury, on account of the extremely strong absorption of the mercury vapour for the exciting resonance line, is easily observed, this can scarcely be expected in the case of chlorine with its hundred million times smaller absorption constant. But there are indirect reasons for the non-thermal absorption of pure chlorine. The thermal increase in volume during radiation is only to be observed in the presence of moisture or other impurities. According to this view, the transformation of absorbed energy to the chemical reacting system does not occur simultaneously with the absorption of the radiation; the process requires, on account of the repeated absorption and emission of a once absorbed energy quantum, a definite time before it is completed. The energy quantum remains, in a sense, in the reacting system until it is entirely used up. The measurement of such short retardations can be carried out by the new Weigert and Kellermann method (A., 1922, ii, 808). The application of this method to the photochemical chlorine-hydrogen reaction has shown a retardation of about 1/100 sec. It is, however, not certain that this measured delay is due to the above effect, since the yield in this reaction is much larger than Einstein's law demands. The delay can also be explained by assuming a long chain of reactions. Many such mechanisms have been put forward which are discussed. A special photoelectric effect is assumed, which may represent the primary

process by which the chlorine-hydrogen reaction is started. This assumption does away with the necessity of assuming excited chlorine molecules and a splitting of the molecules into atoms. It may be concluded that ozone will be decomposed by long wave-length ultra-violet radiation in the absence of any other substance, and that perhaps the radiation absorbed by the chlorine falls in the ozone absorption band and that during the repeated absorption and re-emission it is used up in this weak absorption region.

J. F. S.

The Photochemical Reactivity of Ozone in presence of Other Gases. I. ROBERT OWEN GRIFFITH and WILLIAM JAMES SHUTT (T., 1923, 123, 2752—2767).

The Photochemical Reactivity of Ozone in presence of Other Gases. II. ROBERT OWEN GRIFFITH and JANE MACWILLIE (T., 1923, 123, 2767—2774).

Decomposition of Ammonia by Ultra-violet Rays, and the Law of Photochemical Equivalence. W. KUHN (*Compt. rend.*, 1923, 177, 956—957).—The decomposition of ammonia, prepared by heating its silver chloride derivative, has been studied in quartz vessels, monochromatic light of known wave-length (from 2025—2140) being used as the source of energy. (In complete light, the decomposition proceeds to completion, at a speed proportional to the energy absorbed. Aqueous solutions of the gas undergo no decomposition under similar conditions.) The number of quanta absorbed by 1 mol. of ammonia, undergoing decomposition, varies from 2—2.5, and is independent of the pressure (900—5 mm.). For temperatures of 10—20°, the speed of decomposition is independent of t , and, generally, this speed is not affected by the size of the quartz surfaces (whereas the thermal dissociation is accelerated by quartz surfaces). The speed of decomposition is also unaffected by the addition of metallic sodium, and is therefore independent of the action of minute traces of water. With monochromatic light of $\lambda = 2063$, the number of quanta necessary to decompose 1 mol. of ammonia is 3.4, or as many as 10 if the monochromatisation is very perfect. From the heats of dissociation for $N_2 = N + N(-140,000 \text{ cal.})$, $H_2 = H + H(-84,000 \text{ cal.})$, and $NH_3 = 0.5N_2 + 1.5H_2(-11,000 \text{ cal.})$, whence $NH_3 = N + H_2 + H - 123,000 \text{ cal.}$, and $NH_3 = N + H + H + H - 207,000 \text{ cal.}$, it follows that a quantum $h\nu$ for the ray 2063 corresponds with 128,000 cal. per g.-mol. The energy furnished by the absorption of a quantum suffices for the first, but not for the second change. On these lines may be explained the facts that several quanta are required to decompose 1 mol. of ammonia, and that the speed of decomposition depends on the perfectness of monochromatisation of the ultra-violet radiation.

E. E. T.

The Photochemical Decomposition of Silver Bromide. II. ROBERT SCHWARZ and HEINRICH STOCK (*Z. anorg. Chem.*, 1923, 129, 41—54; cf. A., 1921, ii, 614).—Attempts were made to find the relationship between the age and the photochemical decom-

position of silver bromide, using the mercury lamp as a source of light. Very irregular curves were obtained, however, the irregularities being ascribed to (1) moisture, the loss of which decreased the rate of separation of bromine, and (2) grain size, which increased with age. Colloidal sols act as catalysts; silica is a positive and platinum, zirconium hydroxide, stannic acid, and gelatin negative catalysts.

W. T.

The Formation of Organic Compounds from Inorganic by the Influence of Light. OSKAR BAUDISCH (*Science*, 1923, 57, 451—456).—The observation that cholera bacilli rapidly reduce nitrates to nitrites, the velocity of the reaction being dependent on the bacterial iron content, led to a study of the catalytic effect of iron in the reduction of nitrates and nitrites. Dextrose in alkaline solution reduces nitrites, but not nitrates, and then only in the presence of traces of iron. Ferrous hydrogen carbonate or hydroxide does not reduce alkali nitrates even at 100° in the absence of oxygen; the presence of oxygen, however, causes immediate reduction to nitrite, and there is a direct relation between the amount of oxygen dissolved in the water and the amount of nitrite formed. This "fertilisation" process involves the production of a peroxidic iron compound, nitrite, and the reactive intermediate substance potassium nitrosyl, KNO. The latter substance reacts with aldehydes with the formation of hydroxamic acids, OH·CR.N·OH. It is considered that the magnetic properties of the peroxide are in direct relation to its great chemical activity. The action of potassium pentacyanoperoxoferroate, $K_3[FeO_2(NC)_5]$ in behaving as an oxygen carrier and activator is likened to a simple type of respiration. Whilst light of long wave-length brings about the formation of an alkaline aquo-base from potassium ferrocyanide solution, the reduction of alkali nitrates is effected only by light of short wave-length. In summer sunlight, alkali nitrates can be reduced to nitrite in a short time if small quantities of complex salts, e.g., potassium ferrocyanide, are present. Formaldoxime and formaldehyde in sunlight form cyclic nitrogen compounds which contain pyridine and pyrrole rings and give the typical alkaloidal reactions. An aqueous solution of acetaldoxime and formaldehyde when exposed to sunlight gives a thick, dark brown syrup which has not been investigated. Nitromethane also unites with formaldehyde under the influence of light, or in weakly alkaline solution, *iso*-nitrobutylglycerol being formed intermediately. The author's observations of the formation of formhydroxamic acid, methylamine, alkaloids, and α -amino-acids have been confirmed and extended by Baly. Illumination of alkali nitrates with daylight in the presence of formaldehyde yields gases agreeing qualitatively with those formed by soil bacteria, and (in the presence of iron salts) formhydroxamic acid and formaldoxime. It is thought possible that many soil bacteria and also green leaves utilise nitrous oxide from the air for nitrogen nutrition. Although at considerable altitudes, or by the influence of silent electric discharges, carbon dioxide can be reduced to formaldehyde, which may then react

with nitrous oxide from atmospheric nitrogen and oxygen to yield formhydroxamic acid, it is not thought possible that the reduction can be effected by sunlight at sea level without the aid of chlorophyll.

A. A. E.

Relation between the Energies of Alpha-particles and the Atomic Numbers of the Elements. L. MYSSOWSKY (*Z. Physik*, 1923, **18**, 304—306).—It is shown that the great majority of the radioactive elements can be arranged on four parallel and equidistant straight lines, drawn so that abscissæ represent atomic numbers, and ordinates the respective kinetic energies of the α -particles emitted from the elements. The position of thorium is uncertain. Thorium-*C*, actinium-*C*, uranium-II, and radium-*C* do not lie on the straight lines, and it is pointed out that at these elements the radioactive series branch.

J. S. G. T.

Cathode-ray Furnace. HANS GERDIEN and HANS RIEGGER (*Wiss. Veröffentl. Siemens-Konzern*, 1923, **3**, 226—230).—A cathode-ray furnace, employing an exhausted spherical glass flask of diameter up to 50 cm., silvered externally or surrounded by acidified water, and provided with a cylindrical neck is described. Cathode rays emitted normally from the external electrode described impinge radially on the material to be heated, supported at the centre of the sphere on a rod passing axially through the neck of the flask. The use of an external electrode permits the furnace being operated with high-tension high-frequency current.

J. S. G. T.

Cathodoluminescence of Heated Alumina. D. T. WILBER (*Physical Rev.*, 1922, **20**, 101).—Ordinary powdered alumina, built up into a fritted cone, when freshly prepared shows coloured bands under cathode rays. The component ruby, green, blue, and orange bands appear in areas within restricted temperature limits. The ruby bands are due to the presence of minute traces of chromium. A mixture of alumina and magnesia in molecular proportions with 1% of manganese gave a brilliant green band; alumina and lime with manganese as active metal gave a broad band in the yellow and green. Alumina and lime with copper gave a band in the blue.

A. A. E.

The Excitation of Characteristic X-Rays from certain Metals. FRANK HORTON, URSULA ANDREWES, and ANN CATHERINE DAVIES (*Phil. Mag.*, 1923, [vi], **46**, 721—741).—The authors have investigated the voltages connected with some of the longer wavelength X-ray absorption limits in the case of the elements aluminium, iron, nickel, copper, and zinc, employing for this purpose the excitation potential method (cf. Kurth, A., 1922, ii, 410). The following respective critical values of the potential (expressed in volts) were determined: aluminium, 42, 66, and 107; iron, 73 and 166; nickel, 104 and 178; copper, 112 and 193; zinc, 119 and 200. By extrapolating the Moseley curves for the various absorption limits to low atomic numbers, it was found that the lower and higher values determined in the cases of the metals iron, nickel, copper, and zinc

were respectively associated with $M^{II, III}$ and M^I levels. The changes in the slopes of the M^I and $M^{II, III}$ curves in passing through the observed points support the view that a change in the constitution of the M electronic group occurs during the passage from one of these elements to another. Likewise, the results indicate that the development of the second M sub-group from four electrons to six electrons does not commence before the element cobalt (atomic number 27), and that the similar development of the first M sub-group commences at a lower value of the atomic number. By similar extrapolation of the Moseley curves for the L absorption, it was found that the critical potentials 66 volts and 107 volts found in the case of aluminium are respectively associated with the $L^{II, III}$ and L^I levels. From analogy with the anomalous K absorption limits found by Fricke for titanium, vanadium, and chromium (A., 1921, ii, 6), it is probable that the value, 42 volts, found for aluminium is associated with the displacement of an electron from the second L sub-group to the first M sub-group.

J. S. G. T.

Luminescence Produced by Röntgen Rays. A. JAUBERT DE BEAUJEU (*J. Phys. Radium*, 1923, 4, 257—267).—Particulars are given of the principal wave-lengths and relative intensities of the fluorescence excited in various solid solutions of the rare earths, and in a large number of organic solid substances, by the incidence of Röntgen rays. Amongst the latter substances, aromatic compounds exhibit the phenomenon most markedly, and it is suggested that, in these cases, fluorescence is attributable to the presence of the benzene ring.

J. S. G. T.

The Secondary Corpuscular Rays produced by Homogeneous X-Rays. H. ROBINSON (*Proc. Roy. Soc.*, 1923, [A], 104, 455—479).—In continuation of previous work (A., 1914, ii, 696), the author has investigated the "line spectra" of the secondary corpuscular radiation emitted from targets of bismuth, lead, gold, tungsten (metal and WO_2), barium ($BaCO_3$), iodine (LiI and AgI), tin, silver (metal and AgI), molybdenum, strontium ($SrCO_3$), copper, and various light atoms, including calcium, potassium, sulphur, magnesium, sodium, and oxygen, by the incidence of X-rays corresponding with the copper $K\alpha_1$ radiation. The various measurements are considered to be correct to within 1 part in 1000 parts. In general, the respective values of the energy levels of the emitted radiations agree very closely with those tabulated by Bohr and Coster. The apparatus enabled the three limits of L -radiation to be determined as far down as strontium (38). Five M rings were identified in the case of bismuth (83) and tungsten (74). The N -rings of bismuth were likewise identified. In the case of the heavier elements (barium to molybdenum), the L^{III} level is the most effective in the emission of secondary electrons and L^I the least effective, in agreement with deductions from X-ray data. With decreasing strength of binding, the differences between the effects of the different rings become appreciably less pronounced. In the case of strontium, the three L lines are of approximately

equal intensity, whilst with copper L_1 is just perceptibly the strongest line. The M and N levels likewise show a similar changing over of high intensity from the "softer" to the "harder" subgroups.

J. S. G. T.

Long-range Particles from Radium-active Deposit. GERHARD KIRSCH and HANS PETTERSSON (*Nature*, 1923, **112**, 687).—A reply to Bates and Rogers (this vol., ii, 720). The difference in brightness between the scintillations from α -particles and those from hydrogen particles, viewed under identical conditions, is so conspicuous that no mistake is possible. A small number of scintillations of the α -type was generally observed in addition to the much fainter hydrogen scintillations, especially at the lowest values of absorption. These particles are for the time being assumed to be identical with those found by Rutherford (A., 1919, ii, 258) to be expelled from oxygen. The former view, that the particles are hydrogen particles expelled by artificial disintegration of the glucinum, magnesium, silicon (and probably also lithium) atoms is upheld.

A. A. E.

The Relative Activities of Radioactive Substances in an Unchanged Primary Uranium Mineral. W. P. WIDDOWSON and A. S. RUSSELL (*Phil. Mag.*, 1923, [vi], **46**, 915—929).—The work of Boltwood (A., 1908, ii, 454) on the relative activities of the radioactive constituents of an unchanged primary uranium mineral (pitchblende) has been carefully repeated. The results obtained agree with those previously obtained, indicating the lowness of the relative activity of the mineral to that of its uranium content, but disagree therewith as regards the relative activities of polonium, ionium, radium, and uranium. The values found for these agree closely with those deduced theoretically. The ratio of the activity of the actinium series to that of the radium series is found to be 0.29, in agreement with the result obtained by Hahn and Meitner (A., 1920, ii, 148).

J. S. G. T.

The Relative Deposition of Radium and Barium Salts as a Function of Temperature and Acidity. W. B. PIETENPOL (*Physical Rev.*, 1922, **20**, 199).—It is found that the first crystals formed in a radium-barium solution contain a larger percentage of radium than succeeding crystals. The efficiency and rapidity of the separation by fractional crystallisation may be increased by separating the liquor from the crystals at a point above room temperature. With rapid cooling, a smaller percentage of radium is adsorbed than with slow cooling.

A. A. E.

Ionisation and Resonance Phenomena. CHARLES B. BAZZONI (*J. Franklin Inst.*, 1923, **196**, 627—651).—Bohr's theory of atomic structure and the mechanism of radiation are briefly reviewed, and experimental determinations of resonance and ionisation potentials, more especially in the cases of helium and mercury, and the excitation of resonance spectra, critically examined in relation to the theory. The author concludes that the impact potentials of helium require further study.

J. S. G. T.

The Fundamental Processes concerned in the Thermal Ionisation of Gases. RICHARD BECKER (*Z. Physik*, 1923, **18**, 325—343).—The author discusses the fundamental processes, viz., ionisation due to absorption of radiation, ionisation by electronic collisions, and the disappearance of electrons due to combination either with or without the emission of radiation, concerned in the establishment of equilibrium in a thermally-ionised system, and deduces the equilibrium equation relating to the thermal ionisation of monatomic and univalent gases by the application of statistical mechanics and the quantum theory. J. S. G. T.

New Evidence regarding the Interpretation of Critical Potentials in Hydrogen. P. S. OLMSTEAD (*Physical Rev.*, 1922, **19**, 532—533).—A relatively small amount of atomic hydrogen is produced when a close grid of tungsten wires, introduced close to the gauze in an ionisation tube of the Lenard type, is heated to incandescence. It is shown that the ionising potential of the hydrogen atom is 13.5 volts; the critical potential of ionisation of the molecule, probably without dissociation, is about 11.5 volts, and a weaker effect, ascribed to radiation from the atom, at about 10.2 volts. The strongest effect, dissociation of the molecule and ionisation of one of its parts, is put at 16 volts. A. A. E.

Critical Electron Energies in Hydrogen. FRANK HORTON and ANN CATHERINE DAVIES (*Phil. Mag.*, 1923, [vi], **46**, 872—896).—In continuation of previous work (A., 1920, ii, 215), the authors have made a detailed investigation of the effects of electron collisions with hydrogen, in order to determine more exactly the critical electron energy values, and to ascertain whether the radiation or ionisation occurring at a critical stage is of atomic or molecular origin. The results indicate that critical energy values (expressed in volts) are associated with respective processes as follows: 10.2, $H \rightarrow H(\text{excited})$; 11.9, $H_2 \rightarrow H_2(\text{excited})$; 12.6, $H_2 \rightarrow H + H(\text{excited})$; 13.5, $H \rightarrow H^+ + \text{electron}$; 15.9, $H_2 \rightarrow H + H^+ + \text{electron}$; 22.8, $H_2 \rightarrow H_2^+ + \text{electron}$; 26.1, $H_2 \rightarrow H^+ + \text{electron} + H(\text{excited})$; 29.4, $H_2 \rightarrow 2H^+ + 2 \text{ electrons}$. These deductions are in agreement with the interpretation by Olmstead (this vol., ii, 367) of the critical values observed at 10.2, 12.6, 13.5, and 15.9 volts, but differ in respect of the interpretation of the critical energy stage included between 10.2 and 12.6 volts. The present authors' deduction in this matter is in accord with the value of the resonance potential of normal hydrogen (11.8 volts) deduced by Mohler, Foote, and Kurth (*Physical Rev.*, 1922, **19**, 414) from the consideration of inelastic collision curves. The present experiments establish the existence of a true molecular radiation as distinct from a radiation produced by electronic-molecular encounters at which dissociation and atomic excitation occur. They also support Pauli's suggestion (A., 1922, ii, 703) that the production of positively charged hydrogen molecules requires energy equivalent to about 23 volts. The spectroscopic results obtained are in general agreement with those of Duffendack (this vol., ii, 373), except for the observation of a number of lines of group II of Fulcher's classification,

viz., $\lambda\lambda$ 5916.8, 5931.6, 5938.9, and 6028.2 Å., which were not observed by Duffendack at 23 volts. Moreover, a visible continuous spectrum of hydrogen can be produced in the absence of the Balmer series lines, and it is suggested that this spectrum originates owing to the formation of molecules (H_2 or possibly H_3) by the combination of neutral atoms.

J. S. G. T.

The Lengths of the Free Paths of Slow-moving Electrons in the Rare Gases. H. SPONER (*Z. Physik*, 1923, **18**, 249—257).—Experiments showing that the respective lengths of mean free path of slow-moving electrons in the rare gases, argon, krypton, and xenon increase continuously with decreasing velocity of the electrons until a velocity corresponding with zero accelerating voltage is attained, are described. In the case of krypton at a pressure of 1.2 mm., maximum values of the mean free paths of electrons resulting from inelastic collisions occur when the exciting potential has the value 8.4 ± 0.2 or 9.6 ± 0.2 volts. The corresponding voltages in the case of xenon are 8.0 and 8.8 volts. The ionisation potential of krypton was found to be between 12 and 13 volts; that of xenon was between 11 and 12 volts.

J. S. G. T.

The Lengths of the Free Paths of Slow-moving Electrons in the Vapours of Mercury and Cadmium. R. MINKOWSKI (*Z. Physik*, 1923, **18**, 258—262).—The author shows that, as in the case of the rare gases (see preceding abstract and Ramsauer, A., 1921, ii, 324), the respective lengths of mean free path of the slowest-moving electrons in mercury and cadmium vapours depend, although to a considerably less extent, on the velocities of the electrons. In the case of mercury vapour, maximum values of the mean free paths of electrons resulting from inelastic collisions correspond with values of the exciting potential equal to 4.7, 4.9, 9.8, and 11.6 volts. In cadmium vapour, the corresponding values are 3.7, 3.8, 5.4, 7.4, and 7.6 volts. Attention is, in this connexion, directed to the occurrence in the case of cadmium vapour, of the exciting voltage 3.7 volts, corresponding with the series $1S-2p_3$, a result hitherto observed only in the case of mercury vapour.

J. S. G. T.

Ionising Potentials of Helium and some Multiatomic Gases. C. A. MACKAY (*Phil. Mag.*, 1923, [vi], **46**, 828—835).—The following values (volts) of the ionising potential have been determined for the respective gases: helium, 24.5; nitrogen, 16.3; hydrogen, 15.8; oxygen, 12.5; hydrogen chloride, 13.8; hydrogen bromide, 13.2; hydrogen iodide, 12.8; ammonia, 11.1; water vapour, 13.2. The value for helium is in agreement with the convergence limit of Lyman's spectroscopic series. The value for oxygen is considerably lower than the value, 15.5 volts, found by Foote and Mohler.

J. S. G. T.

The Scattering of Electrons by Aluminium. C. DAVISSON and C. H. KUNSMAN (*Physical Rev.*, 1922, **19**, 534—535; cf. A., 1922, ii, 251).—Analysis of the distribution curves below 200 volts indicates that the L -electrons of aluminium are at a distance of about 3×10^{-9} cm. from the atomic nucleus. Above 200 volts the

distribution is complicated by the scattering effect of oxygen atoms on the surface of the target. A. A. E.

Relations between Supplied Energy, Spectral Intensities, and Alterations in Different Media. L. HAMBURGER (*Trans. Amer. Electrochem. Soc.* [advance copy], 1923, 307—318).—From the proportionality between the energy supplied to discharge tubes, the intensities of the spectral lines emitted and the pressure difference due to the transference of ponderable ions in the discharge, the author concludes that atoms both absorb and emit energy in quanta. The part played by partly ionised atoms in the phenomena of electroluminescence, effects due to collisions of slow-moving electrons with atoms, spectra excited otherwise than electrically, catalytic phenomena, and velocities of reaction are briefly referred to. The dependence of the reduction temperature necessary in the Bucher process for the fixation of nitrogen, on the nature of the carbonate employed is discussed with reference to the ionising and resonance potentials of the alkali and alkaline-earth metals. The unity of optical, chemical, and energy relations contemplated in the quantum theory and the Rutherford-Bohr interpretation of atomic structure indicates that chemical and physical changes do not differ essentially. J. S. G. T.

Problems of Hydrone and Water : the Origin of Electricity in Thunderstorms. G. C. SIMPSON (*Nature*, 1923, 112, 620; cf. Armstrong, this vol., ii, 772).—It is held to be conclusively proved that if there are ascending currents exceeding eight metres per second in the atmosphere, there must be much breaking of rain drops; that when a water drop breaks there is a separation of electricity; that the broken water drops retain a positive charge; that the air attains a negative charge, and that a considerable excess of positive electricity is brought down by rain. Armstrong's views are considered to be completely untenable. A. A. E.

The Electrical Conductivity of Solid Orthophosphoric Acid. MARK RABINOWITSCH (*Z. anorg. Chem.*, 1923, 129, 60—66).—The conductivity of orthophosphoric acid, $2\text{H}_3\text{PO}_4 \cdot \text{H}_2\text{O}$, was studied in the crystalline and supercooled states and found to be of the magnitude of 10^{-4} and 10^{-2} , respectively. The temperature coefficient was positive; a sudden change occurs on solidifying. The decomposition potential is given as 1.70 volts. The ratio of these conductivities is assumed to indicate the degree of loosening of crystal lattices (cf. Hevesy, A., 1922, ii, 623). The conductivity of anhydrous phosphoric acid decreases with the time; this change is associated with some change in the acid. W. T.

The Theory of Electrolytic Ions. XXVIII. The Conductivities of the Arsinic Acids. RICHARD LORENZ and ELISABETH BREHMER (*Z. anorg. Chem.*, 1923, 128, 76—80).—Continuing previous work (A., 1920, ii, 465; this vol., i, 406), the dissociation or affinity constant has been determined for a number of substituted phenylarsinic acids. The constant K is calculated from the formula $\alpha^2/1-\alpha C \cdot 10^{-3}$, and is therefore related to Kohlrausch's constant c ,

which is in *C.G.S.* units, thus: $c \cdot 10^5 = K$. The following values are given for *K* at the molar concentration 1/256: phenylarsinic, 0.027; *p*-hydroxyphenylarsinic, 0.015; *p*-amino-*o*-tolylarsinic, 0.014; *m*-methoxyacetarsanilic, 0.029; *p*-nitrophenylarsinic, 0.137; *o*-nitrophenylarsinic, 0.037; 2-nitroarsanilic, 0.0086; 3-hydroxyarsanilic acid (at 1/512), 0.0067. In general, the affinity constant of phenylarsinic acid is affected in the same way by substituents as benzoic acid. An exception appears in the cases of *o*-nitrophenylarsinic acid and *o*-nitroarsanilic acid, where the expected augmentation of the affinity constant by the *o*-nitro-group is not realised. On account of the low solubilities of 2-nitroarsanilic and 3-hydroxyarsanilic acids, their conductivities and affinity constants could only be determined at high dilutions and, in the case of the latter, owing to its rapid decomposition at the electrodes, the result is only approximate. E. H. R.

Electrical Resistivity of Commercial Aluminium. LÉON GUILLET (*Compt. rend.*, 1923, 177, 953—955).—The purest commercial aluminium has a resistivity of 2.8 micro-ohms per sq. cm./cm. Impurities may cause this figure to become even higher than 3.2 (for 89.5% metal). Silicon has a greater effect on the resistivity than iron, whilst mechanical treatment, even cold hammering, only increases the resistivity very slightly, particularly with the purer specimens of aluminium. In tempering, the more rapid the quenching, the higher the resistivity, probably owing to more silicon being retained in solution under these conditions. E. E. T.

Existence of Ions with a Dual Character. OTTO BLÜH (*Z. physikal. Chem.*, 1923, 106, 341—365).—The dipole theory is briefly discussed, and on the basis of this it is shown that amphoteric electrolytes, so far as they form true ions of dual character, must raise the dielectric constant of the solution containing them. Measurements of the dielectric constant of aqueous solutions of sulphanilic acid, helianthin, *o*-aminobenzoic acid, *p*-aminobenzoic acid, hippuric acid, and benzoic acid show that such dual ions exist in aqueous solutions of amphoteric electrolytes. It is shown that an internal salt and a dual ion are not the same thing. New measurements of the dielectric constant of aqueous solutions of strong electrolytes show that this quantity is lower than that for pure water, a result which accords with the dipole hypothesis, and is opposed to the result of earlier measurements. Water is considered as an amphoteric electrolyte, and the high dielectric constant of this liquid is regarded as a consequence of the presence of dual ions. On the basis of such dual ions, a mechanism of the conduction of an electric current by acids and bases is developed. J. F. S.

Electrical Resistance of Quinoline-Water Systems. MARTIN H. FISCHER (*Kolloid Z.*, 1923, 33, 208—215).—The electrical resistance of quinoline, solutions of water in quinoline, and of quinoline in water, of all concentrations up to a saturated solution, has been measured at 24°. The effect of the addition of acids, bases, salts, and ethyl alcohol on the electrical resistance has been

measured at 22° and 23°. Pure quinoline has a resistance of 400,000 ohms at 24°, and this value falls regularly with the addition of water to the value 80,000 ohms for the saturated solution. The addition of *N*/50-hydrochloric acid decreases the resistance very much, the amount of decrease being greater the greater the amount of acid added. The addition of *N*/50-potassium hydroxide produces a similar, but smaller, decrease in the resistance. Comparing the effect of various acids on the resistance, it is found that sulphuric acid has the greatest effect, and this is followed in order by hydrochloric, oxalic, acetic, and lactic acids. Of the bases, potassium hydroxide has the greatest effect, and is followed in order by sodium, calcium, and ammonium hydroxides. Salts generally reduce the resistance in a marked degree, as also does ethyl alcohol. These results are practically the same for both the water and the quinoline phases.

J. F. S.

Electrometric Measurements with Regard to Ionic Activity.

LEONOR MICHAELIS and KOSAKU KAKINUMA (*Biochem. Z.*, 1923, **141**, 394—409).—Electrometric measurements have been made on acid and alkaline, salt and salt-free solutions with the view of determining the relation between ionic concentration and Bjerrum's activity coefficient (*A.*, 1919, ii, 9; 1920, ii, 79) at varying dilutions. Measurements of the potential differences of pure solutions of hydrochloric acid against a standard acetate electrode showed that in concentrations below *M*/30 the activity coefficient of the hydrogen-ions is unity, and the activity is regarded as being equal to the concentration of the acid. The influence of rubidium, potassium, sodium, and lithium chlorides on the activity of the hydrogen-ions in buffered and unbuffered solutions of hydrochloric acid solutions is in the order given, rubidium showing the least and lithium the greatest influence in increasing the activity. Similar determinations of the influence of salts on the activity of hydrogen-ions in alkaline solutions showed the effect to be greater than that observed in acid solutions. For salt-free solutions of sodium hydroxide of concentrations less than *M*/30 the solute is fully dissociated and the activity of the hydroxyl-ions is unity. From the sum of p_H and p_{OH} of solutions of sodium hydroxide ranging in concentration from *M*/30 to *M*/3000 values of the dissociation constant of water were obtained; pK_w^{17} is given as 14.13 and pK_w^{19} as 14.10. It is concluded that on thermodynamical grounds neutral salts are without influence on the dissociation constant of water, but an exact experimental demonstration is not given.

J. P.

Amphoteric Elements. J. KASARNOWSKY (*Z. anorg. Chem.*, 1923, **128**, 33—44).—The measurement of the normal potential of the system Te/Te'' presents difficulties which have not yet been surmounted, but by applying Nernst's heat theory to the reaction $H_2Te = H_2 + Te + 34,900$ cal. the value has been calculated to be about -0.913 volt. The *E.M.F.* of the system $Te|1 \text{ mol. } Te'''||1 \text{ mol. } Te''|Te$ would be 1.48 volts and the ion product $[Te''']/[Te'']^2$ $0.85 \cdot 10^{-102}$. For the reaction $Te_2'' \rightleftharpoons Te'' + Te$, the value of the constant $K = [Te'']/[Te_2'']$ is $0.39 \cdot 10^{-2}$. In a similar

manner, the normal potential of selenium with respect to its bivalent ion, Se/Se'' , is calculated to be -0.771 volt. The increasing sensitiveness of sulphides, selenides, and tellurides to oxygen is seen to be in the order of the normal potentials of the three elements, the value for sulphur being -0.55 . The value for polonium, extrapolated from that of tellurium, is probably about -1.0 volt. It follows from the extremely small value of the ion products, that a positive ion of an amphoteric element practically cannot exist in presence of negative ions, and *vice versa*. Amphoteric cleavage is a strongly endothermic process. For tellurium, the following values are calculated: $3\text{Te} \rightleftharpoons \text{Te}''' + 2\text{Te}'' - 136,000$ cal. and $5\text{Te} \rightleftharpoons \text{Te}''' + 2\text{Te}_2'' - 129,000$ cal. The formation of ditelluride can then be expressed by the equation: $\text{Te}'' + \text{Te} = \text{Te}_2'' + 3,500$ cal.

E. H. R.

The Potential Surfaces of Ternary Alloys of Cadmium and Mercury with Tin or Lead. ROBERT KREMANN, HERMANN PRAMMER, and LUDWIG HELLY (*Z. anorg. Chem.*, 1923, **127**, 295—315).—The potentials of ternary alloys of cadmium, mercury, and tin and of cadmium, mercury, and lead were measured against a $\text{Hg}/\text{N}-\text{CdSO}_4$ electrode, and the results obtained are discussed with the aid of diagrams for which the original should be consulted.

H. H.

The Electrochemical Behaviour of Alloys of Iron—Chromium, Iron—Molybdenum, and Iron—Aluminium. G. TAMMANN and E. SOTTER (*Z. anorg. Chem.*, 1923, **127**, 257—272).—The potentials of iron—chromium alloys in $\text{N}/10$ -sulphuric acid were measured with anodic and cathodic polarisation. Up to 15% of chromium, the potential is negative to chromium in each case, but above that percentage of chromium the alloy is strongly electro-positive to chromium with cathodic polarisation, and only slightly so with anodic polarisation. The end potential is not reached immediately, and for anodic polarisation the equation $t = t_0 e^{\alpha(\pi - \pi_0)}$ is suggested, where π_0 is the potential at time t_0 and α is a constant. For cathodic polarisation, the case is more complex, there being apparently three distinct periods. Polishing with emery, and heating at 400° decrease the electro-positiveness of the alloys. The presence or absence of air bubbling through the solution affects the potential but little, but the presence of a reducing agent, such as pyrogallol, phosphorus, or quinol, reduces the electropositiveness of cathodically polarised iron—chromium alloys to a remarkable extent. Molybdenum—iron alloys are electronegative to molybdenum up to 65% molybdenum, and then slightly electropositive. For iron—aluminium alloys, the potential slowly falls with time when cathodically polarised, and rises when anodically polarised. It is suggested that passivity depends on the protection of the metal by a layer of oxygen, but that the density of this layer can vary within fairly wide limits.

H. H.

The Galvanic Tensions of Ternary Alloys of Antimony, Zinc, and Bismuth. ROBERT KREMANN, AUGUST LANGSBAUER and HERMANN RAUCH (*Z. anorg. Chem.*, 1923, **127**, 229—238).—The

E.M.F. of some ternary alloys of zinc, antimony, and bismuth were measured against a $\text{Zn}|N\text{-ZnSO}_4$ element. By keeping the ratio bismuth/antimony constant, and varying the proportion of the other component, part of the ternary equilibrium diagram was constructed. Measurements were made with alloys which had been slowly cooled and with the same alloys tempered for twelve hours at 260° . Three cases are distinguished: (a) ternary alloys in which the ratio Sb/Zn is less than 40/60 atom.%, which show practically the potential of zinc; (b) ternary alloys in which the ratio Sb/Zn lies between 40/60 and 50/50 atom.%, which behave as mixtures of the binary compounds Zn_3Sb_2 and ZnSb with bismuth and show a potential about 50–100 millivolts more positive than zinc, and (c) ternary alloys in which the ratio Sb/Zn lies between 50/50 and 100/0 atom.%, which are less noble than zinc. By plotting isopotential lines on the triangular concentration diagram, it is shown that for alloys containing 50/50 atom.% of Zn/Sb , the *E.M.F.* is practically independent of the bismuth content, especially in the case of the tempered alloys. H. H.

The Galvanic Tensions of Ternary Alloys of Bismuth, Cadmium, and Lead. ROBERT KREMANN and AUGUST LANGBAUER (*Z. anorg. Chem.*, 1923, 127, 239–243; cf. preceding abstract).—The *E.M.F.* of ternary alloys of bismuth, cadmium, and lead were measured against a $\text{Cd}|N\text{-CdSO}_4$ element. Triangular concentration diagrams on which isopotential lines were plotted, were constructed as before, and from the results obtained it is found that the potential of the alloy falls abruptly from that of cadmium to that of lead as soon as the percentage by weight of the former in the alloy falls below 4. Bismuth has very little effect on the *E.M.F.* until the Bi/Pb ratio rises to 98/2, when the *E.M.F.* again falls abruptly to that of bismuth. H. H.

A New Type of Reduction–Oxidation System. I. Cysteine and Glutathione. MALCOLM DIXON and JUDA HIRSCH QUASTEL (*T.*, 1923, 123, 2943–2953).

Membrane Potentials and Colloidal Behaviour. A. V. HILL (*J. Gen. Physiol.*, 1923, 6, 91).—A reply to Hitchcock (this vol., ii, 530), in which the author's criticism (this vol., ii, 221) is reiterated. E. S.

Membrane Potentials and Colloidal Behaviour. DAVID I. HITCHCOCK (*J. Gen. Physiol.*, 1923, 6, 93).—A reply to Hill (cf. preceding abstract). E. S.

Temperature Coefficients of Unsaturated Weston Cells. WARREN C. VOSBURGH and MARION EPPLEY (*J. Amer. Chem. Soc.*, 1923, 45, 2268–2277).—The *E.M.F.* of unsaturated Weston cells has been investigated. It is shown that the *E.M.F.* increases in an approximately linear manner as the concentration of cadmium sulphate decreases. The *E.M.F.* values are linear functions of the temperature between 15° and 35° , but not between 35° and 45° . The temperature coefficient between 15° and 35° is found to be a

linear function of the *E.M.F.* It decreased from 0.0000028 volt per degree for cells with an *E.M.F.* of 1.01827 volts to -0.000013 volt per degree for cells with an *E.M.F.* of 1.0210 volts. Normal cells with electrodes made by saturating 0.015*M*-sulphuric acid solution with hydrated cadmium sulphate behave in accordance with Wolff's temperature formula. Mercurous sulphate prepared by reduction of mercuric sulphate with formaldehyde at 100° showed no difference in its behaviour in normal cells from the electrolytic salt. The differential heat of solution of hydrated cadmium sulphate in a slightly acid saturated solution has been calculated, and the following values have been obtained for 0.012*M*-sulphuric acid: 15°, -352 cal./mol., 18°, -431 cal./mol., and 25°, -605 cal./mol.

J. F. S.

Action of Light on Electrodes of Metals possessing Low Solution Pressures. RENÉ AUDUBERT (*Compt. rend.*, 1923, 177, 818—821; cf. Buisson, A., 1900, ii, 519).—Experiments are carried out on the effect of illuminating one of two electrodes formed of the same metal and immersed in the same electrolyte, illumination being effected using an arc lamp (or nitrogen-filled tungsten lamp) with a condenser, and, in some experiments, light filters. Independently of the electrolyte, the illuminated electrode becomes the anode in the case of platinum, copper, and mercury, and the cathode in the case of silver and gold, unless secondary effects (photochemical decomposition of electrolyte, etc.) occur. Thus in presence of ferrous or ferric salts, the illuminated platinum electrode becomes negative or positive, according as oxidation or reduction is dominant, whilst a silver electrode, in hydrochloric acid solution, is covered with silver chloride when illuminated.

Blue rays are much more active than red ones. The sensitivity of metals varies inversely with their solution pressures, and for each metal there appears to be a threshold of excitation which, as metals more and more electropositive are considered, is displaced towards higher frequencies.

The effects produced are independent of the anion, and appear to depend on the layer of kations adsorbed on the electrode, and on the solution-pressure of the kation.

E. E. T.

Intermittent Current Electrolysis. II. Overvoltage Study of the Lead Electrode. SAMUEL GLASSTONE (T., 1923, 123, 2926—2934).

Note on Glasstone's Discussion of Over-voltage Measurement. HERBERT HAWLEY and HENRY JULIUS SALOMON SAND (T., 1923, 123, 2891—2901).

Ions and Ionic Activity. P. DEBYE (*Chem. Weekblad*, 1923, 20, 562—568).—A repetition of the criticisms already advanced against the theory of Ghosh by Prins (this vol., ii, 369) and the author (this vol., ii, 724). The conception of an "electrical atmosphere" round the ion is developed from considerations of energy and potential; the formulæ obtained give values different from, but of the same order of magnitude as those deduced by Ghosh. Mathe-

matical treatment indicates that for a completely dissociated solution the osmotic pressure is determined not only by the concentrations, but also by the valencies of the ions. The addition of a second salt, *B*, to a system consisting of a saturated solution of one salt, *A*, with excess of undissolved *A*, is considered from the energy point of view, and equations are deduced. S. I. L.

Moving Boundary Method for Determining Transport Numbers. DUNCAN A. MACINNES and EDGAR REYNOLDS SMITH (*J. Amer. Chem. Soc.*, 1923, **45**, 2246—2255).—The Denison and Steele method of determining transport numbers (*A.*, 1903, ii, 709; 1906, ii, 68, 329) has been investigated, and a modification developed which involves only a single moving boundary. It is shown that the boundaries move with the theoretical velocities only when the two solutions in contact at a boundary are adjusted to within about 5%, to the relation $C/T = C'/T'$, in which *C* and *C'* are the concentrations and *T* and *T'* are the transport numbers. The correct value of the transport number can therefore be obtained by a series of experiments approaching more and more closely to this relation. Unless the adjustment is obtained, the results are not independent of the composition of the indicator solution, or of the current passing through the apparatus, and may vary widely and erratically from the true values. The transport numbers at 25° have been determined for 0.1*N*-solutions of potassium chloride and potassium bromide, using lithium bromide as indicator solution. The transport number of potassium in potassium chloride is found to be 0.492 ± 0.001 at 25° and in potassium bromide 0.485. These values are compared with the values of Denison and Steele and others. It is shown that the conductivity of the potassium-ion is the same in these two solutions if the correction for viscosity is made.

J. F. S.

The Position of Tellurium in the Voltaic Series. J. KASAR-
NOWSKY (*Z. anorg. Chem.*, 1923, **128**, 17—32).—When tellurium is used as cathode in the electrolysis of potassium hydroxide it dissolves as a univalent element, forming potassium ditelluride, K_2Te_2 . On the other hand, used as anode in the electrolysis of hydrochloric acid, tellurium passes into solution as a quadrivalent metal, forming $TiCl_4$. The author has measured the normal potential of tellurium corresponding with the two ions Te_2'' and Te''' . The potential of the system Te/Te_2'' , determined in potassium hydroxide solution, varies with the concentration according to Nernst's equation; the normal potential is -0.818 volt. The normal potential of the system Te/Te''' is $+0.549 \pm 0.001$ volt. This is the first example of the determination of the normal potentials of an amphoteric element with respect to its positive and negative ions. As a metal, tellurium comes between copper (0.34) and silver (0.80), whilst it is the "noblest" of the metalloids, so far as they have yet been measured. The hypothetical system $Te|N-Te'''/N-Te_2''|Te$ should have an *E.M.F.* of 1.37 volts, and the ion product, calculated from van't Hoff's equation, is $[Te'''] [Te_2'']^2 = 10^{-95}$.

This gives a measure of the amount of dissociation of tellurium into positive and negative ions. E. H. R.

Electrolytic Separation [Deposition] of Alloys. A. H. W. ATEN (*Rec. trav. chim.*, 1923, **42**, 931—938).—A theoretical discussion of the possibility of depositing an alloy by electrolysis. The problem resolves itself into one of discovering a solution of such a composition that the anode will dissolve in the same proportions as the metals are deposited on the cathode. It is not necessary that the anode shall have this composition. The author concludes that the problem, although difficult, may be capable of solution.

H. H.

Chemical Effects Produced by Passing Electric Currents through Thin Artificial Membranes of High Resistance. R. S. LILLIE and S. E. POND (*Proc. Amer. Physiol. Soc., Amer. J. Physiol.*, 1923, **63**, 415—416).—An electric current corresponding with a potential of 10 volts flowing across a caoutchouc membrane of thickness $40\ \mu$ interposed between two electrolyte solutions, one of which is a mixture of ferrous chloride and potassium thiocyanate, causes oxidation of ferrous to ferric iron at the surface of the membrane facing the cathode. CHEMICAL ABSTRACTS.

Anomalies of Chromium and its Behaviour during Electrolysis by Alternating Current. N. ISGARISCHEV and A. OBRUTSCHEVA (*Z. Elektrochem.*, 1923, **29**, 428—434).—The solubility of chromium electrodes in acid, alkaline, and neutral solutions, using direct and alternating current and both types of current simultaneously, has been investigated. The solubility of chromium in sulphuric acid at various temperatures and in the presence of various anions has also been investigated. It is shown that there is no definite transition point at which passive chromium passes into the active condition, as is the case in allotropic changes. The metal can become active at any temperature, the activation depending on the properties of the medium. Chromium is rendered passive by exposure to air, by the action of oxidising agents such as chromic acid, hydrogen peroxide, and potassium permanganate, and by the action of electrolytic oxygen; it is rendered active by electrolytic reduction and by mechanical purification of the surface. Consequently, the passivity of chromium is connected with the formation of a protecting oxide film on the surface. The protecting film is a transparent, colloidal substance, the density and permanence, and consequently the passivating action, of which depend on the nature of the medium, particularly on the presence of those ions, such as chloride- and bromide-ions, which bring about colloidal transitions. Chloride-ions have the greatest disturbing effect on the film and make it permeable to most reagents. Particles of passive chromium become active when brought into contact with active chromium, zinc, or magnesium. Since these metals are all more electro-negative than passive chromium, this action is due to the formation of a galvanic element which liberates hydrogen and consequently reduces the oxide film. The oxide film is also the cause of the

anomalies of chromium. Chromium dissolves as anode to give bi-, ter-, and sexa-valent ions, the amounts of the various types of ion depending on the conditions. J. F. S.

The Electrochemistry of the High Intensity Arc. PRESTON R. BASSETT (*Trans. Amer. Electrochem. Soc.* [advance copy], 1923, 319—338).—The phenomena exhibited by various types of electric arcs operated with currents ranging from 20 to 300 amperes are briefly described. The tendency to produce two arc flames, a positive and a negative, is present in practically all arcs, and in the high-intensity arc this tendency is enhanced, so that the two flames are separate and distinct, and each flame performs a separate function, the positive flame operating as light producer, and the negative as arc maintainer. The positive electrode consists of a core of cerium fluoride and carbon surrounded by a shell of non-graphitizable pure carbon. The negative carbon electrode contains a core of soft carbon. The arc is customarily operated with a current of 150 amperes. The intrinsic brilliance of the arc is from 500 to 1,000 candles per sq. mm., and its temperature about 4,700°. It is suggested that the high intrinsic brilliance of the arc is attributable to the formation of cerium carbide in the arc. J. S. G. T.

Thermal Conductivities of some Metals in the Solid and Liquid States. W. BYRON BROWN (*Physical Rev.*, 1923, 22, 171—179).—In the guard ring method of measurement employed, a cylinder of the metal, electrically heated at one end, was surrounded by a slate tube and a hollow brass cylinder, also heated electrically at one end. The other ends were cooled with running water, and the conductivity calculated from the energy applied to the rod and the temperature gradient. Tables and curves are given for the conductivity of tin, cadmium, thallium, and tin-zinc, tin-lead, lead-antimony, and lead-bismuth alloys. For the pure metals, the following values are abstracted. Tin: 50°, 0.1428; 102°, 0.1404; 209°, 0.1297. Cadmium: 45°, 0.200; 99°, 0.209; 240°, 0.239. Thallium: 45°, 0.0934; 90°, 0.0958; 113°, 0.0976; 125°, 0.0919; 149°, 0.0927. A polymorphic change in thallium at 120° is thus indicated. A. A. E.

Entropy of Diatomic Gases and Rotational Specific Heat. RICHARD C. TOLMAN and RICHARD M. BADGER (*J. Amer. Chem. Soc.*, 1923, 45, 2277—2285).—A direct mathematical method has been developed for determining the theoretical values of the constants S_2 and $C_{298.1}$ in the equations for the entropy of diatomic gases, $S = 7/2 R \log_e T + 3/2 \log_e M - R \log_e p + R \log_e J + S_2$; $S_{(298.1, 1 \text{ atm})} = 3/2 R \log_e M + R \log_e J C_{298.1}$. Six different hypotheses which have been proposed for rotational specific heat all based on the first form of quantum theory, but based on different hypotheses as to a priori probabilities and as to the lowest possible azimuthal quantum number, have been used to determine the theoretical values of S_2 and $C_{298.1}$, and the results compared with the experimental values. In the absence of further evidence, the best values for S_2 and $C_{298.1}$ are 64.92 and 104.57, respectively, the

units being, entropy in calories, temperature in degrees centigrade absolute, pressure in atmospheres, molecular weight in g./mol., moment of inertia in g.cm.²/mol. J. F. S.

The Form of the Melting-point Curves of Series of Binary Mixed Crystals, and the Lattice Parameters of their Components. EUSTACE J. CUY (*Z. anorg. Chem.*, 1923, 128, 241—244).—The maximum departure from the straight line joining the melting points of the components of the curve of the beginning of crystallisation, a temperature range ΔT_m , has been plotted against the relative difference of the two lattice parameters, Δd , given by the expression $\Delta d = (d_A - d_B)/(d_A/2 + d_B/2)$, where d_A and d_B are the parameters of the two components, A and B, for a series of pairs of halides of the alkali metals, and some alloys. The points found lie on a straight line, which for the value $\Delta T_m = 0$ (i.e., when the temperature of beginning of crystallisation lies on the line joining the melting points of the two components) cuts the Δd axis at the value 0.04. S. I. L.

Cryoscopy in $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. Molecular Magnitudes of Malates, Molybdates, and Molybdomalates. E. DARMOIS and J. PÉRIN (*Compt. rend.*, 1923, 177, 762—765; cf. A., 1922, i, 220, 522; Löwenherz, A., 1896, ii, 149, and Boutaric and Leenhardt, A., 1912, ii, 1136).—Sodium sulphate decahydrate is used as a cryoscopic solvent, k being calculated from a study of the $\Delta t/c - \Delta t$ curves for carbamide, sodium chloride, and sodium nitrate. The value of k so found, namely, 32, is then made use of in determining the molecular complexity of various sodium salts, the results being as follows: Sodium malate, $\text{C}_4\text{H}_5\text{O}_5\text{Na}$, sodium molybdate, Na_2MoO_4 , sodium "acid" molybdate, $\text{Na}_6\text{Mo}_7\text{O}_{24}$; sodium dimolybdomalate (hexahydrate) (M found, 1010) is derived from a tetramolybdic acid whilst sodium molybdodimalate (M found, 427) is derived from 2 mols. of malic acid (cf. Klason, A., 1901, ii, 162). Whereas the sodium salts give true molecular weights in sodium sulphate solution, the corresponding ammonium salts are completely dissociated as in aqueous solution. E. E. T.

The Accurate Determination of Elevation of Boiling Point. KAZIMIERZ JABŁCZYŃSKI and STANISŁAW KON (*T.*, 1923, 123, 2953—2963).

Vapour Pressure of Monatomic Elements. RUSSELL W. MILLAR (*J. Amer. Chem. Soc.*, 1923, 45, 2323—2329).—A theoretical paper in which a formula has been derived by means of which the pressure of a monatomic gas in equilibrium with the liquid or solid element can be calculated from specific heat data and one vapour pressure measurement, the latter being required to evaluate the integration constant Z . The equation in its general form is $\log p(\text{atm.}) = (2.5 - [a - \beta]/R) \log T - 2.303\beta/2R \cdot \log T^2 + Z/T + 1/R[1.5R \log w + \alpha \log T_0 + 2.303\beta/2 (\log T_0)^2 - (2.63 + S_0 - (\alpha - \beta) + 2.5R)/2.303]$. This formula has been evaluated for mercury, zinc, sodium, and hydrogen. In the case of mercury, it takes the form $\log p(\text{mm.}) = -0.8443 \log T - 3319.6/T + 10.5134$, and reproduces the

observed values with fair accuracy. For sodium, the equation is $\log p(\text{mm.}) = -1.20 \log T - 5135/T + 11.071$, and in this case the agreement of the calculated value with the experimental value is very much better at low temperatures than at higher temperatures. In the case of zinc, the equation is $\log p(\text{mm.}) = 4.0583 \log T - 0.7845 (\log T)^2 - 6823.1/T + 3.7555$, which reproduces the experimental values with fair accuracy up to 363° . Hydrogen, below 60°Å. , has the heat capacity of a monatomic gas. The formula in this case is $\log p(\text{mm.}) = 7.3725 \log T - 2.0572 (\log T)^2 - 26.8679/T - 1.9280$, which gives fair agreement. J. F. S.

Free Energy of the Thiosulphate-ion. F. RUSSELL BICHOWSKY (*J. Amer. Chem. Soc.*, 1923, **45**, 2225—2235).—A complete thermodynamic investigation of the reaction $\text{S} + \text{CaSO}_3 \cdot 2\text{H}_2\text{O} = \text{CaS}_2\text{O}_3 \text{ aq} + 2\text{H}_2\text{O}$ has been carried out. The reaction is shown to be reversible, and the equilibrium constant has been determined at 141° , 122° , 110° , 100° and 79.8° . Calcium thiosulphate, $\text{CaS}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ dissolves in water at 25° to the extent of 2.28 g. of the crystallised salt per 1,000 g. of solution. The heat of the reaction has been determined experimentally as well as the specific heat, freezing point, and heat of dilution of solutions of calcium thiosulphate. The solubility of the dihydrate of calcium sulphite has been determined at 25° , and the mean value 0.000037 g. mols. per litre obtained. Using the data obtained in the present investigation and other data, the free energy of formation, ΔF_{298° , of the thiosulphate-ion is calculated to be $-125,110$ cal. J. F. S.

The Heats of Combustion of Benzoic Acid, Naphthalene, and Sucrose. P. SCHLÄPFER and W. FIORONI (*Helv. Chim. Acta*, 1923, **6**, 713—729).—The ratios between the heats of combustion of benzoic acid, naphthalene, and sucrose were determined with great exactitude for the purpose of using these substances as calorimeter standards. The heat of combustion of benzoic acid was taken as 6324 cal. per gram weighed in air, and this value was used for determining the water equivalent of the calorimeter. The value so obtained was used in determining the heats of combustion of naphthalene and sucrose both by the ordinary method and the adiabatic method. The most probable values are: naphthalene 9613.7, and sucrose 3945.7 cal. per gram. E. H. R.

The Adiabatic Cooling of Water and the Temperature of its Maximum Density as a Function of Pressure. NICOLAI ANTONOVITCH PUSHIN and ELIJAH VASILJEVICH GREBENSHCHIKOV (*T.*, 1923, **123**, 2717—2725).

Some Thermal Properties of Gases. I. Density of the Coexistent Phases of Dimethyl Ether. ETTORE CARDOSO and AUGUSTO ACQUAVIVA COPPOLA (*J. Chim. Phys.*, 1923, **20**, 337—346).—The density of the liquid and gaseous phases of dimethyl ether have been experimentally determined from 0.20° to 126.50° . Extrapolation of the value for 126.90° , that is, for the critical temperature, leads to the value 0.2714 ± 0.0003 for the critical density. J. F. S.

Some Thermal Properties of Gases. II. Critical Constants and the Vapour Pressure of Dimethyl Ether. ETTORE CARDOSO and ALFREDO BRUNO (*J. Chim. Phys.*, 1923, 20, 347—351; cf. preceding abstract).—The critical pressure and temperature and the vapour pressure of dimethyl ether have been determined at temperatures 126.9° to 0.0°. The following experimentally determined data are recorded: $t_c = 126.90^\circ \pm 0.05^\circ$, $p_c = 52.00 \pm 0.05$ atm., vapour pressure at 122.20°, 47.67 atm.; 117.80°, 44.06; 116.82°, 43.41; 113.75°, 41.24; 110.57°, 38.82; 99.90°, 32.14; 90.25°, 26.80; 80.10°, 22.14; 64.68°, 15.95; 56.02°, 13.11; 49.75°, 11.22; 46.13°, 10.31; 33.55°, 7.49; 25.40°, 6.05; 16.80°, 4.58; 9.25°, 3.58; 0.00°, 2.52. The vapour pressure is expressed by the equation $\log p = 0.40654 + 0.016082t - 0.000069963t^2 + 0.00000019343t^3$. The differential coefficient is given by $dp/dt = p(0.037031 - 0.00032220t + 0.0000013362t^2)$. J. F. S.

Wetting of Glasses by Mercury. EARLE E. SCHUMACHER (*J. Amer. Chem. Soc.*, 1923, 45, 2255—2261).—An attempt has been made to cause mercury to wet glass and quartz after their surfaces have been freed from gas by heating at 550° in a vacuum. Fairly good wetting can generally be obtained on quartz after this treatment, but it can only be obtained occasionally on Pyrex glass and on lime soda glass. The difficulty in causing mercury to wet glass appears to become greater as the alkali-content of the glass becomes greater. The term "wetting" is used in the sense that wetting is complete when the angle of contact between liquid and solid is zero and the meniscus is concave, and that the liquid does not wet the glass in cases where the angle of contact is zero and the meniscus is convex. In the present work, wetting was considered to have taken place when the meniscus of the mercury was less convex at the conclusion of the experiment than it was at the start. J. F. S.

The Nature of Charcoal "Sorption." H. HORTON SHELTON (*Physical Rev.*, 1922, 19, 253).—The dual nature of sorption (McBain, A., 1919, ii, 449) by charcoal is demonstrated by the fact that when the pressure-time curve for gases, or the concentration-time curve for solutions, is plotted, there are evidently two distinct parts separated by a bend. The second action, however, begins only after the first is nearly complete. Since solution should begin as soon as adsorption, it is suggested that the second part is due to diffusion into the more inaccessible channels; this cannot be expected to take place to any extent until the easily accessible or directly exposed portions are saturated. A. A. E.

Adsorption of Uranium- X_1 and Thorium by Charcoal. H. FREUNDLICH and MARIE WRESCHNER (*Z. physikal. Chem.*, 1923, 106, 366—377).—Uranium- X_1 is completely adsorbed by charcoal from a solution of a uranium salt, but if a small quantity of a thorium salt is added the uranium- X_1 is not adsorbed at all. It was shown previously that if the thorium nitrate used in the above experiment is previously shaken with charcoal, it loses, to a great extent, its power of displacing the adsorption of uranium- X_1 (A.,

1916, ii, 70). This result is confirmed in the present paper; it is also shown that a solution of thorium nitrate which has been shaken with charcoal behaves like a solution of thorium nitrate which has passed through a dialysis membrane or one from which the colloidal particles has been removed by cataphoresis. This leads to the view that the colloidal particles in thorium nitrate are responsible to a large extent for the displacement of the adsorption of uranium- X_1 by charcoal, and that when these particles are removed by adsorption, dialysis, or cataphoresis the displacing action of thorium nitrate ceases. This explanation is in keeping with the fact that when an acid, colloid-free solution of thorium nitrate after treatment with charcoal is evaporated to dryness and redissolved, it has the same displacing effect as an untreated solution of thorium nitrate. The explanation is that the colloid particles are not removed from acid solutions by charcoal, and on solution after evaporation these are again peptised. Uranium- X_1 is also partly adsorbed as colloidal particles, and this would explain the very long time required for setting up the adsorption equilibrium and the reversible nature of the displacement by thorium, whilst other adsorptives such as benzoic acid and strychnine nitrate are not reversibly displaced.

J. F. S.

Adsorption. III. Peptisation and the Reversal of the Charge on some Hydroxides. K. C. SEN and N. R. DHAR (*Kolloid Z.*, 1923, **33**, 193—202; cf. A., 1922, ii, 205).—The peptisation of the hydroxides of iron, mercury, cobalt, copper, nickel, manganese, cadmium, thorium, and cerium by means of solutions of non-electrolytes such as sucrose, dextrose, laevulose, galactose, lactose, mannose, dextrin, starch, and glycerol, has been investigated, in most cases quantitatively. It is found that peptisation only takes place when the alkali hydroxide is added to a mixture of a salt of the metal and the peptising agent. In some cases, it is found that a slight excess of alkali over that required for the formation of the hydroxide assists the peptisation. An increase in the concentration of the salt requires a proportional increase in the peptising agent for complete peptisation. In all cases, the peptisation is chiefly specific, although there is a similarity in the action of the various peptising agents. It is found generally that the hydroxide prepared from sulphates, that is, in the presence of sulphat-ions, is less easily peptised than the same hydroxide in the presence of chloride- or nitrate-ions. Freshly precipitated ferric hydroxide passes into a negatively charged colloid in the presence of arsenious acid. In the presence of an excess of alkali and either glycerol or sucrose, the charge of the colloid is negative, but on adding the alkali slowly to a mixture of ferric chloride and sucrose or glycerol the colloid passes through three definite stages. At first it is positively charged, then it coagulates, and finally it passes into a negative colloid.

J. F. S.

The Dissociation Constant of Lithium Hydroxide and the Second Dissociation Constant of Salicylic Acid. I. M. KOLTHOFF (*Rec. trav. chim.*, 1923, **42**, 969—972).—The “dis-

sociation constant" of lithium hydroxide was found to be approximately 0.5. Sodium salicylate may be supposed to ionise in two stages: $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{OH} \rightleftharpoons \text{Na}^+ + \text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{O}'$ and $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{O}' \rightleftharpoons \text{O}'\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{O}' + \text{H}^+$. For the second of these equilibria, the dissociation constant is 3.6×10^{-14} . H. H.

The [Second] Dissociation Constant of the Hydroxides of the Alkaline Earth Metals. I. M. KOLTHOFF (*Rec. trav. chim.*, 1923, **42**, 973—979).—The second dissociation constant, that for the equilibrium $\text{MOH}^+ \rightleftharpoons \text{M}^{++} + \text{OH}'$, was measured for the hydroxides of barium, strontium, calcium, and magnesium. The values found were: $\text{Ba}(\text{OH})_2$, 0.19 ± 0.02 ; $\text{Sr}(\text{OH})_2$, 0.15 ± 0.01 ; $\text{Ca}(\text{OH})_2$, 0.086 ± 0.005 ; $\text{Mg}(\text{OH})_2$, 0.004 ± 0.001 . H. H.

Nature of Non-dissociated Acids. H. VON HALBAN (*Z. Elektrochem.*, 1923, **29**, 434—444).—A theoretical paper in which the author discusses and criticises Hantzsch's theory of ionisation (this vol., ii, 475). It is shown that Hantzsch's conception of the pseudo-acid may not be extended to acids generally, nor may it be applied to electrolytes as a whole. J. F. S.

Kinetic Theory of Osmotic Pressure. GÉZA SCHAY (*Z. physikal. Chem.*, 1923, **106**, 378—385).—A theoretical paper in which, on the basis of van der Waals's views, a kinetic hypothesis of solutions of non-electrolytes is developed, and in this connexion it is shown that cause of the osmotic phenomena is not to be sought in a pressure exerted by the dissolved molecules, but rather in a pressure difference of the solvent. The osmotic pressure formula put forward by Sackur has been developed theoretically, and two other possible formulæ have been derived. J. F. S.

Concentrated Salt Solutions. R. O. HERZOG and W. BERGEN-THUN (*Annalen*, 1923, **433**, 117—121).—The addition of a small quantity of sucrose to a solution of calcium chloride of about 7*N*-concentration causes an increase in the boiling point which is less than that calculated by Raoult's equation. The boiling point of a more concentrated solution is, however, decreased, whilst for certain concentrations there is no effect. A depression of the boiling point is observed when lactose or mannitol is added to 8.09*N*-calcium chloride, or when dextrose is added to a 8.09*N*-solution; also by the addition of sucrose to solutions of lithium chloride or calcium thiocyanate. Very little departure from the calculated increase in boiling point is observed when sugar is added to 5.3*N*-sodium chloride solution. A series of figures is quoted for calcium chloride solutions. Since the work of dilution and the heat of dilution are practically equal, conclusions respecting the nature of the complexes formed cannot be drawn without the aid of further assumptions.

The distribution of cellobiose octa-acetate between chloroform and calcium thiocyanate of the normalities, 90.8, 8.68, and 7.90, has been measured. For a given concentration of salt solution the partition coefficient remains constant; the relative solubility in the aqueous solution decreases rapidly with the concentration of the salt.

W. S. N.

X-Rays and Crystal Structure. SIR W. H. BRAGG (*Nature*, 1923, 112, 618).—A brief discussion of the facts revealed by the X-ray method of crystal analysis, and the limitations of the method. The significance of the term "molecule" is considered in relation to crystal structure. A. A. E.

[**X-Ray Analysis of Crystals.**] SIR W. H. BRAGG (*J. Franklin Inst.*, 1923, 196, 675—677).—In reply to adverse criticism by Wyckoff (this vol., ii, 300) of the results obtained by the method of X-ray analysis of crystals, on the ground that this method pays insufficient attention to the theory of space groups, the author points out that whereas the older methods, depending on observations of form, enable the class of a crystal nearly always to be determined, but not its space-group, the method of X-ray analysis likewise enables the crystal class to be determined, and in addition permits, in a large number of cases, data referring to the appropriate space group being ascertained. The conclusions of mathematical crystallography can only prove the possibility of what X-rays actually find, and the author contends that it is unreasonable to reject results because they have been obtained without the use of the terms of the theory of space-groups, since the terms naturally used in X-ray analysis are equally effective in expressing the laws of symmetry. The argument is supported by reference to resorcinol, assigned on the basis of its asymmetric molecular structure, ascertained by X-ray analysis to the space-group C_{2v}^{10} . In the absence of knowledge of the asymmetric character of the molecule, the crystal might equally well be assigned to the space group Q_h^{12} . J. S. G. T.

Stability, in Presence of Water, of a certain Number of Binary Mixtures. N. PERRAKIS (*Compt. rend.*, 1923, 177, 879—882).—A determination of the quantity of water, which, added to a definite weight of a binary mixture, at constant temperature, causes the appearance of a second layer. The mixtures chosen were: (a) ethyl alcohol with one of the following: diphenyl ether, benzene, *o*-cresol, or phenol, (b) benzene with one of the following: methyl, ethyl, isopropyl, or *n*-butyl alcohols. The results are discussed in terms of miscibility and solubility relationships. E. E. T.

Liesegang Rings. III. Effect of Light and Hydrogen-ion Concentration on the Formation of Colloidal Gold in Silicic Acid Gel. Rhythmic Bands of Purple of Cassius. EARL C. H. DAVIES (*J. Amer. Chem. Soc.*, 1923, 45, 2261—2268; cf. A., 1922, ii, 140).—A number of experiments are described which show that gels made with silicic acid and gold chloride and a reducing agent are remarkably affected by light, the effect being the production of a banded structure. The light of small wave-length is the active portion of the light in producing these effects. The results obtained in the present work remove Bancroft's objection ("App. Colloid Chemistry," p. 259), to Holmes's diffusion hypothesis of Liesegang ring formation (A., 1918, ii, 392). A further series of experiments shows that there is a distinct relationship between the hydrogen-ion concentration and the size of the "pockets"

in which the gold is formed. The effect of light on the reduction of gold is well shown by the following experiment. To 25 c.c. of 3*N*-hydrochloric acid, 2 c.c. of 1% solution of gold chloride are added, and then slowly and with shaking 25 c.c. of water glass (*d* 1.16). The liquid is filtered into test-tubes and allowed to set for three days. It is then covered with black paper and 5 c.c. of saturated oxalic acid solution are added to each tube, and placed in a dark room for three weeks for diffusion to take place. When a tube is brought into bright sunlight, when first opened there will be only a few crystals of gold, but after fifty seconds' exposure to light there will be a flash of colour in the tube. Narrow but rhythmic bands of purple of Cassius may be obtained as follows. To one of the tubes of gel described above add 3 c.c. of a mixture of 10 g. of anhydrous stannous chloride and 0.1 g. of stannic chloride in 90 c.c. of water, and allow to diffuse, when bands will be produced.

J. F. S.

High-speed Stirring as an Aid to Chemical Action. C. H. MILLIGAN and E. EMMET REED (*Ind. Eng. Chem.*, 1923, 15, 1048—1049).—The speed of many chemical reactions depends on (1) the speed of mutual solution of the reagents, (2) the reaction velocity. If the former is greater than the latter, as in the action of sulphur dioxide on benzene in presence of aluminium chloride, then the progress of the reaction is unaffected by stirring. An investigation of the reverse case as exemplified by the absorption of ethylene in benzene in presence of aluminium chloride and the absorption of hydrogen in cotton-seed oil in presence of nickel gave results showing great acceleration; this is expressed by the equation $v = a + br$, in which v is the rate of gas absorption and r the rate of stirring. In these experiments, the speed of the stirrer head, which was a perforated disk with bell-shaped projection underneath, into which the gas was delivered, was varied between 0 and 14,000 r.p.m.

C. I.

The Radiation Hypothesis of the Velocity of Chemical Reaction. A. KISS (*Chem. Weekblad*, 1923, 20, 585—589).—By applying to the recent results deduced from the quantum theory by Perrin and others the formula of Arrhenius for the dependence of reaction velocity on temperature, namely $k = se^{-a/T}$, where s and a are constants, the equation $Q/RT^2 = \rho/T^2(\nu_2 - \nu_1)$, where ν_2 and ν_1 are the frequencies of the radiations bringing about the forward and backward changes in a reversible monomolecular reaction, ρ is Planck's constant 0.5×10^{-10} (C.G.S.), and T the absolute temperature, is deduced. This equation for a reversible unimolecular change is independent of the nature or number of molecular collisions, but in applying the same reasoning to reactions of a higher order, the latter factors must be taken into account. From the kinetic theory, regarding molecules in collision as new molecules, equations can be deduced in the same way for these reactions also.

The frequencies of the activating radiations may thus be deduced from the heats of reaction, and checked by the absorption spectra.

The theory indicates that an exothermic reaction is much more sensitive to temperature change than an endothermic reaction.

S. I. L.

A Homogeneous Gas Reaction. The Thermal Decomposition of Chlorine Monoxide. I. CYRIL NORMAN HINSHELWOOD and CHARLES ROSS PRICHARD (T., 1923, **123**, 2730—2738).

Two Heterogeneous Gas Reactions. CYRIL NORMAN HINSHELWOOD and CHARLES ROSS PRICHARD (T., 1923, **123**, 2725—2729).

The Velocity of the Action of Oxygen, Nitric Oxide, and Nitrous Oxide on Metals. E. SCHRÖDER and G. TAMMANN (*Z. anorg. Chem.*, 1923, **128**, 179—206).—The rate of oxidation of iron and nickel, as measured by the formation of films at high temperatures on thin plates (this vol., ii, 831), in an atmosphere of oxygen, is independent of the pressure, except at very low pressures; the initial velocity at the same temperature, plotted against the pressure of the gas, gives a curve very similar to the adsorption isotherm of gases by charcoal, indicating that the oxygen is adsorbed by the surface film of oxide. With copper, on the other hand, oxidation is more rapid at low pressures than at high pressures; whilst at the beginning the rate of formation of the oxide skin is lower at low pressures, this skin is permeable to the gas at low pressures, but becomes impermeable at high pressures, so that the velocity of oxidation rapidly falls off as the pressure rises.

At normal pressure, the rate of oxidation of iron in air, oxygen, or nitric oxide is the same at equal temperatures; in nitrous oxide, the rate is lower. The action of both nitric and nitrous oxides on nickel gives rise at first to a slightly permeable skin, which becomes permeable at a definite thickness, $280\ \mu\mu$ measured as air (to obtain absolute thickness, divide by the coefficient of refraction of the oxide film), after which the course of the action becomes similar to that in a mixture of oxygen and nitric oxide in which the partial pressure of the oxygen is greater than 150 mm. S. I. L.

The Discontinuity of the Hydration Process. WILLIAM A. DAVIS and J. VARGAS EYRE (*Proc. Roy. Soc.*, 1923, [A], **104**, 512—537).—The authors have determined the rates of hydration of very different substances, including salts, *e.g.*, calcium sulphate, copper sulphate, and gelatin and fibrous forms of cellulose. The results indicate that under the same conditions of relative humidity the hydration curves for different substances differ very considerably in character. Thus in the case of copper sulphate, the curve showing the percentage of moisture absorbed at short intervals is characterised by long linear portions and short parabolic arcs. The curve for calcium sulphate shows a preponderance of parabolic portions, whilst cellulosic materials are characterised by the almost complete absence of linear portions of the hydration curve. Substances exposed in an atmosphere saturated with water vapour give entirely different hydration curves from those obtained when the same substances are exposed in a drier atmosphere, *e.g.*, 88% humidity.

In some cases, hydration may proceed at a slower rate, over a long period of time, in the atmosphere of greater humidity. Notwithstanding the tendency of a powdery anhydrous salt to "set" to a hard cake as hydration proceeds, the rate of hydration is not affected. The "set" mass continues to absorb water, as though it existed in the form of an open-mesh structure freely permeable to water vapour. Empirical equations for successive parabolic portions of the hydration curves are deduced by simple graphical methods.

J. S. G. T.

Chemical Dynamics of Autocatalytic Processes. Dynamics of the Oxidation of Arsenious Acid by Bromic Acid. JERZY STANISŁAW CHODKOWSKI (*Roczniki Chemji*, 1923, 2, 183—270).—It has been suggested by Schilov (A., 1903, ii, 276) that the oxidation of arsenious acid by bromic acid is too slow to be measurable except in the presence of sulphurous acid, although in the presence of excess of hydrogen-ions the reaction begins after a long period of induction. It is now shown that at 40°, in the presence of an excess of hydrogen-ions, the reaction proceeds spontaneously and at a measurable rate; the reaction is an autocatalytic one of the second order, according to the equation $dx^1/dt = kax^1(1-x^1)$; the velocity constant is equal to 9.7 at 30.7° and in presence of 1/10 mol. of sulphuric acid. The arsenious acid does not appear to exert any influence on the reaction and merely acts as an indicator of the reaction between bromic and hydrobromic acid; the products of this reaction, bromous and hypobromous acid, then oxidise the arsenious acid present. The initial production of hydrobromic acid must, however, be due to the interaction of arsenious acid with bromic acid. The action of sulphuric acid is proportional to the square of the concentration of hydrogen-ions; the addition of neutral sulphates which reduce this concentration retards the reaction. The addition of hydrogen bromide causes the reaction to proceed in accordance with the formula $dx^1/dt = ka(b^1+x^1) \cdot (1-x^1)$, where b^1 is the concentration of the hydrobromic acid, x the initial concentration of bromic acid; the velocity constant remains the same. Hydriodic acid has a similar although much greater action, whilst the addition of chlorine-ions has a much smaller effect; from experiments in which neutral potassium halides were added it can be concluded that the relative accelerating effects of potassium chloride, bromide, and iodide are as 1 : 15 : 3,000. The addition of hydrogen chloride, owing to the simultaneous influence of both hydrogen- and chlorine-ions, has a much greater effect than that of sulphuric acid, whilst arsenic acid, which is the final product of the reaction, also acts as a positive catalyst, although nine times weaker than an equivalent quantity of sulphuric acid. The thermal coefficient of the reaction is normal and amounts to 2.14.

G. A. R. K.

The Mechanism of Reduction. III. H. J. PRINS (*Rec. trav. chim.*, 1923, 42, 942—953; cf. this vol., ii, 548).—In continuation of his previous work, the author has studied the influence of the structure and purity of zinc on the reduction of nitrobenzene in acetic acid solution. The action is practically independent of the

crystalline state of the metal, except in the case of the mechanically strained outer layer. At 53° , hydrogen is evolved during the reduction, with a velocity which is constant and independent of the reduction reaction, until about one-fourth of the surface of the metal becomes covered with reaction products.

The velocity of reduction is a linear function of the nitrobenzene concentration up to a critical value of the latter; in this region the surface of the metal remains bare. At higher concentrations a portion, θ , of the surface becomes covered with reaction products, and it is found that the equilibrium velocity is given by the equation $V_{eq} = K_1 c(1 - \theta)$, so that there can be no reaction on the covered part of the metal. It is supposed that the protective layer is zinc acetate adsorbed by the zinc.

H. H.

Measurement and Calculation of Reaction Velocity. H. VON EULER and ERIK RUDBERG (*Z. anorg. Chem.*, 1923, 127, 244—256; cf. A., 1922, i, 219, and ii, 40).—The influence of the concentration of hydrogen-ions on the velocity of hydrolysis of acetamide and of sucrose was studied. The first case was treated as a bimolecular reaction and the fall of hydrogen-ion concentration with time noted. Electrometric measurements with sulphuric acid and acetamide gave $K_b = 3 \times 10^{-15}$ at the ordinary temperature, in good agreement with earlier values. An attempt was made, but unsuccessfully, by using sodium hydroxide, to measure K_a for acetamide.

Similarly, the effect of p_H on the hydrolysis of sucrose was studied, and it is pointed out that special precautions have to be taken with regard to absorption of carbon dioxide from the air or alkali from glass vessels, if the p_H lies above 4. In these cases, electrometric control is essential. From their results, the authors consider that sucrose has the dissociation constant $K_b = 1 \times 10^{-19}$ or 10^{-20} , and they support Dushman's view (A., 1921, ii, 315) that $K = e^{-h\nu/RT}$, where ν is a frequency probably associated with electrons within the molecule.

H. H.

Kinetics of the Conversion of Creatine into Creatinine in Hydrochloric Acid Solutions. GRAHAM EDGAR and R. A. WAKEFIELD (*J. Amer. Chem. Soc.*, 1923, 45, 2242—2245).—Measurements have been made of the rate of conversion of creatine into creatinine in hydrochloric acid solutions of concentrations 0.19*N*, 0.38*N*, and 0.76*N* at 25° , 57° , 78° , and 100° . The reaction is strictly unimolecular and the velocity increases with increasing concentration of acid. The temperature coefficient is given by Arrhenius's equation, in which the critical increment E has a mean value of 20,000 cal. and is independent of the acid concentration. The velocity constant can be expressed by the equations $\log_e K = -E/RT + C$ and $\log_{10} K = -4368/T + C^1$, where C and C^1 are constants depending on the concentration of the acid. J. F. S.

Catalytic Oxidation of Carbon Monoxide. I. Efficiency of the Catalysts Manganese Dioxide, Cupric Oxide, and Mixtures of these Oxides. J. A. ALMQUIST and WILLIAM C. BRAY (*J. Amer. Chem. Soc.*, 1923, 45, 2305—2322).—Temperature—

efficiency curves have been obtained for three series of partly hydrated porous catalysts of manganese dioxide and cupric oxide. A very definite improvement in the efficiency is caused by the addition of a small amount of either oxide to the other. Partial dehydration is necessary to bring a catalyst to a region of maximum activity, but the water content may then be lowered to a relatively small value by slow dehydration with but little change in the efficiency. Continued dehydration, however, finally lowers the efficiency, and causes loss of oxygen (except in the case of copper oxide). The efficiency of a catalyst is independent of the carbon monoxide concentration between 0.1 and 0.6%, and is practically unchanged by the presence at higher concentration of carbon dioxide, the product of the reaction. Water vapour has a marked poisoning effect which is reversible. It is probable that under steady state conditions the oxygen content of a catalyst is practically constant whether the catalyst is operating at low or high efficiency. A catalyst is reduced when treated with carbon monoxide in the absence of oxygen at a temperature at which it would act as a catalyst. The activity of a mixed catalyst is permanently impaired by this reduction, even when much of the lost oxygen is restored on subsequent operation as a catalyst. An hypothesis of the mixture effect in this case is put forward.

J. F. S.

Catalysis. XVIII. The Phenomenon of Induction. N. R. DHAR (*Z. anorg. Chem.*, 1923, 128, 207—211).—A discussion of the results of Skrabal (A., 1915, ii, 533; 1922, ii, 488), the author, and others on the reactions between iodic acid and hydriodic and sulphurous acid. The latter may be resolved into two reactions, (1) the reduction to hydriodic acid, which is slow but much influenced by change of temperature, and (2) oxidation of the hydriodic acid so formed by iodic acid left unchanged, which is very quick, but only slightly influenced by temperature; the second reaction is, however, slowed down by the presence of hydrogen-ions due to the formation of sulphuric acid in the first reaction. The whole reaction is therefore autocatalytic. If arsenious acid is used in place of sulphurous acid, the reduction (1) is much slower and even more strongly influenced by temperature. With other reducing agents there is no induction period, iodine being continuously liberated.

The reaction between a thiosulphate and salts of antimony, silver, bismuth, etc., has now been studied, and found also to have an induction period, depending on the temperature and concentrations; probably there are two reactions involved here also, thio-sulphuric acid being first transformed into hydrogen sulphide and tetrathionic acid.

In the hydrogenation of unsaturated organic compounds in presence of colloidal metals, it is suggested that reaction of the hydrogen with oxygen adsorbed or occluded in the metal induces the reduction of the organic body. Similarly the observation of Venkataramaih (*Nature*, 1920, 106, 46) that permanganate is reduced when a mixture of hydrogen and oxygen is exploded over

it may be explained not by the formation of active hydrogen, but as a reaction induced by the reaction between the hydrogen and oxygen. S. I. L.

Catalysis. XIX. Photochemical Catalysis. A. K. SANYAL and N. R. DHAR (*Z. anorg. Chem.*, 1923, **128**, 212—217).—The reaction between mercuric chloride and ammonium oxalate in sunlight has been studied, and it is found that the velocity of reaction is independent of the concentration of the former, *i.e.*, the reaction is unimolecular, although in absence of light it is bimolecular (see Dhar, T., 1917, **111**, 750). With ferric chloride and ammonium oxalate, reaction is extremely slow in the dark, even on boiling, but proceeds normally at the ordinary temperature if the mixture has been exposed to light for a short time. Carbon dioxide retards both reactions. Iron salts exercise a strong positive catalytic effect on all reactions between oxalates and oxidising agents.

Many salts of lead, bismuth, and mercury are sensitive to tropical sunlight, darkening in colour; this effect is accelerated by foreign substances, especially those having the same anion as the salt employed. Halide salts of these metals show loss of the halogen after exposure, lead bromide losing 8—10% of its bromine after seventy-five hours' exposure.

Various mixtures of gases exposed to tropical sunlight react at the ordinary temperature. S. I. L.

Catalysis. XX. The Relation between the Order of a Reaction and its Temperature Coefficient. N. R. DHAR (*Z. anorg. Chem.*, 1923, **128**, 218—228).—The temperature coefficient diminishes with the order of reaction, being greatest for nil-molecular reactions, lower for unimolecular, and lower still for multimolecular reactions. Pseudo-unimolecular reactions are generally really bimolecular, and have moderately high temperature coefficients; the real and not the apparent order of reaction determines the temperature coefficient. S. I. L.

Catalysis. XXI. The Action of Neutral Salts. N. R. DHAR (*Z. anorg. Chem.*, 1923, **128**, 229—240).—The effect of various neutral salts on the reactions between (a) oxalic acid and chromic acid, (b) formic acid and chromic acid, (c) sodium formate and iodine, (d) sodium formate and mercuric chloride, and (e) sodium formate and silver nitrate has been studied. Some salts retard, others accelerate, the effect being specific for each salt, and more pronounced in dilute than in concentrated solutions; the order of reaction is not affected, nor is the temperature coefficient; the effect of the salt is not modified by change of temperature. S. I. L.

Catalytic Combination of Ethylene and Hydrogen in the Presence of Metallic Copper. II. Measurements of Reaction Velocity at 150°, 200°, and 250°. ROBERT N. PEASE (*J. Amer. Chem. Soc.*, 1923, **45**, 2235—2242; cf. this vol., ii, 472).—A continuation of previous work (*loc. cit.*). The velocity of combination of ethylene with hydrogen in the presence of copper has been determined at 150°, 200°, and 250°. The results show that in this range

of temperature the reaction is more nearly bimolecular than at lower temperatures, the combination at 0° is approximately unimolecular with respect to hydrogen, and is somewhat inhibited by excess of ethylene. The more nearly normal character of the reaction at the higher temperature is believed to be due to the fact that in these circumstances the reacting gases are not adsorbed to a measurable extent by the catalysts. The temperature coefficient of the velocity is much smaller at the higher temperatures, and decreases with increasing temperature. These facts are explained in a qualitative manner by taking into account the decrease of adsorption with increasing temperature and the normal increase in the velocity of the surface action.

J. F. S.

Studies of Electrovalency. III. The Catalytic Activation of Molecules and the Reaction of Ethylene and Bromine.
RONALD GEORGE WREYFORD NORRISH (T., 1923, 123, 3006—3018).

The Origin of the Chemical Elements. A. VON WEINBERG (*Z. angew. Chem.*, 1923, 36, 525—529).—An account of Bohr's recent theory of the orbits of revolution of electrons in the atoms from $\text{Li}=3$ to $\text{U}=92$ is given. The 3rd, 4th, 5th, and 6th electrons (Li , Be , B , C) describe elongated ellipses, the figure in the last instance regaining the symmetry of a tetrahedron. On further addition of electrons, the latter in consequence of the forces now present describe circles within the figure and with 8 added electrons the completely symmetrical neon is obtained. Continuing, the 11th electron describes an ellipse related to the neon complex as the 3rd electron was related to the helium nucleus and period III of the periodic system is obtained. In period IV the 8 elements Sc to Ni are formed by addition of electrons to the inner orbit and then follows a series similar to that of the earlier periods, and similarly with series V. This theory does not attempt to afford an explanation of the origin of the different elements. In framing a theory of this process, it is necessary to assume a universe filled with hydrogen nuclei and electrons of mass $1.649 \cdot 10^{-24}$ g. and $0.8996 \cdot 10^{-27}$ g., respectively, and also to assume the validity of the ordinary conceptions of mechanics such as inertia and centrifugal force, also of the Coulomb conception of electrical charges. It is, however, doubtful whether the helium atom can properly be considered as made up of 4 hydrogen nuclei and 2 electrons, although the atomic weight relation $4 : 1.008$ can be explained on Einstein's hypothesis by loss of energy in association. The author prefers to treat the helium nucleus as differing radically from other complex nuclei and develops a theory analysing the atoms of the different elements in terms of hydrogen and helium nuclei. Meitner's differentiation of the nuclei of radioactive elements into a central nucleus carrying the atomic charge and a neutral part is extended by him to all complex nuclei and the elements tabulated with the hydrogen and helium nuclei in the two parts shown separately. The nuclei in the neutral part are presumed to revolve around the central nucleus attended by their own electrons. Elements having odd atomic

numbers will necessarily include a hydrogen nucleus in the central nucleus. Isotopes differ only in the components of the neutral part, and hence their chemical properties which depend on the orbits of the electrons about the central nucleus are identical. The elements from which Rutherford removed hydrogen nuclei by bombardment with helium nuclei (B, N, F, Na, Al, and P) are the simpler atoms having hydrogen nuclei in the neutral part, so that, strictly speaking, he only effected the interconversion of isotopes. Such isotopes as those of chlorine in which one helium nucleus in the neutral part is replaced by two hydrogen nuclei, could not be generated from each other, which is in accordance with the constant composition of chlorine in nature. This theory leads to the conception of the origin of the elements, not by the random encounter of complex nuclei with electrons, but by the combination of hydrogen and helium atoms, of which some remain intact in the neutral part and others, completely ionised, join the central nucleus, their electrons adding themselves to the main swarm. The non-existence of elements above uranium is explained as follows. The higher the charge of the nucleus, the smaller is the diameter of the innermost electronic orbit, both on account of the increased attraction of the nucleus and the increased repulsion of the outer electrons. In the case of uranium, the radius of this orbit has fallen to the order of $1 \cdot 10^{-13}$, which is about the radius of the nucleus itself, so that more complicated systems could have no stable existence. This synthetic view of the origin of the elements, which is also supported by the evidence of ionisation of elements at very high temperatures, as in stellar spectra, affords a rational explanation of the existence of radioactive elements in the world to-day.

C. I.

The Bohr Atom. J. D. MAIN SMITH (*Chemistry and Industry*, 1923, **42**, 1073—1078).—The author discusses briefly the inadequacy of Bohr's theory of atomic structure and electron valency in its application to the explanation of chemical phenomena, instancing and illustrating the inability of the theory to explain the structure or the existence of certain simple compounds, *e.g.*, carbon monoxide, and its failure to account for the chemical activities of elements. Whilst the theory is incapable of general application in chemistry, it is applicable to all cases where simple atomic ions are concerned. The postulates concerning atomic linking and the number of co-valencies associated with an atom, introduced by Sidgwick in his extension of the Bohr theory to co-ordination compounds (T., 1923, **123**, 725) are examined critically, and the author concludes that they scarcely furnish a sufficient basis on which a consistent explanation of chemical phenomena can be built. Thus the author contends that there is no evidence to support the assumption of the existence of co-valencies, and shows, *inter alia*, that nine of the fourteen elements from lithium to chlorine are not in accord as regards respective values of the maximum co-ordination numbers predicted by application of the second postulate. Co-ordination numbers greater than 8, contrary to Bohr's theory,

are rare in chemistry, and, where they do occur cannot be predicted by the postulate, which is regarded as being inconsistent with the fundamental feature of Bohr's theory, which determines the electronic path about the nucleus in terms of the principal and secondary quantum numbers. The resolution of the "actual number of electrons" attached to an atom into groups is admissible only when such number is equal to Bohr's ionic numbers; otherwise the groups have no necessary reality. The extended theory assigns an anomalous position to hydrogen, for it disposes two of the four co-valency electrons in orbits to which their quantum number does not relate. Difficulties attending the application of the co-valency postulate appear to originate in the assumption that two shared electrons can be simultaneously effective in two atomic structures. Shared electrons must react as if only one at a time were effective in any one quantum orbit, and provision must be made for a harmonic reaction between shared and unshared electrons having the same quantum number.

J. S. G. T.

Application of the Adiabatic Hypothesis to the Model of Ortho-helium. OTTO HALPERN (*Z. Physik*, 1923, **18**, 344—351).—The author shows mathematically that Bohr's application of the adiabatic hypothesis (this vol., ii, 478) to the model of ortho-helium due to Landé, and comprising a coplanar system of electrons, is unjustifiable, and attributes to this misapplication the discrepancy between observed and calculated values of terms in the spectral series relating to ortho-helium.

J. S. G. T.

An Explanation of the Theory of the Rotation of the Atomic Nucleus. IV. HERBERT HENSTOCK (*Chem. News*, 1923, **127**, 241—243, 259—260; cf. this vol., ii, 400, 477, 679).—The octet of the nitrogen atom is probably distorted as far as the number of electrons present will allow. Two such distorted atoms when placed in juxtaposition in such a manner that the nuclei are orientated at right angles to one another form a model of the nitrogen molecule. There are no free valencies, and since no cube face is opened up to form the triple bond, the molecule must be very stable. The shape of the positive nitrogen atom is identical with that of the distorted carbon atom in carbon monoxide. This similarity, and the equality of the number of electrons present in the two molecules, may account for the property which nitrogen has of absorbing energy when present in an explosive mixture of carbon monoxide and oxygen (Bone, Newitt, and Townsend, *Proc. Roy. Soc.*, 1923, [A], **103**, 205). Nitrous oxide appears as $\text{N}:\text{N}:\text{O}$, which explains its easy reduction to nitrogen and its non-formation of hyponitrous acid with water.

In the second paper the structures of the oxides of nitrogen are discussed from the point of view of the author's theory (this vol., ii, 400, 477, 679).

E. H. R.

The Ion of the Hydrogen Molecule, according to the Quantum Theory. K. F. NIESSEN (*Arch. Néerland*, 1923, **7**, 12—59).—Considering the ion of the hydrogen molecule as constituted of an

electron moving about two positive nuclei permanently at rest, the author, following the analysis developed by Jacobi in the analogous case of motion about two centres of force, determines mathematically the electronic trajectories which are mechanically possible. From such paths are selected those which are stable and conform with stability of the nuclei in accordance with classical mechanics; these may be quantised in accordance with the ideas developed by Bohr and Sommerfeld. It is shown that when three quantum numbers are associated with the trajectories, symmetrical paths about the nuclei are alone stable. An ion executing such a path does not emit a rotation spectrum, and whether the motion be symmetrical or asymmetrical, no vibration spectrum is emitted.

J. S. G. T.

Quantum Theory of the Hydrogen Molecule. L. NORDHEIM (*Z. Physik*, 1923, **19**, 69—94; cf. A., 1922, ii, 703).—Employing the method developed by Born and Pauli for the calculation of perturbed motions and utilising the principles applicable to degenerate dynamical systems as determined by Born and Heisen (this vol., ii, 478) and by Nordheim, the author discusses analytically the motion of two electrons each moving about its respective associated positive nucleus—a model representing the neutral hydrogen molecule. In the first part of the analysis, the distance between the nuclei is considered to be so large that each electron may be conceived as describing a Keplerian ellipse about the appropriate nucleus. Under these conditions it is shown that ten configurations of the electronic orbits are possible. Five of these are ruled out by the consideration that the energy associated with them is positive, indicating repulsion between them and the nuclei. Two of the remaining five electronic configurations comprise coplanar circular orbits executed either in the same or opposite directions about their respective nuclei. Two others comprise orbits inclined respectively both at 60° , or one at 60° and one at 120° , to the line joining the nuclei, whilst the remaining configuration consists of electronic orbits executed in parallel planes perpendicular to the line joining the nuclei. The respective positions of the electrons in their respective orbits are given. A consideration of the stability of dynamical systems leads to the conclusion, in agreement with the result found by Kramers (this vol., ii, 312), that no model of the hydrogen molecule consisting of two identical atomic systems can be inherently stable. A consideration of the perturbations in the respective electronic orbits in the various configurations due to the proximity of the second nucleus—a factor taken into account in the latter part of the analysis—leads to the conclusion that whilst three of the five electronic configurations referred to suffer perturbations in such manner as still to yield inherently stable systems, these three do not conform with experimental results in the matter of nuclear distance and molecular energy of combination. The greatest agreement is found in the case of the Bohr-Debye model, constituting one of the five models, and comprising two coplanar circular

electronic orbits executed in the same direction by electrons having a relative phase difference of 180° . The remaining two models, which, regarded from the physical point of view, have most to commend them, are rejected, as the type of their electronic motions is entirely altered by perturbations prior to the establishment of equilibrium.

J. S. G. T.

Radii of the Atoms of the Alkali Metal Vapours. S. H. ANDERSON (*Physical Rev.*, 1922, 20, 200).—By assuming that the ionising potential is one-half of the potential of a point on the orbit of the valency electron, and that the distribution of the electrons in the kernel is that suggested by Bury (A., 1922, ii, 43) and Bohr (A., 1922, ii, 277), the radii of the valency electrons of the alkali metals are computed as follows: lithium, 1.379×10^{-8} cm.; sodium 1.80; potassium, 2.21; rubidium, 2.45; caesium, 2.695. When plotted against the integral numbers 2, 3, 4, 5, and 6, these values are uniformly distributed about a straight line. On passing from one metal to the next higher in the periodic table, an extra electron shell is therefore added to the atomic structure, and the shells are evenly spaced.

A. A. E.

The Radii of the Alkali- and Halogen-ions and of the Atoms of Inert Gases. WHEELER P. DAVEY (*Physical Rev.*, 1923, [ii], 22, 211–230).—An analysis of the author's measurements (this vol., ii, 413) of the ionic distances in the lattices of the alkali halides leads to the following conclusions: (1) These ions are packed as if they were nearly spherical. (2) The heavier ions have packing radii which are nearly constant, *i.e.*, independent of the ions with which they are combined. (3) The radii of potassium-, rubidium-, and caesium-ions are approximately equal to those of the negative ions with the same number of electrons, chlorine, bromine, and iodine, respectively. The approximation is the closer the greater the atomic number. Assuming that (1) and (2) hold rigidly, and that the radii of caesium- and iodine-ions are equal, the radii of the ions ($\times 10^{-8}$ cm.) are computed to be as follows: caesium and iodine, 1.974; rubidium, 1.679; bromine, 1.737; potassium, 1.548; chlorine, 1.589; sodium, 1.1 to 1.2; fluorine, 1.0 to 1.2. These values are in general agreement with those obtained by Landé, Richards, and Saha, but not by Bragg. If it is assumed that for each inert gas the radius is the mean of those for the alkali- and halogen-ions with the same number of electrons, the packing radii are computed to be as follows: xenon, 1.97; krypton, 1.71; argon, 1.57; neon, 1.15. These results are only 0 to 0.27 unit higher than those obtained by Rankine from viscosity measurements. Derived values for the "atomic volume per electron" are approximately constant for the inert gases except in the case of argon, where it is low. In a note, it is argued that Wyckoff's value of 1.081 Å. for the radius of the chlorine-ion (this vol., ii, 311) is actually that of the neutral atom of chlorine.

A. A. E.

Theory of Residual Affinity and its Application to Organic Chemistry. I. The Fundamental Principles of the Theory.

A. ORÉKHOV (*Rev. gén. Sci. pur. Appl.*, **34**, 264—270; from *Chem. Zentr.*, 1923, iii, 279).—The author discusses Werner's theories of reciprocal desaturation of valencies in relation to simple, double, and treble linkings. It is concluded that in long carbon chains the linkings are variable and that periodic changes in properties occur.

G. W. R.

The Electronic Theory of Valency. II. Intra-molecular Ionisation in Organic Compounds. III. The Transmission of Chemical Affinity by Single Bonds. T. MARTIN LOWRY

(*Phil. Mag.*, 1923, [vi], **46**, 964—976, 1013—1020).—II. In continuation of previous work (this vol., ii, 480), the author shows that the theory of intramolecular ionisation can be extended to organic compounds, if it be assumed that double bonds can assume a form in which one carbon atom carries eight *L*-electrons, and the other six only, one pair of electrons being shared. This type of double bond is thus constituted of one co-valency and one electro-valency. On this assumption, ethane, ethylene, and acetylene

have the respective formulæ $\begin{array}{ccc} \text{CH}_3-\text{CH}_3 & \overset{+}{\text{CH}_2}-\overset{-}{\text{CH}_2} & \overset{+}{\text{CH}}=\overset{-}{\text{CH}} \\ \text{CH}_3-\text{CH}_3 & \text{CH}_2=\text{CH}_2 & \text{CH}\equiv\text{CH} \end{array}$

the barb, —, denoting an electro-valency passing from the positively to the negatively charged atom. This extension of the theory brings the reactivity of organic compounds into line with the activity of inorganic ions and makes it possible to regard all chemical action as ultimately ionic in character. The resting forms of molecules are not necessarily identical with their ionised or reactive forms. It is probable that organic compounds may be divided into two groups according as the normal structure of the molecule is polar and therefore reactive, or is non-polar and must undergo isomeric change into a polar form before it can react. Thus zinc methyl, sodium ethoxide, and methylethylaniline oxide probably have permanently ionised structures. In general, a compound which requires "activating" by heat or a catalyst, etc., before it will react is probably in a non-polar condition. It is pointed out that the theory of mixed double bonds affords a new interpretation, which is supported by experimental evidence, of the phenomena of conjugation discussed by Thiele, and of other phenomena. The properties of "multipolar ions," *i.e.*, ions which in addition to the electrification required to give the net charge of the ion possess additional positive and negative charges, afford a new interpretation of the phenomenon of tautomerism, and explain the readiness with which tautomeric ions yield co-ordination-compounds.

III. The author examines whether the two mechanisms discussed in previous parts are adequate to explain all the facts in reference to the transmission of chemical affinity through chains of atoms, or whether an additional mechanism is required. The existence of an unexplained residue of facts necessitating an additional mechanism is regarded as unproved, and the work of Lapworth

(T., 1922, 121, 416) and of Flürscheim (T., 1909, 95, 718) is examined in this connexion. It is pointed out that the reactivity of the methyl group in ethyl crotonate agrees with the theory of polar double bonds. It cannot be used as a proof of the existence of polarised single bonds, as it is interpreted simply in terms of Thiele's theory of conjugation. The small fluctuations observed in the strengths of unsaturated acids as the double bond is moved along the chain may be attributed to steric influences, depending on the configuration of the chain rather than on a reversal of polarity in alternate atoms. The fact that amino-acids are sometimes stronger than the acids from which they are derived is attributed to the acylous character of the amino-group: this is usually masked by the direct neutralising action of the basic group. The special mechanism devised by Flürscheim to explain the apparent anomaly is therefore unnecessary. The author concludes that alternate polarities are characteristic of conjugated systems, and it is not yet proved that they can be developed in chains of single bonds, where both acylous and basylous groups produce effects of constant sign.

J. S. G. T.

Co-ordination and Acidity. T. M. LOWRY (*Chemistry and Industry*, 1923, 42, 1048—1052).—Hydrogen is unique in that its combination with other atoms can only be represented by a single type of valency. A naked proton cannot lead an isolated existence, but will probably attach itself to any octet which is not too fully occupied by other atoms. From this point of view, the water in aqueous hydrochloric acid functions as an acceptor of hydrogen-

ions: $\text{H}_2\text{O} + \text{HCl} \rightleftharpoons \text{OH}_3^+ + \text{Cl}^-$. It is now suggested that water may take a more active part in the ionisation of acids by combining with the anion to form a co-ordinated complex anion and expelling the hydrogen-ion in the same way as the chlorine-ions are successively expelled from the triammine $[\text{CoCl}_3, 3\text{NH}_3]$ by molecules of ammonia, with eventual formation of $[\text{Co}, 6\text{NH}_3]\text{Cl}_3$. The final stage in the ionisation of sulphuric acid might then be represented by $[\text{SO}_4, x\text{H}_2\text{O}]\text{H}_2$. This theory of the relation between hydration and ionisation accords with the hygroscopic character of strong acids. The theory may be regarded as an extension of Werner's theory of acids and bases.

E. H. R.

The Polarisation of Double Bonds. A. LAPWORTH and R. ROBINSON (*Nature*, 1923, 112, 722).—Thomson (this vol., ii, 682) suggests that in such a system as $\text{Cl}-+\text{C}_1-+\text{C}_2-+\text{C}_3-+\text{C}_4-+\text{C}_5$ the existence of the electrostatic doublet between Cl and C₁ will cause electrons to crowd into C₁ from C₂ and into C₃ from C₄, bringing about an alternating condition in the chain. For the same reason, however, that electrons pass from C₂ into C₁, it would appear that they should also pass from C₃ into C₂, and the effect would then be continuous, although diminishing in degree along the chain. If it is held that electrons may pass from one carbon atom to another if these are joined by a double bond, but not if they are joined by a single bond, the acceptance

of Kekulé's benzene formula in its simplest form is necessary. Moreover, Thomson's method of deduction of the alternate effect leads in numerous cases to results which are negatived by experiment. In this connexion, the behaviour of vinyl chloride and that of the group $C_3=C_2-C_1=O$ are discussed. The classification of atoms as "chemically active" or "chemically inert," according as there is a defect or excess of electrons, respectively, is considered to be unsatisfactory, since both types appear to be reactive under the correct conditions. A. A. E.

A Useful Substitute for Ground Joints in Vacuum Technique. A. VON ANTROPOFF (*Ber.*, 1923, 56, [B], 2137—2138).—The principle of the mercury seal is utilised, but a fusible mixture of colophony, turpentine, and linseed oil is used as seal and is allowed to set solid before use. This mixture has the advantage of transparency. If the contents of the vacuum vessel must not come in contact with this mixture, a mercury seal covered with the colophony mixture may be employed. H. H.

Apparatus for Absorbing and Washing Gases. K. KELLER (*Chem. Ztg.*, 1923, 47, 506).—The apparatus consists of a cylindrical tube, closed at the bottom and fitted with a rubber stopper; the inlet tube for the gas extends just below the stopper, whilst the exit tube reaches into the liquid contained in the lower part of the cylinder. The exit tube is provided with a bulb below the stopper, and a spiral tube extends from the side of this bulb to just below the surface of the liquid. The gas entering the apparatus is forced upwards through this spiral tube, carrying with it a quantity of the liquid; if any liquid reaches the bulb it passes downwards through the central part of the tube below the bulb, whilst the washed gas leaves the bulb through the upper part of the delivery tube. W. P. S.

Extraction Apparatus with Device for the Recovery of Solvent. TWISSELMANN (*Chem. Ztg.*, 1923, 47, 506).—A plain cylindrical tube (similar to the body of a Soxhlet extractor, but without a siphon tube) contains the substance to be extracted. The top of this tube is connected with a vertical condenser by a tapped tube provided with a large bulb above the tap, and a side tube (for the vapour of the solvent) extends from below the tap to the lower part of the condenser. During the extraction, the tap is open so that the condensed solvent passes through the substance in the extraction tube and thence to the extraction flask; when the extraction is complete, the tap is turned and the condensed solvent is collected in the bulb above the tap. W. P. S.

The Filtration of Viscous Liquids. A. GUTBIER and E. SAUER (*Z. anorg. Chem.*, 1923, 128, 15—16).—For the filtration of highly viscous liquids, such as 10—20% glue solution, the so-called "cellulose filter" is particularly useful. The substance is obtainable in square tablets which must be broken up as small as possible and placed in a capacious flask with hot water, and shaken until a uniform pulp is obtained. As a support for the

filter, a perforated porcelain plate or Buchner funnel may be used, covered with copper or nickel wire-netting. The pulped filter material is poured quickly on to the support, sucked dry, and well pressed down. The cake formed on the support should be 2—3 cm. thick. E. H. R.

A Simple Lecture Experiment for Obtaining Neon and Helium from the Air and Demonstrating the Absorbent Power of Charcoal. A. VON ANTROPOFF (*Ber.*, 1923, 56, [B], 2135—2137).—A tube containing well-dried coconut charcoal is fused on to a vacuum tube fitted with electrodes. The other end of the charcoal tube is drawn out into a long, fine capillary and sealed. An induction coil is connected to the vacuum tube and the charcoal plunged into liquid air. Very soon the tube becomes luminous and then again dark as the air is condensed in the charcoal. Then the capillary is broken and air allowed to stream slowly into the tube through the cooled charcoal. The other components are absorbed and the spectrum of neon and helium may be demonstrated. H. H.

Inorganic Chemistry.

The Presence of Chlorine in Synthetic Hydrochloric Acid.

B. NEUMANN (*Z. angew. Chem.*, 1923, **36**, 529—531).—A calculation of the theoretical temperature developed by the combination of equivalent volumes of hydrogen and chlorine gives the figure of 2648°, at which the degree of dissociation of hydrogen and chlorine may be 2%; but as the gases combine again very rapidly on cooling, this cannot account for the occasional presence of free chlorine in synthetic hydrogen chloride. It is due to the dilution of the chlorine with air and the employment of insufficient hydrogen to satisfy both the chlorine and oxygen present. In this case, the relation $K = [\text{H}_2\text{O}]^2[\text{Cl}_2]^2/[\text{HCl}]^4[\text{O}_2]$ obtains, and the value of K at different temperatures has been experimentally determined, $\log k$ at 25° being = 13.28, at 600° = 0, at 1984° = -4.30, according to Treadwell. There are also the relations $K = (x/2[1-x])^4 \cdot 1/p_{\text{O}_2}$, in which x is the relative proportion of chlorine mols. to hydrogen chloride mols. (Haber) and $\log k = 6034/T - 6.972$ (Treadwell). From these, for a gas mixture of given composition (initial and final) the value of T , the temperature of reaction, can be calculated. Results are tabulated for chlorine-air mixtures of various compositions, the hydrogen in each case being the equivalent of the chlorine. With excessive dilution, the heat of reaction will be insufficient to carry the reaction on, and the conclusion is drawn that for combustible mixtures the chlorine content of the final gas mixture will range between 0.5% and 5%.

C. I.

Absorption of Atmospheric Gases by Water. J. H. COSTE (*Analyst*, 1923, **48**, 433—435; cf. A., 1917, ii, 463; 1918, ii, 265).—A graph is given showing the volumes of oxygen and nitrogen at *N.T.P.* dissolved by 1 litre of water of any salinity from 0 to 20 g. of chloride-ions per kg. of water. W. P. S.

A Simplified Graphical Representation of the Yield and Concentration Afforded by Ozone Apparatus. HANS BECKER (*Wiss. Veröffentl. Siemens-Konzern*, 1923, **3**, 243—247).—The yield, *A*, in g. of ozone produced per kw. hour is shown to be related to the concentration *c* and the limiting concentration *C* of ozone produced, by the linear equation $A = A_0(1 - c/C)$. Moreover, the energy employed, W_{Rt} , per cubic metre of oxygen treated is given by $W_{Rt} = c/A$. These two linear relations are plotted on a diagram employing rectangular co-ordinates, the former appearing as straight lines drawn with values of *A* and *c* as ordinates and abscissæ respectively, whilst the latter is represented by a series of straight lines radiating from the origin and inclined to the axis of ordinates at respective angles given by $\tan^{-1} c/A$. From the diagram, the concentration of ozone, the yield and power employed in an apparatus for producing ozone may be read off directly.

J. S. G. T.

Behaviour of Rhombic Sulphur at High Temperatures and Pressures. H. ROSE and O. MÜGGE (*Nach. K. Ges. Wiss. Göttingen*, 1922, **10**, 105—107; from *Chem. Zentr.*, 1923, iii, 288).—The deformability and plasticity of rhombic sulphur are not appreciably increased by heating at temperatures up to 281° under pressures of 1,000 to 19,600 kg. per sq. cm. The data of Tammann up to 3,143 kg. per sq. cm. pressure and 190° were confirmed by the authors. At higher pressures, the fusion curve of rhombic sulphur rises. At 19,300 kg. per sq. cm. it has m. p. 263°.

G. W. R.

The Formation of Sulphur by the Action of Sulphur Dioxide on the Sulphides of Calcium, Zinc, and Iron. LOTHAR WÖHLER, F. MARTIN, and E. SCHMIDT (*Z. anorg. Chem.*, 1923, **127**, 273—294).—Sulphur dioxide acts on calcium sulphide at temperatures below 1,000° to give the sulphate and sulphur, but the reaction is soon brought to a standstill owing to the formation of a protective layer of sulphate on the pieces of sulphide. By working at temperatures above 1,000°, this can be avoided, as the reaction products are lime and sulphur. The low temperature reaction can, however, be accelerated by the addition of triferrie tetroxide, which acts as a catalyst. Zinc blende reacts with sulphur dioxide to give the oxide and sulphur, but here again the reaction velocity rapidly diminishes owing to the formation of a protective layer, in this case of basic sulphide. Both sulphides of iron react with sulphur dioxide to give triferrie tetroxide and sulphur. The reaction is rapid and complete, being catalytically accelerated by the oxide.

H. H.

Sulphurous Acid and its Salts. I. The Decomposition of Sulphurous Acid and its Salts in Aqueous Solution. F. FOERSTER, F. LANGE, O. DROSSBACH, and W. SEIDEL (*Z. anorg. Chem.*, 1923, **128**, 245—342).—The spontaneous decomposition of sulphurous acid, forming sulphuric acid and sulphur, proceeds extremely slowly, requiring at 100° several days and at 150° about two days for completion. The change is autocatalytic, being accelerated by the sulphur and retarded by hydrogen-ions; the latter effect masks the former as the change proceeds. Dilute solutions decompose more quickly and completely than concentrated solutions, whilst in acid solutions the decomposition is inhibited, being completely suppressed in 2*N*-hydrochloric acid solution.

The first stages in the decomposition are probably (b) $2\text{HSO}_3' \rightarrow \text{SO}_4'' + \text{SO} + \text{H}_2\text{O}$, and (c) $2\text{SO} + \text{H}_2\text{O} \rightleftharpoons \text{S}_2\text{O}_3'' + 2\text{H}'$, (b) being extremely slow. The positive catalytic action of sulphur is probably due to the formation of thiosulphate, (d) $\text{HSO}_3' + \text{S} \rightleftharpoons \text{S}_2\text{O}_3'' + \text{H}'$, which is very rapid in comparison with (b) and (c), and gives rise to penta-, tetra-, and tri-thionic acids, thus, (e) $5\text{S}_2\text{O}_3'' + 6\text{H}' \rightarrow 2\text{S}_5\text{O}_6'' + 3\text{H}_2\text{O}$, (f) $\text{S}_5\text{O}_6'' + \text{HSO}_3' \rightarrow \text{S}_4\text{O}_6'' + \text{S}_2\text{O}_3'' + \text{H}'$, (g) $\text{S}_4\text{O}_6'' + \text{HSO}_3' \rightarrow \text{S}_3\text{O}_6'' + \text{S}_2\text{O}_3'' + \text{H}'$, and finally to sulphuric acid, (h) $\text{S}_3\text{O}_6'' + \text{H}_2\text{O} \rightarrow \text{SO}_4'' + \text{S}_2\text{O}_3'' + 2\text{H}'$, all these changes (e) to (h), proceeding very rapidly in comparison with (b); the intermediate polythionic acids increase rapidly in the solution at the beginning. The thiosulphuric acid formed is, however, transformed back to sulphurous acid by hydrogen-ions, $\text{S}_2\text{O}_3'' + \text{H}' \rightarrow \text{HSO}_3' + \text{S}$, which reaction prevents the changes (d) to (h) and brings the decomposition to a halt.

The strong positive catalytic effect of hydriodic acid on the decomposition is ascribed to the formation of complex ions. The decomposition of the metal hydrogen sulphites is different from that of the acid itself in that until the decomposition is far advanced the concentration of hydrogen-ions remains low, being that of a hydrogen sulphite-sulphurous acid solution; the change is therefore very strongly positively autocatalytic, and is greatly hastened by addition of sulphur or polythionates. If sulphur dioxide is allowed to escape from the solution, as by boiling a strong sodium hydrogen sulphite solution in an open vessel, polythionic acids are not formed, the mechanism following (b) and (c) above being $\text{S}_2\text{O}_3'' + \text{H}_2\text{O} \rightarrow \text{SO}_4'' + \text{H}_2\text{S}$, $\text{S}_2\text{O}_3'' + 2\text{H}' \rightarrow \text{SO}_2 + \text{S} + \text{H}_2\text{O}$, and $2\text{H}_2\text{S} + \text{SO}_2 = 3\text{S} + 2\text{H}_2\text{O}$.

Selenium and selenious acid act as powerful positive catalysts, forming the selenosulphuric-ion SeSO_3'' in the solution. Potassium selenosulphate and selenodithionate have been prepared in the pure state, and indications of the existence of selenium analogues of the polythionic acids obtained. The mechanism of the series of changes (c) to (h) when selenium dioxide is substituted for sulphur dioxide has been examined.

Tellurium when free from selenium has no catalytic activity with regard to the decomposition of hydrogen sulphites. S. I. L.

Preparation of Sulphuryl Chloride. SIR WILLIAM J. POPE (*Rec. trav. chim.*, 1923, **42**, 939—941; cf. T., 1920, **117**, 1410).—Bone charcoal or activated wood charcoal forms a most convenient

catalyst for promoting the union of sulphur dioxide and chlorine to form sulphuryl chloride. Combination occurs instantaneously, and, provided that the reaction vessel is cooled to 30°, the chloride is condensed and may be drained away as rapidly as it is formed. There seems to be no limit to the life of the catalyst. H. H.

The Alteration of Thiosulphate Solutions. F. FEIGL (*Ber.*, 1923, **56**, [B], 2086—2088; cf. this vol., ii, 483, and A., 1922, ii, 873).—It is suggested that the alteration of thiosulphate solutions on keeping may be due to the decomposition of the thiosulphate into sulphate and sulphur which, under the influence of hydrogenions or of carbon dioxide, combine to form the co-ordination

complex, $\begin{bmatrix} \text{SO} \\ \text{S} \\ \text{OO} \end{bmatrix} \text{Na}_2$.

H. H.

The Preparation and Properties of Selenium Trioxide and Chloroselenic Acid. RICHARD ROBERT LE GEYT WORSLEY and HERBERT BRERETON BAKER (*T.*, 1923, **123**, 2870—2875).

Ammoniates as Binary Systems. III. Water-Ammonia. FRITZ FRIEDRICHS (*Z. anorg. Chem.*, 1923, **127**, 228).—The author cannot confirm the existence of the two hydrates of ammonia described previously by Rupert (*A.*, 1909, ii, 726). H. H.

The Catalytic Oxidation of Ammonia and Hydrogen Cyanide. I. JÓZEF ZAWADZKI (*Roczniki Chemji*, 1923, **11**, 145—157).—A full summary is given of the work published on the subject by different authors and the results are compared and criticised. G. A. R. K.

The Catalytic Oxidation of Ammonia and Hydrogen Cyanide. II. JÓZEF ZAWADZKI and JAN WOLMER (*Roczniki Chemji*, 1923, **2**, 158—182).—The oxidation of ammonia and hydrogen cyanide was carried out in an electrically heated quartz tube containing platinum or ferric oxide as a catalyst, using concentrated sulphuric acid to absorb the products of the reaction.

Most of the experiments with ammonia were carried out with a platinum catalyst in the form of gauze (400 per sq. cm.); the ferric oxide catalyst did not give good results. The effect of different temperatures, rates of flow of gas, and partial pressures of ammonia were studied, and the results are expressed in the form of curves. These show that at temperatures below 750° the yield of oxides of nitrogen increases with an increase in the rate of flow, that is, with a shortening of the time of contact between the reacting gases and the catalyst; the increase in yield reaches a maximum and then diminishes (for rates of flow from 2 to 42 litres per hour), but at temperatures above 750° the increase is continuous. It is also found that the greater the rate of flow the higher the optimum temperature of the reaction. There seems to be no absolute optimum temperature for this reaction; a short contact with the catalyst and a high temperature appear to be the most favourable conditions. The effect of the partial pressure of ammonia

in the reaction mixture is not very great. The relative amounts of nitric oxide and nitric peroxide formed depend entirely on the extent to which the nitric oxide in the reaction product undergoes oxidation.

The experiments with hydrogen cyanide in the presence of ferric oxide show that the yield of oxides of nitrogen increases with increase of temperature up to 780° ; the rate of flow of the reaction mixture is of secondary importance; a few experiments carried out with the platinum catalyst mentioned above show that the yields are comparable with those obtained in the oxidation of ammonia under similar conditions, and an increase in the rate of flow of the gases is beneficial at high temperatures.

The mechanism of the catalytic oxidation of ammonia is discussed, and it is suggested that the first step is the dissociation of the ammonia into its constituent elements; the atomic nitrogen then combines with oxygen to form nitric oxide, provided the temperature is not too high to allow the existence of this compound; otherwise the reaction $N+N=N_2$ will proceed at the expense of the reaction $N+O=NO$, and it is on the relative rates of these two reactions that the yield of the desired product depends. The view put forward by Neumann and Rose (A., 1920, ii, 247) that the formation of nitrogen at higher temperatures is due to the direct oxidation of the ammonia to nitrogen and water is criticised, because in that case the reaction should be independent of the rate of flow of the gases and show a definite optimum temperature, whereas it is now shown that equally good results can be obtained with higher temperatures than those used by Neumann and Rose (500°), provided the flow is suitably accelerated. It is also shown that nitric oxide decomposes quite appreciably (12.2 % at 800°) under conditions similar to those used, and this decomposition is greatly assisted by contact with a platinum catalyst.

The reason of the poor yields at temperatures below 500° may perhaps be attributable to the reaction between ammonia and nitrogen trioxide and peroxide, whilst at higher temperatures these oxides dissociate into oxygen and nitric oxide. G. A. R. K.

Action of Sulphur Chloride on Ammonia, and on Organic Bases. ALEXANDER KILLEN MACBETH and HUGH GRAHAM (*Proc. Roy. Irish Acad.*, 1923, **36**, 31—40).—By adding an ice-cold chloroform solution of ammonia to sulphur monochloride in the same solvent, nitrogen sulphide is obtained according to the equation: $12\text{SCl} + 16\text{NH}_3 = \text{N}_4\text{S}_4 + 12\text{NH}_4\text{Cl} + 4\text{S}_2$. Other sulphides of nitrogen, however, are formed, for after precipitation of the sulphide, N_4S_4 , by the addition of alcohol, the mother-liquors may be concentrated to obtain nitrogen pentasulphide, N_2S_5 , and also *hexasulphamide*, S_6NH_2 , which crystallises in colourless, square plates, m. p. 105° , insoluble in water, but soluble in organic solvents. This compound gives a coloration with alcoholic potassium hydroxide and with alcoholic solutions of organic bases. It is thought that this coloration may be due to the formation of a salt of a nitrogen-sulphur acid, but attempts to obtain such an acid or its salts were unsuccessful. H. H.

Ammoniates as Binary Systems. II. Hydrazine-Ammonia. FRITZ FRIEDRICHS (*Z. anorg. Chem.*, 1923, **127**, 221—227; cf. A., 1921, ii, 503).—Carefully purified hydrazine has m. p. $+1.8^{\circ}$, as determined by a dilatometric method. The three-dimensional pressure-temperature-concentration diagram for the system hydrazine-ammonia has been completely mapped out, and it is shown that no compound of the two components is formed. H. H.

The Atomic Weight of Boron. ALFRED STOCK and ERNST KUSS (*Z. anorg. Chem.*, 1923, **128**, 49—75).—The accepted atomic weight of boron, 10.90, is probably too high. According to Aston, boron contains two isotopes of atomic weights 10 and 11, in such proportions that the experimental atomic weight should be about 10.75 ± 0.07 . Baxter and Scott have recently found 10.83 ± 0.01 by analysis of the chloride and bromide (A., 1922, ii, 285), and Hönigschmid and Birckenbach (this vol., ii, 559) adopt the value 10.82, also from the chloride. The authors have now made use of the gaseous boron hydride, B_2H_6 , for the atomic weight determination, by measuring the volume of hydrogen formed by reaction of a known weight of the gas with water: $B_2H_6 + 6H_2O = 2H_3BO_3 + 6H_2$. This reaction is shown to proceed quantitatively. The hydride, B_2H_6 , was prepared by heating B_4H_{10} to 95° for five hours, followed by fractional distillation at low temperatures. As a result of six concordant experiments, the atomic weight of boron is found to be 10.8055 ± 0.0015 . This is the lowest value so far obtained.

The atomic weight of silicon was determined in a similar manner, using the reaction of silicon hydride, with sodium hydroxide: $SiH_4 + 2NaOH = Na_2SiO_3 + 4H_2$. This work was carried out before the methods of precision finally adopted in the work on boron had been fully developed. Three closely agreeing experiments gave the mean atomic weight for silicon 28.15, which is considerably lower than the accepted value (28.3). E. H. R.

The Coefficients of Viscosity and Slip of Carbon Dioxide by the Oil Drop Method, and the Law of Motion of an Oil Drop in Carbon Dioxide, Oxygen, and Helium at Low Pressures. JAMES M. EGLIN (*Physical Rev.*, 1923, **22**, 161—170).—The coefficient of viscosity of carbon dioxide, determined by the oil drop method, is 1.478×10^{-4} at 23° and 760 mm. A. A. E.

The Interaction of Potassium Tetroxide with Ice and with Dilute Sulphuric Acid. HERBERT HAWLEY and HENRY JULIUS SALOMON SAND (*T.*, 1923, **123**, 2891—2896).

A Study of Secondary Valency by Means of X-Rays. GEORGE L. CLARK and WILLIAM DUANE (*Physical Rev.*, 1922, **20**, 85—86; cf. A., 1922, ii, 483).—Potassium tri-iodide, preserved against sensible decomposition, was analysed by the X-ray method and found to be centred cubic, with an iodine atom going to the centre of each of the original unit cubes of potassium iodide, thereby increasing

the edge length from 3.532 to 4.680×10^{-8} cm. The number of molecules per unit cube was found experimentally to be 0.4986 .

A. A. E.

Promoter Action in the Decomposition of Potassium Chlorate. HARVEY A. NEVILLE (*J. Amer. Chem. Soc.*, 1923, **45**, 2330—2333).—The fact that commercial manganese dioxide is a more effective catalyst in the decomposition of potassium chlorate than the pure material is shown to be due to the presence of 8.8% of ferric oxide in the commercial article. Experiments with mixtures of these two oxides confirm this view, and show that each oxide is a promoter of the other. The action of cupric oxide and manganese dioxide as mutual promoters is also shown experimentally. J. F. S.

The Melting-point (Solidus) Curve for Mixtures of Potassium Nitrate and Sodium Nitrate. WALTER MATTHEW MADGIN and HENRY VINCENT AIRD BRISCOE (*T.*, 1923, **123**, 2914—2916).

The Structure of Crystals of Sodium Bromate and Sodium Chlorate. L. VÉGARD (*Z. Physik*, 1923, **18**, 379—381).—The author replies to criticism by Kolkmeijer, Bijvoet, and Karssen (this vol., ii, 414) of the structures attributed by him to crystals of sodium bromate and sodium chlorate. Considerations of the relative numbers and intensities of lines in the respective X-ray spectra, and of the experimental determination of these intensities lead the author to conclude that the structures proposed by him are to be preferred to those suggested by his critics. J. S. G. T.

Investigation with X-Rays of the Structure of Crystals of Sodium Chlorate and Sodium Bromate. A. KARSEN (*Rec. trav. chim.*, 1923, **42**, 904—930).—An attempt to decide between the models proposed by the author and others (A., 1921, ii, 200) and those proposed by Dickinson and Goodhue (A., 1922, ii, 145). It is concluded that with the present uncertain underlying assumptions no final choice can be made. H. H.

Heterogeneous Equilibria in the Ternary System Sodium Sulphite-Sodium Sulphate-Water. ALBERT CHERBURY DAVID RIVETT and NEIL BANNATYNE LEWIS (*Rec. trav. chim.*, 1923, **42**, 954—963).—Isotherms in the ternary system sodium sulphate-sodium sulphite-water were obtained at 0.1° , 17.5° , 25° , and 37.5° . The stable systems at the three lower temperatures show two series of mixed crystals, one between the heptahydrates, and one between the decahydrates of the salts. At 25° , there is also a metastable system of mixed crystals of the anhydrous salts. At 37.5° , the stable system is one in which there are three series of mixed crystals between the anhydrous salts. H. H.

X-Ray Investigation of the Crystal Structure of Lithium and Lithium Hydride. J. M. BIJVOET (*Rec. trav. chim.*, 1923, **42**, 859—903).—The elementary cell of lithium is found to be a centred cube with an edge of 3.50 \AA ., each cell containing two atoms: the "atomic domain" is 3.04 \AA . in diameter. A lattice of stationary valency electrons does not explain the results obtained,

and it is thought possible that the valency electron rotates round the nucleus, or possibly between the nuclei, in planes perpendicular to the trigonal axes.

Lithium hydride also crystallises in cubes with four LiH groups per unit cell of side 4.10 Å. Two models appear to fit the facts: (a) with atoms at the points of the lattice with radii of the same order of magnitude as found by Bohr for the free atoms: (b) with positive lithium-ions and negative hydrogen-ions at the points of the lattice, the electrons rotating round the nuclei in planes perpendicular to the non-intersecting trigonal axis. In this case, the radius of the lithium⁺-ion is about 0.05*a*, and of the H⁻-ion is about 0.58*a*. This structure, of course, implies a heteropolar binding in the hydride, as against a homopolar linking in the metal. H. H.

Crystal Structures of Lithium Iodide and Rubidium Fluoride. R. W. G. WYCKOFF and EUGEN W. POSNJAK (*J. Washington Acad. Sci.*, 1923, **13**, 393—397).—An apparent discrepancy in the results obtained by the authors (A., 1922, ii, 214, 499) and by Davey (this vol., ii, 413) for the crystal structure of lithium fluoride as determined by X-ray analysis, is attributed to the probability that the material employed by the latter was not the anhydrous salt. Additional X-ray data referring to lithium iodide are given. It is pointed out that the observed intensities of the diffraction lines obtained with the material used are different from those calculated for the assigned structure, and that the calculated interatomic distances associated with this structure do not agree with those to be anticipated from a consideration of "atomic radii" determined by W. L. Bragg (A., 1920, ii, 537). The structure of lithium iodide, as determined by the authors from observations on the fused material, gives a "sodium chloride arrangement" of the atoms for which the atomic distance, Li to I, is in substantial agreement with that to be anticipated from the additive rule, viz., 3.015 Å. Accepting this structure, the only outstanding discrepancy between calculated and anticipated values of atomic distances amongst the alkali halides would be that associated with the crystal structure of rubidium fluoride, additional data for which are given. J. S. G. T.

Aqueous Solutions of Ammonium Hydrogen Carbonate. CLAUDE BONNIER (*Compt. rend.*, 1923, **177**, 685—688).—A study of the effect, on the gaseous pressure produced in closed vessels, by aqueous solutions of ammonium hydrogen carbonate, of (1) the concentration of the solution, and (2) the relation between the volumes of liquid and gaseous phases (cf., also, Dibbits, A., 1875, 421, and Berthelot and André, A., 1887, 11). The results are expressed by means of curves, which should be consulted for details. E. E. T.

Rendering Thin Silver Films on Glass Visible. J. ESTERMANN and O. STERN (*Z. physikal. Chem.*, 1923, **106**, 399—402).—Gerlach and Stern have shown previously that invisible silver films may be rendered visible by physical development (*Z. Physik*,

1921, 8, 110; 1922, 9, 349, 353). The present paper deals with experiments designed to ascertain the minimum thickness of silver which can be detected in this manner. The silver films were produced from a silver-plated platinum wire which on heating emits a stream of silver atoms; these pass through a small hole in a platinum screen and on to the glass. The thickness of the film may be calculated by the formula $d = d_0 \cdot \rho^2 / r^2$, where d_0 is the thickness of the silver on the platinum wire, ρ the radius of the hole in the screen, r the distance of the screen from the glass plate, and d the thickness of the film. The plate of glass after exposure is placed in a solution of 1—2% quinol containing a little gum arabic and then 1—2 drops of 1% silver nitrate are added. After a few minutes, the film commences to show. It is shown that the thinnest film detectable by this method is 2×10^{-9} cm. Holding the film in cadmium vapour also develops it, the limit of the method being the same as above. Experiments with copper films produced in the same manner show that a film of this metal of the same thickness as the silver can be detected by the same method. J. F. S.

Structure of Thin Silver Precipitates. J. ESTERMANN (*Z. physikal. Chem.*, 1923, 106, 403—406).—In an earlier paper (preceding abstract) a method is described whereby thin silver films were rendered visible by a physical development which consisted in depositing silver or cadmium on the film. It is now shown that the developed film in some cases could be removed as a foil, but in others it remained as mere spots of silver of a grey or brown colour. The silver films have therefore been examined ultramicroscopically. It is shown that films 3×10^{-9} cm. thick are made up of definite individual particles. Since an ultramicroscopic particle must consist of at least 1,000 atoms, it follows that these crystals cannot be formed from silver deposited in the position where the crystal is found. It is suggested that the silver atoms are adsorbed on the glass and that by collisions with other atoms in the adsorption layer the crystals are built up. The author's experiments indicate that the mean free path of the silver atoms is of the order of 100 atomic diameters. J. F. S.

Reduction of Silver Salts by Means of Manganous Salts. GIUSEPPE BARBERI (*Gazzetta*, 1923, 53, 645—648).—The black, pulverulent precipitate formed on addition of 0.1N-ammoniacal silver nitrate solution to 0.1N-manganous sulphate solution at the ordinary temperature consists of a mixture of manganese dioxide and silver (cf. Wöhler, *Annalen*, 1837, 41, 344). If the former solution contains only sufficient ammonia to dissolve the silver hydroxide first formed, the precipitate will have the composition $\text{MnO}_2 + 2\text{Ag}$. Rose's statement that the compound $\text{Mn}_2\text{O}_3 \cdot \text{Ag}_4\text{O}$ is formed under these conditions (*Annalen*, 1857, 101, 229) is erroneous. T. H. P.

The Action of an Aqueous Solution of Sodium Hyposulphite (Hydrosulphite) on Silver Chloride. The Recovery of Silver from Silver Chloride Residues. J. B. FIRTH and J. HIGSON (*J. Soc. Chem. Ind.*, 1923, 42, 427—429t).—Solid silver chloride is

acted on to a small extent by dilute solutions (2—6%) of sodium hyposulphite. Stronger solutions (12—24%) are more active, the action increasing with rising temperature up to about 50°, then falling off at still higher temperatures, probably on account of decomposition of the hyposulphite. Under the most favourable conditions, using a 24% solution at 50°, the product consists of 10.05% unchanged silver chloride, 88.92% of silver, and 1.95% of sulphur (as Ag_2S). The product is therefore a mixture of silver and silver sulphide. A solution of silver chloride in sodium thio-sulphate is immediately reduced in the cold by sodium hyposulphite to silver sulphide, whilst an ammoniacal solution of silver chloride is reduced quantitatively to metallic silver. These two reactions can be applied for the recovery of silver from silver chloride residues.

E. H. R.

Transference of the Acid Radicle in the Solid Phase. II. J. ARVID HEDVAL and JOSEF HEUBERGER (*Z. anorg. Chem.*, 1923, **128**, 1—14).—The displacement of a basic oxide from a salt by a more basic oxide, as observed in the case of carbonates when they are heated with an oxide more basic than that present in the salt (A., 1922, ii, 766) has now been found to occur with sulphates. The sulphates examined included those of strontium, calcium, magnesium, zinc, copper, cobalt, and iron (Fe'' and Fe''') and the oxides used were those of barium, strontium, calcium, and magnesium. Reaction between the salt and oxide was detected from the heating curve. The reaction temperature was lowest with barium oxide, varying from 328—370° with different salts; with strontium oxide, it varied from 410—451°, and with calcium oxide from 516—584°, except in one case, with ferrous sulphate, when it was as low as 444°. Magnesium oxide required the highest temperatures as a rule, and these are not determinable with so high a degree of accuracy as in the other cases on account of the low heats of reaction. In all the cases observed, reaction occurs at a temperature much below the decomposition temperature of the salt. Reaction can only occur when the heat of reaction is positive, and is not reversible. The extent to which the reaction proceeds was determined in the case of copper sulphate. Using molecular proportions, with BaO , 12.2% remained unchanged, with SrO , 11.8%, and with CaO , 38.9%. When the proportion of oxide was increased, the proportion of copper sulphate left unchanged was correspondingly diminished. The reaction is to be regarded as a true solid phase reaction between space lattices in contact at a suitable temperature.

E. H. R.

The Crystal Structure of Strontium Selenide. MABEL K. SLATTERY (*Physical Rev.*, 1922, **20**, 84).—Strontium selenide, prepared by heating the selenate to redness in a current of hydrogen, was examined by the powder method. The unit structure is a cube of dimensions 3.10 Å., the alternate corners being occupied by strontium- and selenium-ions.

A. A. E.

Action of Barium Chloride on Sulphate in Fused Salts. HOWARD E. BATSFORD (*Ind. Eng. Chem.*, 1923, **15**, 1044)—If a

small proportion of barium chloride is added to a fused mixture of sodium and calcium chlorides, any sulphate present as impurity is quantitatively precipitated and the freezing point of the fused mixture is unaltered. C. I.

Quantitative Decomposition of Natural Fluorspar by Fusion with Excess of Sodium Carbonate. C. C. PALIT (*Z. anorg. Chem.*, 1923, **128**, 350—354).—Whilst freshly precipitated calcium fluoride is completely decomposed by the carbonate fusion within two hours, it was found that one fusion left a quantity of mineral fluorspar undecomposed, the amount so left varying with the degree of fineness of the pulverised mineral, the amount of sodium carbonate used, and the duration of the fusion. The residue from a single fusion of fluorspar was never less than 5.8% of the weight taken, but this residue may be completely decomposed by a second fusion with sodium carbonate. S. I. L.

The Vapour Pressure of Cadmium and its Alloys with Zinc. ALFRED CHARLES EGERTON and FRANK VICTOR RALEIGH (*T.*, 1923, **123**, 3024—3032).

Constitution and Evolution of Oxides and Metallic Hydroxides. PAUL PASCAL (*Compt. rend.*, 1923, **177**, 765—768).—The measurement of specific magnetic susceptibility allows a clear distinction to be made between water present as (1) hydroxyl or (2) solvent of crystallisation, etc. In this way, the dehydration of various hydroxides has been studied. Cadmium hydroxide, when heated, passes irreversibly into the oxide, magnesium hydroxide, however, undergoing the corresponding change reversibly. In the case of zinc hydroxide, although dehydration is irreversible, water lost by the hydroxide is partly adsorbed by the oxide. Magnetic analysis enables these changes to be followed clearly, whereas they would not be detected by ordinary methods. Whilst zinc hydroxide, on drying at 160°, is partly converted into oxide, the latter, if resulting from the dehydration of the hydroxide at 205°, still retains 2—3% of water. E. E. T.

Cadmium Sulphide and the Estimation of Cadmium. ALFRED CHARLES EGERTON and FRANK VICTOR RALEIGH (*T.*, 1923, **123**, 3019—3024).

The Isotopes of Lead. A. S. RUSSELL (*Nature*, 1923, **112**, 619—620).—The author's analysis of the complexity of elements (this vol., ii, 748) leads to the somewhat surprising conclusion that common lead consists principally of mass-numbers 204, 205, 206, 207, 208, and 210, of which probably 206 and 208 are the chief. Of these isotopes, 206, 208, 210, and possibly 207 are end-products of radioactive series; consequently this analysis, if confirmed experimentally, can of itself neither confirm nor support the view that common lead may be of radioactive origin. The odd mass-number 205 may possibly be an isobare. Minor additions to and corrections of previous results are given. A. A. E.

Adsorption of Gases by Copper. ROBERT N. PEASE (*J. Amer. Chem. Soc.*, 1923, **45**, 2296—2305).—The adsorption isotherms of hydrogen, ethylene, ethane, carbon monoxide, and nitrogen at 0° and up to one atmosphere pressure have been determined. The results are discussed and the specific character of the adsorption is pointed out. The effect of poisoning the copper with mercury on the adsorption of hydrogen, ethylene, and carbon monoxide and also of partly deactivating copper, by heating, on the adsorption of hydrogen and ethylene, has been ascertained. In both cases, it has been found that the strong adsorption at low pressures has been markedly decreased whilst the additional adsorption at higher pressures has been little affected. From these results and certain incidental observations, it is concluded that the adsorption is due to specific adsorbing centres on the copper surface rather than to the copper surface as a whole. These centres, it seems reasonable to suppose, are regions of high curvature, or "peaks," on the surface. J. F. S.

Metallic Cementation. H. WEISS (*Ann. Chim.*, 1923, [ix], **20**, 131—195; cf. this vol., ii, 678).—The rate at which alloys, initially not in equilibrium, attain homogeneity was studied in the cases of copper-tin, silver-antimony, and copper-arsenic, the last-mentioned being in the form of a prehistoric axe containing 1.25% of arsenic. The results obtained may be adequately expressed as an exponential function of the absolute temperature and for the temperature range covered by experiment by $v=I/\theta=K\alpha^T$, where θ is time, T absolute temperature and K and α are constants (cf. Tammann and Schönert, A., 1922, ii, 772). The author is of opinion that his experiments do not distinguish clearly between the influence of temperature and that of concentration, but that the latter appears to be one of the controlling factors in those temperature regions in which cementation occurs in practice. No tendency to the attainment of homogeneity could be observed initially in the prehistoric specimen, but a more delicate experimental method is required in order to justify extrapolation of results to include phenomena occurring at the ordinary temperature. The various causes which may impair the accuracy of the experimental work are discussed, together with their bearing on the results which might be obtained by extrapolation, and it is shown that a possible interpretation would indicate the cessation of penetration on reduction of the temperature to 280°. Five alloys (silver-antimony, copper-antimony, silver-tin, gold-antimony, gold-lead) in which penetration occurs in the form of propagation of a chemical reaction were studied from the point of view of the time factor, and the general conclusion drawn is embodied in the equation $\theta=mx+n/2 \cdot x^2$. As the time taken by the chemical reaction is negligible in comparison with that required for penetration, mx may be omitted and θ becomes $n/2 \cdot x^2$, where $n/2$ is the time required for formation of a homogeneous layer 1 mm. in thickness and x the thickness of the layer formed. The propagation of a zone of given concentration is thus proportional to the

square root of the time if the conditions remain unchanged. The size of the crystals formed and the possibility of the existence of regions which differ in stability may affect the results obtained. The author states that he does not claim to have thrown light on the mechanism of penetration, but the results show that the phenomena observed appear to become capricious as the temperature decreases. A few observations, admittedly incomplete, on the mutual penetration of crystalline salts were made. H. J. E.

The Equilibrium Diagram of the System Cuprous Sulphide-Ferrous Sulphide. C. B. CARPENTER and C. R. HAYWARD (*Eng. Mining J. Press*, 1923, **115**, 1055—1061).—The diagram is of the type obtained when the two components of the system are completely soluble in each other when liquid, but only partly so when solid. The two branches of the curve intersect at the eutectic point (995°, 68% FeS). Solid solutions are formed with limits of solubility at 92.5% FeS and 50% Cu₂S, respectively; compounds are not formed. Ferrous sulphide has f. p. 1163°, and cuprous sulphide has f. p. 1,128°. A transformation occurs in the solid state at 950°, due probably to a dimorphic change in the crystal habit of cuprous sulphide. In the range 15—45% FeS, if the mass is heated considerably above its melting point, loss of sulphur by volatilisation, and consequent interaction of iron with cuprous sulphide, leads to the separation of copper. A matte of 32% Cu (60% FeS) gradually lost sulphur when maintained at 1,100°. Photomicrographs are given, and the experimental procedure is described. CHEMICAL ABSTRACTS.

Separation of the Rare Earths by Basic Precipitation. V. Preparation of Cerium-, Lanthanum-, and Coloured Earths from Thorium-free Monazite Sand. WILHELM PRANDTL and JOSEPH LÖSCH (*Z. anorg. Chem.*, 1923, **127**, 209—214; cf. A., 1922, ii, 769).—The crude sand is dissolved in concentrated nitric acid and potassium bromate solution added to precipitate the cerium. The filtrates are concentrated, and this process is repeated until all the cerium is removed. The coloured earths (samarium, neodymium, and praseodymium) are then fractionally precipitated by the addition of ammonium and cadmium nitrates. The lanthanum appears in the final precipitates.

H. H.

Double Carbonates of Sodium and Metals of the Cerium Group. F. ZAMBONINI and G. CAROBBI (*Atti R. Accad. Lincei*, 1923, [v], **32**, ii, 125—130).—Contrary to the statement of Meyer (A., 1904, ii, 734), these double carbonates are easily obtained crystalline and have the general formula $M_2(CO_3)_3 \cdot Na_2CO_3 \cdot 12H_2O$. The lanthanum sodium compound forms microscopic spherulites which, left in the mother-liquor, change either to slender, microscopic needles, mostly united in parallel bundles, or to irregular lamellar aggregates. The cerium sodium compound forms minute spherulites changing, in the mother-liquor, to bundles of needles and lamellar aggregates. The praseodymium sodium compound

forms either pale green complicated aggregates resembling minute lamellæ or bundles of needles. The neodymium sodium compound forms aggregates of needles. The samarium sodium compound, $\text{SmNa}(\text{CO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Cleve, A., 1885, 636, gave $8\text{H}_2\text{O}$), forms characteristic minute rosettes. T. H. P.

The Crystal Structure of Mercury. L. W. MCKEEHAN and P. P. CIOFFI (*Physical Rev.*, 1922, 19, 444—446).—Hull's powder method was employed in connexion with a thin coat of minute mercury droplets condensed on the outer surface of a paraffin- or shellac-coated rotating glass capillary tube, the mercury being maintained at about -115° by the vapour from boiling liquid air. The lattice appears to be rhombohedral, with the axial ratio 1.94. The calculated density, if one atom is associated with each cell, is 13.97 g./cm.^3 ; that computed from Mallet's and Dewar's results is 14.29 g./cm.^3 . The disparity may indicate that a closer packing of atoms can occur in large ingots than in microscopic droplets. A. A. E.

Dynamic Allotropy of Mercuric Iodide. A. DAMIENS (*Compt. rend.*, 1923, 177, 816—818).—It is shown that Smits's theory of dynamic allotropy (cf. A., 1915, ii, 262, and A., 1917, ii, 174), as applied to mercuric iodide, is contradictory to the law of the displacement of equilibrium, and that the results of his experiments on the rapid cooling of heated mercuric iodide are incomplete. According to Smits, the speed of reconversion (into the red variety) of yellow mercuric iodide, heated at temperatures above the transition point (127°), and subsequently cooled in liquid air, is greater the higher the temperature of heating. Whilst this is now confirmed for a first heating and cooling of commercial or precipitated iodide, it is not confirmed for a second or third heating and cooling; with well-developed crystals of the iodide, or with a sample that has previously been fused, reconversion to the red form takes place instantaneously on cooling, independently of the temperature of heating, even where this is as low as 135° . Smits's results are readily explained; the higher the temperature at which heating of microcrystalline iodide is effected, the higher the percentage of large crystals in a sample, owing to increased sublimation, and hence the accelerated recovery on cooling. E. E. T.

Mechanism of the Reduction of Permanganate and its Physico-chemical Basis. VI. Mangani-manganate as an Intermediate Product of the Reduction of Manganate. JOSEF HOLLUTA (*Z. physikal. Chem.*, 1923, 106, 324—340; cf. A., 1922, ii, 771, this vol., ii, 744).—The absorption spectra of manganate and mangani-manganate have been investigated and it is found that absorption spectra of these two substances differ sufficiently for the measurement of the spectrum of a strong alkaline solution of these substances to indicate their presence or absence from a reaction mixture. It is shown to be likely that the measurements of the absorption spectrum of manganate made hitherto have been effected with solutions containing also mangani-manganate. The

course of the reduction of manganate in strongly alkaline solution has been investigated, and it is found that in solutions which are 4.0*N* with respect to alkali an intermediate compound is formed, the bright blue solutions of which give a similar absorption spectrum to that given by mangani-manganate described by Auger and Billy (A., 1904, ii, 262). The appearance of this compound during the reduction coincides with the formation of quinquevalent manganese. The results of the previous paper (*loc. cit.*) have been confirmed from measurements in faintly alkaline solution. In strongly alkaline solution, the reduction of manganate occurs in two phases, which is explained by the formation of mangani-manganate as an intermediate stage. The first phase of the reduction, namely, the formation of mangani-manganate, is accelerated by hydroxyl-ions, whilst the second phase, namely, the reduction of the mangani-manganate, is retarded by hydroxyl-ions.

J. F. S.

The Corrosion of Iron in Water and in Neutral Salt Solutions. JOHN ALBERT NEWTON FRIEND (T., 1923, 123, 2996—2999).

Ferric Oxide Sols Prepared from Iron Carbonyl. H. FREUNDLICH and S. WOSNESSENSKY (*Kolloid Z.*, 1923, 33, 222—227).—A clear reddish-brown ferric oxide sol, which is very stable, can be prepared by the oxidation of iron pentacarbonyl. This is effected by shaking the pentacarbonyl with very dilute solutions of hydrogen peroxide. Since in the oxidation the only other products are carbon dioxide, carbon monoxide, and oxygen, the only electrolyte present is carbonic acid, and if this is removed or if the sol is boiled the sol coagulates readily. The coagulum obtained in this way can be readily peptised to form a positive sol by leading a stream of carbon dioxide through it, or by the addition of hydrochloric, nitric, or picric acid, aluminium chloride or ferric chloride. The positive sol can be converted into a negative sol by the addition of sodium hydroxide. The coagulum produced by the addition of electrolytes cannot be again peptised by carbon dioxide. The sol obtained directly from the pentacarbonyl gives the usual precipitation values of a positive sol, but these are considerably smaller than the values obtained with ferric oxide sols prepared by more usual methods. The latter are therefore more stable, and consequently, the sols obtained by peptising the coagulum from the pentacarbonyl sols with ferric chloride are much more stable than sols containing no ferric chloride. A similar result was obtained with sols obtained by using aluminium chloride as peptising agent, but in this case the sols were not so stable as the ferric chloride sols. The lack of stability was much more marked in the case of sols prepared by the use of lanthanum nitrate as peptising agent. The sol from iron pentacarbonyl can be sensitised by the addition of small quantities of albumin, but larger quantities of albumin peptise the ferric oxide coagulum to form a negative sol.

J. F. S.

The Oxidation of Iron Sulphate Solutions in Air. PRAMOD KISER BANERJEE (*Z. anorg. Chem.*, 1923, **128**, 343—349).—Oxidation of ferrous sulphate solutions exposed to air proceeds extremely slowly; by analysis of samples withdrawn at intervals over a period of sixty-two days, it was found that the order of the reaction approaches more nearly that of a unimolecular than that of a bimolecular reaction. Potassium sulphate exerts an accelerating effect, but the sulphates of all other metals tried, and sulphuric acid itself, exert retarding effects, the maximum retarding effect being that of copper sulphate. At higher temperatures, the reaction appears to be very nearly unimolecular. S. I. L.

Precipitation Reactions of Nickel and Cobalt Sulphate Solutions with Zinc or Cadmium at 100°. ROBERT KREMANN, FRANZ ANGELBERGER, FRANZ BAKALARZ, RUDOLF RÖHRICH, and CAMILLO STÖGER (*Z. anorg. Chem.*, 1923, **127**, 316—342).—Zinc or cadmium in the form of turnings or small cylinders was added to solutions containing about 1.4 mol./litre of nickel sulphate or about 0.09 mol./litre of cobalt sulphate. At room temperature, the precipitate contained both metals together with much hydroxide. At 100°, hydroxide is still produced, but in less quantity. It was found that the amount of hydroxide produced increases with the ratio precipitating metal/precipitated metal. It was also found that the surface of the precipitating metal influenced the composition of the precipitate in that as the surface of the precipitating metal increased the percentage of precipitated metal in the precipitate also increased. Measurements were also made of the *E.M.F.* of the precipitated metal/solution against a normal electrode. H. H.

β -Cobalt Iodide. ERWIN BIRK and WILHELM BILTZ (*Z. anorg. Chem.*, 1923, **128**, 45—48).—When ordinary anhydrous cobalt iodide is heated in an evacuated glass tube at 570—575°, at which temperature it boils, part of it sublimes, forming black crystals of the iodide, part decomposes, and a small quantity is deposited high up the tube as a yellow powder. The yellow powder is a second form of cobalt iodide, termed β -cobalt iodide. It is extremely hygroscopic, and dissolves in water to give a bright yellow solution from which chloroform removes free iodine, leaving a colourless solution. This solution will remain colourless for some time, but when warmed or concentrated it acquires the rose colour of an ordinary cobalt iodide solution. Attempts to prepare distinctive hydrates or ammoniates of the β -salt were not successful. E. H. R.

The Binary System Tungsten-Molybdenum. W. GEISS and J. A. M. VAN LIEMPT (*Z. anorg. Chem.*, 1923, **128**, 355—360).—The pure metals in powder form were compressed together in various proportions, and heated to sintering, the melting points of the alloys so obtained being determined by passing currents through filaments of standard cross-section. The melting points all lie on the straight line connecting the melting points of the

pure elements, and the alloys all appear to have homogeneous structures, thus showing that a continuous series of mixed crystals is formed. This conclusion was confirmed by determinations of the temperature coefficients ($\alpha_{30}^{100^\circ}$) of the electrical conductivities, and is in agreement with the remarkable similarity existing between the elements in all respects.

The temperature coefficient may be used to estimate molybdenum in an otherwise pure tungsten; 1% by weight of the former reduces the coefficient by about 10%.

S. I. L.

The Precipitation of Tungstic Acid [Tungsten Trioxide]. J. A. M. VAN LIEMPT (*Z. anorg. Chem.*, 1923, **127**, 215—220; cf. A., 1922, ii, 773).—The influence of temperature and concentration of acid on the precipitation of tungsten trioxide was studied. The precipitate consists of a mixture of the white and the yellow forms of the trioxide, together with an adsorption compound with water. Temperature has little effect on the precipitation, but in order to obtain the precipitate in a granular and easily manipulated form, it is advisable to use hydrochloric or nitric acid in high concentration, and in excess.

H. H.

The Ammines of Bivalent Tin. WILHELM BILTZ and WILHELM FISCHER (*Z. anorg. Chem.*, 1923, **129**, 1—14).—The following compounds were investigated, the temperature at which the dissociation pressure equals 100 mm. and the heats of dissociation per molecule of ammonia having been determined. $\text{SnCl}_2 \cdot 9\text{NH}_3$, -55° , 7.6 Cal.; $\text{SnCl}_2 \cdot 4\text{NH}_3$, -15° , 9.3 Cal.; $\text{SnBr}_2 \cdot 9\text{NH}_3$, -57° , 7.55 Cal.; $\text{SnBr}_2 \cdot 5\text{NH}_3$, -2° , 9.8 Cal.; $\text{SnBr}_2 \cdot 3\text{NH}_3$, 66° , 12.5 Cal.; $\text{SnBr}_2 \cdot 2\text{NH}_3$, -102° , 13.6 Cal.; $\text{SnI}_2 \cdot 10\text{NH}_3$ or 9NH_3 , -48° , 7.9 Cal.; $\text{SnI}_2 \cdot 5\text{NH}_3$, 10° , 10.2 Cal.; $\text{SnI}_2 \cdot 3\text{NH}_3$, 55° , 11.9 Cal.; $\text{SnI}_2 \cdot 2\text{NH}_3$, 94° , 13.3 Cal.; $\text{SnI}_2 \cdot \text{NH}_3$, 157° , 16 Cal. Heats of solution in 1% hydrochloric acid of $\text{SnCl}_2 + 0.8$ Cal., $\text{SnBr}_2 - 1.6$ Cal., $\text{SnI}_2 - 5.8$ Cal. Heats of formation were measured tensimetrically and calorimetrically and the results agreed well. Decrease in the stability of the complexes in passing from the chloride to the bromide and to the iodide was not observed. For the compounds with the higher co-ordination numbers, the authors suggest the formation of two shells of ammonia around the central atom, and in the case of stannous bromide the co-ordination numbers are assumed to be 3+2 and 3+6. The preparation of all the compounds is described. All except $\text{SnCl}_2 \cdot 4\text{NH}_3$ and $\text{SnI}_2 \cdot 2\text{NH}_3$ are new compounds.

W. T.

The Binary Halides of the Quadrivalent Elements. I. Quadrivalent Tin. MATHIAS G. RÄDER (*Z. anorg. Chem.*, 1923, **130**, 325—332).—Examination of the melting-point curves of mixtures of pure stannic bromide and iodide, and analysis of the crystals first separated on cooling, show that no mixed halogen compounds as described in the literature really exist. The method given by Lenormand (A., 1899, ii, 33, 745) for the preparation of SnBr_2I_2 by heating stannous bromide with excess of iodine in sealed tubes at 100° is found in fact to yield an equimolecular mixture of stannic bromide and stannic iodide.

S. I. L.

The Reduction of Inorganic Halides. II. The Reduction of Titanium Tetrachloride. OTTO RUFF and FRANZ NEUMANN (*Z. anorg. Chem.*, 1923, **128**, 81—95).—The reduction of titanium tetrachloride with different elements was studied. Sodium amalgam reduces it slowly to dichloride in the cold, but if the action is too prolonged, trichloride is formed by interaction of the dichloride with tetrachloride. Magnesium, zinc, aluminium, arsenic, and antimony reduce the tetrachloride to trichloride, the reaction being accelerated by a small quantity of anhydrous aluminium chloride; phosphorus and sulphur reduce the tetrachloride only in presence of aluminium chloride. Reduction of titanium tetrachloride with aluminium powder in presence of aluminium chloride affords a new and effective method for preparing titanium trichloride. The reaction is carried out in a closed, evacuated tube at 200—250°. The trichloride obtained, freed from tetrachloride and from aluminium chloride by distillation, is in a finely divided, non-crystalline form, of a bright violet colour. It is very sensitive to oxygen and moist air. When heated with sulphur, it forms titanium chlorosulphides of varying composition, $Ti_5Cl_4S_{12}$ to $Ti_4Cl_2S_{12}$, and it also forms similar compounds with selenium. When titanium trichloride is heated at 425° at less than 1 mm. pressure, it volatilises practically unchanged and the trichloride crystallises on the colder parts of the tube in dark violet prisms. At 450° and above, the trichloride decomposes (at <1 mm. pressure) into tetrachloride and dichloride. The dichloride remains as a black powder when the trichloride is heated at 475° and the tetrachloride vapour is pumped away as it is formed. Titanium dichloride is extraordinarily reactive, takes fire in moist air, and decomposes water at once with evolution of hydrogen. It is not volatile at 600° at very low pressures.

E. H. R.

Reduction of Inorganic Halides. III. The Reduction of Zirconium Tetrachloride. OTTO RUFF and RICHARD WALLSTEIN (*Z. anorg. Chem.*, 1923, **128**, 96—116).—Zirconium tetrachloride can be reduced by a number of metals and metalloids, including aluminium, magnesium, zinc, arsenic, antimony, lead, tin, mercury, bismuth, and phosphorus, to a greater or less extent, at temperatures above 250° in presence of aluminium chloride, in absence of air. The most suitable reducing agent is aluminium powder in presence of aluminium chloride at 300°. At this temperature, zirconium tetrachloride does not react with alumina, but zirconia reacts completely with aluminium chloride according to the equation: $3ZrO_2 + 4Al_2Cl_3 \rightarrow 3ZrCl_4 + 2Al_2O_3$. When zirconium tetrachloride is heated in a vacuum at this temperature with the theoretical quantity of aluminium for the reaction $3ZrCl_4 + Al = 3ZrCl_3 + AlCl_3$, and the aluminium chloride and unchanged zirconium tetrachloride are removed by sublimation, a residue is left consisting largely of *zirconium trichloride*, which, however, cannot be obtained in a pure condition. The trichloride is a brown, microcrystalline solid, d^{18} 3.0. It is rapidly oxidised by air to

oxychloride and decomposes water with evolution of hydrogen and formation of ZrOCl_2 . Concentrated hydrochloric acid retards the reaction with water, and a brown solution of zirconium trichloride is obtained which slowly loses its colour as oxidation proceeds. When heated in absence of air at about 330° , the trichloride decomposes into a mixture of di- and tetra-chloride: $2\text{ZrCl}_3 = \text{ZrCl}_2 + \text{ZrCl}_4$, and when the tetrachloride is removed as fast as it is formed by a vacuum pump, the *dichloride* remains as a black, amorphous substance, d^{18}_4 3.6. It is practically insoluble in air-free water, and is only slowly decomposed by moist air or water. It is oxidised by concentrated acids with evolution of hydrogen and formation of the quadrivalent zirconium salt. Above 600° , it decomposes into zirconium tetrachloride and zirconium.

E. H. R.

Crystal Structures of Vanadium, Germanium, and Graphite.

ALBERT W. HULL (*Physical Rev.*, 1922, **20**, 113).—The powder method of examination shows that vanadium has a body-centred cubic lattice of side 3.04 \AA , distance between nearest atoms 2.63 \AA , ideal density 5.96. Germanium has the same crystal structure as diamond; corresponding values are 5.63 \AA , 1.218 \AA , and 5.36. It is confirmed that the lattice of graphite is of the hexagonal close-packed type, and not rhombohedral as found by Debye.

A. A. E.

Dispersoid Synthesis of Gold. I. P. P. VON WEIMARN (*Kolloid Z.*, 1923, **33**, 228—247).—A general preliminary communication in which after a discussion of dispersoid synthesis, an account is given of experiments on the dispersoid synthesis of gold by the formaldehyde method, the phosphorus method, the citrate or tartrate method, and the glycerol method. In the general discussion, the author examines the conditions which control the size of the colloidal particles, and the reversibility and the stability of sols. The influence of impurities and added foreign substances is also discussed. The stability, size of particles, colour, and other characteristics of gold sols prepared under various conditions by the above-named methods are discussed.

J. F. S.

Mineralogical Chemistry.

Presence of Anhydrous Sodium Sulphate among the Products of the Present Activity of Vesuvius. FERRUCCIO ZAMBONINI (*Atti R. Accad. Lincei*, 1923, [v], **32**, ii, 122—124).—The products of the present activity of Vesuvius include anhydrous sodium sulphate in the form of thénardite. T. H. P.

The Existence of Brochantite in Katanga. ALFRED SCHOEP and GEORGES BUYSE (*Bull. Soc. Belge Géol.*, 1923, **33**, 72—73; *Bull. Soc. Chim. Belg.*, 1923, **32**, 342—343).—Minute, greenish-

blue needles on quartz crystals in a sample of copper ore have the optical constants of brochantite and gave :

CuO.	SO ₃ .	H ₂ O.	sp. gr.
69.11	17.07	13.81	3.88

L. J. S.

The Presence of Carnotite in the Congo. ALFRED SCHOEP and ÉMILE RICHET (*Bull. Soc. Belge Géol.*, 1923, **32** [for 1922], 150—152; *Bull. Soc. Chim. Belg.*, 1923, **32**, 340—341).—A yellow, crystalline powder in red sandstone from Katanga is proved to be carnotite. The minute crystals are rhombic scales with an angle of 77—78.5°; the optic axial plane is parallel to the shorter diagonal and the acute negative bisectrix normal to the plate. The material dissolves in hydrochloric acid to a blood-red solution, this colour (due to vanadium) being lost on heating.

L. J. S.

A Black Mineral Associated with Carnotite from the Congo. ALFRED SCHOEP (*Bull. Soc. Belge Géol.*, 1923, **33**, 85—86; *Bull. Soc. Chim. Belg.*, 1923, **32**, 344—345).—A red, calcareous sandstone containing carnotite (preceding abstract) shows black lenticles and irregular stains. The lenticles dissolve in strong hydrochloric acid with evolution of chlorine yielding a green solution. Analysis gave :

SiO ₂ .	CoO.	Fe ₂ O ₃ .	Mn ₂ O ₄ .
44.15	2.18	4.70	3.60

The remainder being water and calcium and magnesium carbonates. The black colloidal material is compared with heubachite, transvaalite, etc.

L. J. S.

Chinkolobwite. A New Uranium Mineral from Katanga. ALFRED SCHOEP (*Bull. Soc. Belge Géol.*, 1923, **33**, 87—88; *Bull. Soc. Chim. Belg.*, 1923, **32**, 345—346).—A specimen of massive soddite (A., 1922, ii, 451) from Chinkolobwe, is partly covered with a felt of fine needles of a canary-yellow colour. These at first sight resemble the prismatic type of soddite, but they show a lower birefringence and other differences in their optical characters. Microchemical tests show the presence of uranium and silica, and the mineral is perhaps dimorphous with soddite, 12UO₃.5SiO₂.14H₂O.

L. J. S.

Analytical Chemistry.

A New Absorption Pipette for Gas Analysis. SIDNEY WALTER SAUNDERS (T., 1923, **123**, 2826—2828).

Volumetric Analysis. M. EMM. POZZI-ESCOT (*Ann. Chim. Analyt.*, 1923, [ii], **5**, 293).—Fabaron has recently (*ibid.*, 161) suggested the use of graduated tubes for measuring the volumes of precipitates, but the author points out that he had described this method previously (A., 1908, ii, 539). W. P. S.

Replacement of Iodine by Ferric Chloride in Volumetric Analysis. KARL JELLINEK and LEO WINOGRADOFF (*Z. anorg. Chem.*, 1923, 129, 15—32).—This new method is based on the reaction $2\text{FeCl}_3 + \text{Na}_2\text{S}_2\text{O}_3 = 2\text{FeCl}_2 + 2\text{NaCl} + \text{Na}_2\text{S}_4\text{O}_6$, and can be employed for the estimation of oxidising and reducing agents. The titrations must be carried out with hot solutions and in an atmosphere of carbon dioxide. The solutions recommended are 0.1*N*-ferric chloride+0.2% hydrochloric acid and 0.1*N*-sodium thiosulphate+0.1% sodium carbonate. The ferric solution is kept at 50—60° and the thiosulphate solution run in from a burette; this causes the formation of a violet coloration probably due to the formation of the unstable ferric thiosulphate, which rapidly disappears; the end-point is reached when no further coloration is produced; the presence of more than 0.5% hydrochloric acid makes the colour very indistinct. Thiocyanate or potassium iodide starch paper cannot be employed as indicators for the complete reduction of ferric-ion in this case, but the disappearance of the characteristic colours with phenols gave good results, *e.g.*, 1 c.c. saturated solution of salicylic acid. The end-point was also sharply given by the decoloration of methylene-blue, this being due to the presence of thiosulphuric acid; still better results were obtained by using a mixture of methylene-blue and magenta (5 drops of a 0.5% solution of aqueous methylene-blue and 3 drops of saturated aqueous magenta). Attempts to use as the end-point the decoloration of organic dyes by the sulphur dioxide formed did not give satisfactory results. Details are given of the estimation of potassium permanganate, potassium chlorate, manganese dioxide, tin (in white metal), and sulphides. Unsatisfactory results were obtained in the estimation of nitrates, hydrogen peroxide, and sulphites. W. T.

New Methods in Alkalimetry and Acidimetry, and in Oxidimetry. Hydrolytic Precipitation Analysis and Mercurimetry. K. JELLINEK and P. KREBS (*Z. anorg. Chem.*, 1923, 130, 263—324).—In place of the usual organic colour indicators, the following inorganic salts may be used in titrations of acids and alkalis: (a) Lead salts for all alkalis, and for acids other than sulphuric; (b) copper salts for all acids with ammonia; (c) silver salts for all acids other than the halogen acids, and for all alkalis other than ammonia, and (d) ferric thiocyanate for all strong acids and alkalis. With (a), (b), and (c) the quantity of indicator used must be as small as possible; excess of alkali is added to the acid solution containing the indicator, and the excess titrated back until the cloudiness due to precipitation of the heavy metal hydroxide disappears. The average results with (a) are 0.6% too high in determining the alkali, with (b) 0.6% too high, and with (c) 2.5% too high; these average errors must be taken into account for very accurate estimations. Using (d), the average error is only 0.1%; the indicator is used in the form of 1 drop of a 0.25% ferric chloride solution and 10 drops of a 10% potassium thiocyanate solution.

A suitable method for the titration of ferrous and stannous salts consists in oxidation with hydrogen peroxide solution, using as indicator a titanous salt in presence of sulphuric acid. To reduce the coloration due to the ferric salt formed, orthophosphoric acid is added, the error being 0.5%; with tin salts, the average error is negligible. Ferrous salts are titrated in the cold, tin salts at a high temperature. The method is unsuitable for arsenic and antimony salts, and for oxalates.

A titration method for the estimation of cadmium and nickel consists in precipitating as hydroxide by means of excess of standard alkali at the boiling point. After cooling, a few drops of silver nitrate are added, and the liquid is titrated with standard acid until the yellow coloration disappears. A comparison solution is required in each case, and a separate determination of the amount of alkali required to make the original solution neutral must also be made. For cadmium, the results are very accurate; for nickel, the average error is +0.3%, probably due to oxidation.

The hydrolytic precipitation method described by Jellinek and Czerwinski (this vol., ii, 878) has been further examined for the estimation of (1) lead by means of potassium chromate, and extended to (2) disodium hydrogen arsenite, (3) disodium sulphide, (4) sodium carbonate, and (5) potassium cyanide as precipitation reagents. The solutions to be titrated must be exactly neutralised in each case. Method (2) was found unsuitable for zinc, but suitable for lead and cadmium, the discrepancies being within the limits of experimental error. Phenolphthalein is employed as indicator, and comparison solutions without indicator must be used. Precipitation is effected at the boiling point, and the arsenite solution must be standardised each time against the pure metal salt solution. With (3), very accurate results are obtained for zinc salts, and the analysis may be applied to the estimation of zinc in white metals and other alloys. The indicator used is methyl-red, and the sodium sulphide solution must be standardised by means of pure zinc at fortnightly intervals. The method is rapid and convenient. Both zinc and lead may also be estimated accurately with (4), using phenolphthalein as indicator; the neutralised solution is boiled with excess of the carbonate solution, the excess being titrated back at 100° with a standard zinc or lead solution, respectively, until the red coloration disappears. Comparison solutions must be employed. Neither of these metals can be accurately estimated by means of (5), but with silver excellent results are obtained; phenolphthalein is used as indicator, and precipitation carried out at the boiling point.

Mercuric salts may also be estimated by means of (5), the cyanide solution being added at the boiling point until the indicator, phenolphthalein, becomes rose-coloured. A constant error of 3.1% (low) is observed, but if the cyanide be standardised by means of a mercuric salt, this error automatically disappears. By reason of the slight dissociation of mercuric salts, these promise to be of great value in connexion with this method of analysis.

S. I. L.

Use of Calcium Carbonate in Volumetric Analysis. E. KORDES (*Z. anal. Chem.*, 1923, **63**, 117—120).—For the estimation of free chlorine in solutions which cannot be titrated directly, the chlorine may be expelled by generating carbon dioxide in the solution by the action of hydrochloric acid on thick pieces of calcium carbonate (marble) and collecting the evolved gases in potassium iodide. In estimating the available oxygen in manganese dioxide, for instance, a weighed quantity of the substance is introduced into a conical flask together with two thick pieces of marble and hydrochloric acid is dropped on to the dioxide by means of a dropping funnel. When the latter has dissolved, after gentle heating, if necessary, the flask is inclined so that the marble comes into contact with the liquid. The carbon dioxide evolved sweeps the chlorine formed in the first stage into receiving flasks containing potassium iodide and the liberated iodine is titrated as usual. The whole process takes ten minutes against the forty-five minutes consumed if carbon dioxide is passed through the apparatus in the usual way. A. R. P.

Use of the Mercury Electrode for Electrometric Titration of Halides, Cyanides, Sulphides, and Thiosulphates. I. M. KOLTHOFF and E. J. A. H. VERZYL (*Rec. trav. chim.*, 1923, **42**, 1055—1064).—Methods are described for the potentiometric estimation of chlorides, bromides, iodides, cyanides, sulphides, and thiosulphates. The alteration of the *E.M.F.* of the solution (Δa) in contact with a mercury electrode with a small change in concentration of mercuric chloride (Δc) is measured, and the end-point is indicated when $\Delta a/\Delta c$ reaches its maximum value. Chlorides and bromides can be determined, but not together in the same solution. Iodides can be estimated even in great dilution, but large quantities of bromides interfere. Cyanides and thiocyanates can be estimated. Sulphides may be estimated in great dilution, especially in alkaline solution, but strong solutions are best titrated with silver nitrate. Salts with bivalent anions depress the results slightly. Thiosulphates and sulphides may be estimated in mixtures of the two, provided neutral solutions are employed. H. H.

Estimation of Sulphur in Cast Iron. SANSEI KITAJIMA (*Rikwagaku Kenkyujo Ihô*, 1923, **2**, 243—258).—The author has examined the usual method of estimating sulphur in iron, by dissolving in hydrochloric acid and determining the amount of hydrogen sulphide evolved, and finds that the rate at which the hydrochloric acid is added to the sample has a considerable effect on the result. Hydrochloric acid (*d* 1.19—1.20) diluted with twice its volume of water is to be used for the operation and 10 c.c. of cadmium chloride solution (prepared from 120 grams of cadmium chloride, 1,500 c.c. of water, and 600 c.c. of ammonia, *d* 0.90) diluted with 35 c.c. of water. The volume of the solution for the titration should be about 70 c.c. for 5 grams of the sample. If the evolved hydrogen sulphide is passed through a quartz tube heated to redness before entering the cadmium chloride solution, the result is slightly higher and more constant; in this case the results obtained

by the titration and by weighing as barium sulphate after oxidising the cadmium sulphide with $\frac{1}{2}$ bromine water are almost identical. The solution and residue remaining in the flask after the evolution has ceased are almost free from sulphur. K. K.

Estimation of Sulphate at Great Dilutions by Hahn's Method. I. M. KOLTHOFF and M. J. VAN CITTERT (*Pharm. Weekblad*, 1923, **60**, 1177—1190).—A critical examination has been made of Hahn's method (this vol., ii, 39, 339). The present authors filter the barium sulphate through a wad of cotton, as suggested by Winkler (*Z. angew. Chem.*, 1917, **30**, 251), and carry out the final washing with alcohol. The method gives results 1.0—1.3% too low, but by working in acetic acid or neutral solution instead of in hydrochloric acid solution a high degree of accuracy is obtained. Barium chloride gives better results than barium nitrate.

The alkali metals and aluminium and ferric salts do not affect the results, but calcium interferes unless the precipitation is carried out in *N*/10-hydrochloric acid solution. Nitrates have little influence, but the presence of phosphates make the results too high. If the operation is carried out at atmospheric temperature, the errors are much higher; this is also the case if the reagents are heated in a sealed tube above 260°. S. I. L.

Limitations of the Reaction between Ammonia and Sodium Hypobromite. DINSHAW RATTONJI NANJI and WILLIAM SIMPSON SHAW (*Analyst*, 1923, **48**, 473—477).—Critical examination of the hypobromite method showed that it was untrustworthy for the estimation of ammonia, particularly for small quantities of the latter. When dealing with amounts of ammonia varying from 3 to 17 mg., the results obtained were from 2 to 7% too high. Traces of nitrates and nitrites were always formed as by-products of the reaction. W. P. S.

Cause of Error in the Jodlbauer Method of Estimating Total Nitrogen. JEAN BORDAS (*Compt. rend.*, 1923, **177**, 696—697).—The Jodlbauer method gives a low result with complex fertilisers, etc., containing tannins. These, as well as pyrogallol, quinol, and pyrocatechol (but not resorcinol or non-reducing diphenols) effect partial reduction of nitrate in presence of concentrated sulphuric acid, perceptible evolution of nitrous fumes occurring. The methods of Dumas, of Salle, or of Devarda (followed by a Kjeldahl determination of nitrogen not present as nitrate) are to be preferred in these cases. E. E. T.

The Determination of Protein Nitrogen according to Stutzer. S. KOSTYTSHEV (*Z. physiol. Chem.*, 1923, **130**, 34—38).—Stutzer's method for determining protein nitrogen, in which the proteins are precipitated by heating with copper hydroxide, is inaccurate. Nitrogen other than protein nitrogen is precipitated by the reagent. W. O. K.

Analysis of Monosodium Phosphate and Phosphoric Acid.

FRANK X. MOERK and EDWARD J. HUGHES (*Amer. J. Pharm.*, 1923, **95**, 671—678).—The following volumetric method is described: 40 c.c. of *N*/10-silver nitrate solution and 0.2 c.c. of methyl-red solution are treated with dilute sodium hydroxide solution until the red coloration changes to yellow; 10 c.c. of the phosphate solution (containing about 0.2 g. of the salt) are then added, and the mixture is titrated with *N*/10-sodium hydroxide solution. The reaction proceeds according to the equation $\text{NaH}_2\text{PO}_4 + 3\text{AgNO}_3 + 2\text{NaOH} = \text{Ag}_3\text{PO}_4 + 3\text{NaNO}_3 + 2\text{H}_2\text{O}$. One hundred c.c. of 10% sodium chloride solution and 0.2 c.c. of phenolphthalein solution are treated with sodium hydroxide solution until a distinct red coloration is obtained; the solution is divided into two equal parts, to one is added 10 c.c. of the phosphate solution and the mixture is titrated with *N*/10-sodium hydroxide solution until the coloration is equal to that of the reserved portion. The equation for this titration is $\text{NaH}_2\text{PO}_4 + \text{NaOH} = \text{Na}_2\text{HPO}_4 + \text{H}_2\text{O}$. If the two titrations yield the same percentage of monosodium phosphate, the sample is free from disodium phosphate and phosphoric acid; a higher percentage by the phenolphthalein method indicates the presence of free phosphoric acid, whilst a higher percentage by the methyl-red method denotes the presence of disodium phosphate in the sample. The quantities of free phosphoric acid and disodium phosphate may be calculated from the results obtained. The sodium chloride solution used must not contain calcium salts and the sodium hydroxide solution must be free from carbonate. The method may be applied to phosphoric acid. W. P. S.

Chemistry of the Reinsch Test for Arsenic and Antimony, and its Extension to Bismuth. B. S. EVANS (*Analyst*, 1923, **48**, 417—429).—The results obtained in an investigation of the Reinsch test favour the hypothesis that the reaction is due to reduction of the arsenic, antimony, or bismuth salt by a film of hydrogen on the surface of the copper, the hydrides formed in the first two instances combining with the copper to form arsenide or antimonide, respectively. When oxidation of the cuprous chloride formed is prevented by carrying out the test in an atmosphere of carbon dioxide, the deposition of the three elements is complete; in the case of relatively large amounts of antimony, the deposit may be so dense that the reaction ceases, and the solution may need to be treated with two or three successive pieces of copper foil. With small quantities (1 to 5 mg.) of bismuth better results are obtained by using acetic acid and sodium chloride in place of sulphuric acid and sodium chloride. W. P. S.

Estimation of Arsenic in Arsenobenzenes. F. DE MYT-TENAERE [with VAN BOECKEL, MUSET, and DUMONT] (*Chim. et Ind.*, 1923, **10**, 403—410).—About 0.2 g. of the arseno-compound is dissolved in 5 c.c. of water, 10 c.c. of hydrogen peroxide (10 vols.), and 10 c.c. of 50% sulphuric acid are added and the mixture is boiled until the excess of peroxide is decomposed; a further 5 c.c. of hydrogen peroxide are then added, and the heating is continued

until sulphuric acid fumes are evolved. After cooling, the mixture is diluted with 10 c.c. of water, a slight excess of 1% potassium permanganate solution is added, and the pink coloration is discharged by the addition of a drop of oxalic acid solution; 20 c.c. of 25% potassium iodide solution are added, the mixture is heated on a water-bath for twenty minutes, cooled, and decolorised exactly by the addition of *N*/10-sodium thiosulphate solution. Twenty-five c.c. of saturated sodium carbonate solution and an excess of sodium hydrogen carbonate are then added, and the solution is titrated with *N*/10-iodine solution. Each c.c. of the latter solution is equivalent to 0.003749 g. of arsenic. The quantity of arsenic present should be from 19 to 21%, and the ratio arsenic/nitrogen should not be less than 5.6. W. P. S.

A New Gas Combustion Furnace. THOMAS J. HEDLEY (*J. Soc. Chem. Ind.*, 1923, **42**, 432—433T).—A somewhat fuller description of the furnace previously described (T., 1921, **119**, 1242). E. H. R.

Estimation of Carbon Monoxide in Air. VIKTOR ANDRISKA (*Z. Unters. Nahr. Genussm.*, 1923, **46**, 43—46).—Weltzl's tannin reaction with defibrinated blood solution in which carbon monoxide has been absorbed from the air is developed into a quantitative method of determining carbon monoxide in air. The sensitiveness of the test was found to be 1% of the volume of blood solution (1 part of blood to 4 parts of water) employed, so that 100 c.c. of blood solution will detect 1 c.c. of carbon monoxide. Absorption vessels are not suitable for estimating small proportions of carbon monoxide in air, as losses occur. A more complete absorption is obtained by shaking up the blood solution with one hundred times its volume of air in a closed vessel. A hollow stopper capable of containing 50 c.c. of blood solution, which can be fitted to a 5-litre flask, is illustrated. This is so designed that the blood solution is projected into the flask in a thin stream, so as to effect a complete absorption of the carbon monoxide. After absorption is complete (3 hours), known volumes of the blood solution are diluted with known volumes of the fresh blood solution, the total volume of the mixture being in each case 5 c.c. Fifteen c.c. of a freshly prepared 1% tannin solution are added to each mixture and that mixture noted, the colour of which can just be differentiated from the blank test with fresh blood solution only, after remaining for twenty-four hours. In this way, accurate estimations of carbon monoxide in air are possible down to 0.02%. H. C. R.

A Microchemical Method for the Analysis of Carbonates. MIECZYSLAW DOMINIKIEWICZ (*Roczniki Chemji*, 1923, **3**, 165—176).—Naturally occurring carbonates can be divided into two groups according to their behaviour on heating on platinum foil below red heat; the first group includes those which are not visibly changed by this treatment (calcite, aragonite, lublinit, dolomite, magnesite, witherite, strontianite, baryocalcite, etc.) and those which change colour under the same conditions (siderite, rhodochrosite, oligonite, ankerite, brennerite, cernosite, plumbocalcite, smith-

sonite, and calcites and dolomites containing iron or manganese); naturally coloured minerals such as malachite are not taken into consideration.

Of the minerals of the first groups only two—strontianite and witherite—are completely unaffected by heating; the remainder suffer some degree of dissociation with the formation of oxides which can be detected by suitable reagents. The grains of mineral are treated, after heating, with an alcoholic solution of alizarin (0.1%); those which contain an oxide are coloured bluish-red, whilst strontianite and witherite remain colourless. Dianil-green in aqueous solution can also be used for the same purpose, but the use of 1% alcoholic phenolphthalein is preferable because it allows a further distinction to be made between the minerals of this group. The coloured phenolphthalein salt formed with magnesium is insoluble in alcohol and only slowly dissolves in water, whilst the calcium salt is readily soluble. Magnesite is thus readily recognised because the grains of mineral become coloured, but the solution remains colourless; the solution slowly becomes pink in the case of dolomite, whilst an immediate coloration is obtained with calcite, etc. Dolomite can, moreover, be distinguished from magnesite, because the latter, when heated and then warmed for ten minutes with 5% aqueous sodium hydroxide followed by a 0.1% aqueous solution of the ammonium salt of 2:4:6:7-tetrahydroxyfluoran (Liebermann, A., 1901, i, 595), is coloured crimson, whilst dolomite remains colourless. Predacite, when heated on platinum foil for a few seconds below red heat and then treated with phenolphthalein, is coloured in places only, and the alcoholic solution remains colourless, as the mineral is composed of a mixture of calcite and brucite, the former of which is not decomposed by this treatment; staining with tetrahydroxyfluoran after treatment with alkali produces a similar effect. Calcite can be distinguished from aragonite by heating the mineral for two minutes with 0.25% aqueous cobalt nitrate (compare Meigen, A., 1901, ii, 692), washing, and staining with tetrahydroxyfluoran. On heating with dilute ammonia, aragonite remains crimson, whilst calcite is decolorised. Ferrous sulphate (1%) can replace cobalt nitrate in this test, the dye being used in alkaline solution; aragonite is coloured blue, but calcite remains colourless. Calcite, aragonite, witherite, and strontianite are coloured violet when treated after heating with 0.3% ferric chloride for twelve seconds, followed by a neutral solution of the dye and finally ammonia; dolomite is unaffected.

In order to distinguish witherite from strontianite, the mineral is warmed for one to two minutes with 0.5% chromic acid, when witherite is coloured yellow; the colour can be intensified by subsequent treatment with a lake-forming dye such as chromotrope-2B.

Of the minerals of the second group, siderite and rhodochrosite become black and lustrous on heating, and the former is also magnetic; calcites and dolomites containing iron or manganese become light brown to black; smithsonite shows a yellow coloration while hot, and becomes colourless or black on cooling, whilst cerussite is coloured light-brown and does not change on cooling.

They can also be distinguished by warming with 5% aqueous sodium hydroxide for fifteen to twenty minutes and with tetrahydroxyfluoran for five to ten minutes. The colours produced are: siderite, purplish-brown; rhodochrosite, brownish-crimson; smithsonite, orange. A further test consists in heating for ten to fifteen minutes with 5% sodium hydroxide and a drop of bromine, then with sodium hydroxide alone, and finally with a saturated solution of benzidine in acetic acid; minerals containing manganese are coloured an intense blue (*e.g.*, rhodochrosite).

In a few cases it was found that iron present in some dolomites and calcites was not detected by the tetrahydroxyfluoran test; it is suggested that the iron was present in the form of a definite double carbonate, similar to the calcium magnesium carbonate which constitutes dolomite.

Smithsonite can be recognised by Lemberg's method (*Z. deutsch. Geolog. Ges.*, 1887, 357) in addition to the above, and this also applies to cerussite. The latter and also plumbocalcite can, however, be recognised by the benzidine test described above; an intense blue coloration, changing to violet, is observed in these cases.

G. A. R. K.

Sodium 6-Chloro-5-nitro-*m*-toluenesulphonate—a New Reagent for Potassium. HERBERT DAVIES and WILLIAM DAVIES (*T.*, 1923, **123**, 2976—2982).

Quantitative Analysis by Hydrolytic Precipitation. K. JELLINEK and J. CZERWINSKI (*Z. anorg. Chem.*, 1923, **30**, 253—262).—If to a slightly acid solution of barium chloride coloured red by addition of methyl-orange, excess of potassium chromate solution is added, the colour changes from red to yellow; as soon as the equivalent quantity of potassium chromate has been added, any excess is hydrolysed and the solution acquires an alkaline reaction. Consideration of the degrees of dissociation and of the hydrogen-ion concentrations of the common indicators shows that high degrees of accuracy may be expected by applying the principle to any case in which soluble combinations of weak acid with strong base or strong acid with weak base may be utilised. Thus barium chloride may be estimated by means of potassium chromate, using methyl-red, with an error of 0.06%; by adding a known excess of barium chloride, sulphates may be similarly estimated. Cadmium salts do not interfere. Similarly, lead nitrate may be estimated by means of potassium chromate, using methyl-red. The titrations are carried out in porcelain dishes. The new method allows of rapid and accurate titrations in many cases in which gravimetric analysis is tedious and difficult.

S. I. L.

The Separation of Magnesium from the Alkali Metals by Means of Organic Bases. GUNHILD HEMMING (*Z. anorg. Chem.*, 1923, **130**, 333—342).—A solution of guanidine (prepared by addition of a slightly insufficient amount of barium hydroxide to the carbonate) precipitates magnesia quantitatively in presence of the alkali metals if excess be used; ammonium salts interfere.

The method may be employed in titration, but since guanidine solutions do not keep well, standard solutions of the carbonate and baryta may be employed. Piperidine does not give quite such good results, but the solution may be kept without change. Aliphatic amines are not so suitable, the errors being greater.

S. I. L.

A New Microchemical Reaction for the Estimation of Zinc. G. SPACU and R. RIPAN (*Bul. Șoc. Științe Cluj*, 1922, **1**, 576—580; from *Chem. Zentr.*, 1923, iv, 185; cf. this vol., ii, 699).—The double compound of the composition $[\text{Zn}(\text{C}_5\text{H}_5\text{N})_2](\text{CNS})_2$ formed by the reaction of ammonium thiocyanate and pyridine with a zinc salt is dissolved by repeated extraction with small quantities of chloroform. After evaporation to dryness of the chloroform solution, the residue is weighed.

G. W. R.

The Electrometric Titration of Zinc and Cadmium. FRIEDR. MÜLLER (*Z. anorg. Chem.*, 1923, **128**, 125—130).—In confirmation of the results of Hedrich (*Diss. Dresden*, 1919) it is found that zinc can be titrated electrometrically with potassium ferrocyanide, using a platinum indicator-electrode, with an accuracy of 0.2—0.3%; the precipitate is $\text{K}_2\text{Zn}_3(\text{FeC}_6\text{N}_6)_2$, and the results are best with hot neutral solutions. Cadmium may be similarly titrated, the precipitate being $\text{K}_2\text{Cd}(\text{FeC}_6\text{N}_6)$. With sodium ferrocyanide, cadmium gives accurate results, but with zinc poor results were obtained. No advantage is gained by addition of salts of rubidium, caesium, or lithium. Zinc in presence of cadmium may be accurately titrated with potassium ferrocyanide, but the cadmium can be estimated in the solution only by the use of an empirical factor.

S. I. L.

Estimation of Zinc and Lead in Presence of Large Amounts of Carbon. W. KAHLBAUM (*Eng. Min. J. Press*, 1923, **116**, 110—111).—The carbonaceous matter is destroyed in 0.5 g. of the material by heating with 5—10 g. of sodium peroxide in a mild steel bomb of Parr's type. The mass after reaction is extracted with water, and the insoluble hydroxides are dissolved in dilute acid. For the estimation of zinc, 5 g. of ammonium chloride, 20 c.c. of ammonia solution, and a little hydrogen peroxide are added, the liquid is filtered, and titrated with potassium ferrocyanide solution. Lead is estimated by the molybdate method or, if present in only a small quantity, electrolytically.

CHEMICAL ABSTRACTS.

A New Reaction for Cadmium. G. SPACU (*Bul. Șoc. Științe Cluj*, 1922, **1**, 538—541; from *Chem. Zentr.*, 1923, iv, 187).—By the addition of potassium thiocyanate solution to an aqueous solution of a cadmium salt in the presence of pyridine, a white crystalline precipitate having the composition $[\text{Cd}(\text{C}_5\text{H}_5\text{N})_2](\text{CNS})_2$ is obtained. It is soluble in excess of pyridine and is decomposed by acids. By this reaction, 0.02 g. of cadmium per litre may be detected.

G. W. R.

The Estimation of Lead as Cyanide. W. HERZ and EBERHARD NEUKIRCH (*Z. anorg. Chem.*, 1923, **130**, 343—344).—Lead is pre-

cipitated quantitatively in the cold by gradual addition of considerable excess of normal sodium cyanide solution; the precipitate is collected, dried, and weighed as $\text{Pb}(\text{CN})_2$. Neither copper nor silver interferes.

S. I. L.

Nature of the Oxide Produced on the Anode during the Electrolysis of Thallous Sulphate. A. GUTBIER and W. DIETERLE (*Z. Elektrochem.*, 1923, **29**, 457—467).—The authors have examined the methods of Heiberg (A., 1903, ii, 614) and of Gallo and Cenni (A., 1908, ii, 986) for the electrolytic estimation of thallium, which consists in the deposition of the oxide on the anode. It is shown that the oxide invariably contains sulphuric acid. Consequently, neither method is trustworthy for the exact estimation of thallium. It is shown that thallium may be estimated by the electro-deposition of oxide as follows: thallous sulphate is dissolved in 100 c.c. of water in a roughened platinum dish, 0.1—1.5 c.c. of 2*N*-sulphuric acid and 5—9 c.c. of ethyl alcohol are added, and the solution is electrolysed at 53—58°, when the oxide Tl_2O_3 is deposited quantitatively. It is shown that the anodic product is definitely Tl_2O_3 , and not Tl_3O_5 , as suggested by Gallo and Cenni (*loc. cit.*).

J. F. S.

A New Specific Reagent for the Estimation of Copper. F. FEIGL (*Ber.*, 1923, **56**, [B], 2083—2085).—The name "Cupron" is proposed for benzoinoxime, which precipitates copper quantitatively from neutral or ammoniacal solution. The precipitate is sap-green in colour, and is insoluble in water, alcohol, dilute ammonia, acetic acid, or tartaric acid. It is easily soluble in dilute mineral acids, and fairly soluble in concentrated ammonia. The reagent is specific for copper in ammoniacal or tartrate solution, in that iron, lead, cobalt, nickel, zinc, and aluminium are not precipitated. It is sensitive to one part of copper in 33,000 parts, and the annexed

co-ordination formula
$$\begin{array}{c} \text{Ph}-\text{C}=\text{C}-\text{Ph} \\ | \quad | \\ \text{O} \quad \text{ON} \\ \diagdown \quad \diagup \\ \text{Cu} \end{array}$$
 is proposed for the copper

derivative. This contains 22.02% Cu and may be dried in the air oven at 110°.

H. H.

Simultaneous Electrometric Estimation of Copper and Silver by Means of Potassium Thiocyanate. ERICH MÜLLER and ARTHUR RUDOLPH (*Z. anal. Chem.*, 1923, **63**, 102—111).—Copper may be determined electrometrically by measuring the change of potential between a copper indicator electrode and the usual normal calomel electrode at 70° in a solution containing sodium hydrogen sulphite to which standard potassium thiocyanate is slowly added. The solution must contain more copper than corresponds with a *M*/100-solution; the results are always about 0.7% too high. Silver gives good results when similarly titrated at the ordinary temperature, using a silver indicator electrode. As the presence of sulphites interferes with the simultaneous determination of both metals in a solution, the silver is titrated, first using a silver

indicator electrode; the solution is then filtered, a copper electrode inserted, the requisite sodium hydrogen sulphite added, and the copper then titrated as above. By a compensation of errors the results for copper are quite good under these conditions.

A. R. P.

The Electrometric Estimation of Manganese. ERICH MÜLLER and OTTO WAHLE (*Z. anorg. Chem.*, 1923, **129**, 33—40).—Volhard's method of the titration of a manganous salt by means of permanganate $2\text{MnO}_4' + 3\text{Mn}'' + 2\text{H}_2\text{O} = 5\text{MnO}_2 + 4\text{H}'$ can be carried out electrometrically. The presence of a zinc salt, potassium nitrate, or another electrolyte is shown to be necessary (cf. Sarkar and Dhar, A., 1922, ii, 398). The values obtained are rather low. Near the end-point, an interval of seven minutes is necessary for a constant *E.M.F.* In the presence of hydrogen fluoride, the reaction is as follows: $\text{MnO}_4' + 4\text{Mn}'' + 8\text{H}' = 5\text{Mn}''' + 4\text{H}_2\text{O}$ (cf. Müller and Kopp, A., 1910, ii, 957). In this case, the end-point is sharp, but depends on the composition of the solution. The best results are obtained by using 10 c.c. of 4*N*-sulphuric acid and 8 g. of potassium fluoride per 100 c.c. of the solution. The authors hope to extend the applicability of this method to the analysis of a mixture of ferrous iron and manganese.

W. T.

The Separation of Tin from Other Metals. N. HOWELL FURMAN (*Ind. Eng. Chem.*, 1923, **15**, 1071—1073).—An investigation of the precipitation of stannic tin by means of cupferron from such a solution as would be obtained in the McCay method of separating tin and antimony (A., 1909, ii, 351, 1910, ii, 1003) showed that this method of treatment is rapid and accurate. The precipitate on stirring for thirty to forty-five minutes becomes compact and brittle, and is then easy to filter and wash. Manganese, nickel, cobalt, and zinc, if present, remain in the filtrate.

The separation of tin and antimony by precipitation with hydrogen sulphide in dilute hydrofluoric acid solution is incomplete unless the antimony is all in the tervalent state. The method of electrolytic precipitation of tin from the solution obtained in the McCay method, as recommended by Kling and Lassieur (A., 1920, ii, 452), has been found to be extremely slow and unsatisfactory.

C. I.

Oxidimetric Studies on Antimony. J. KNOP (*Z. anal. Chem.*, 1923, **63**, 81—102).—A large number of titrations of antimony with potassium permanganate under varying conditions have been carried out in order to ascertain those giving the most satisfactory results. Under widely varying conditions of acidity either of hydrochloric or of sulphuric acid or of both, results were obtained which gave only 98.5% of the total antimony if the calculations were based on an atomic weight of 120.2. Every possible source of error was investigated without obtaining any more satisfactory result. Consequently, further series of tests were made by adding an excess of potassium dichromate solution and titrating this excess with ferrous sulphate, using diphenylamine as internal indicator or ferricyanide as external indicator. From the mean of many

very concordant results, again only 98·5% of the antimony present was found and no possible source of error could be discovered. All the results obtained agree with the old atomic weight of 121·9 for antimony, and this seems to confirm the value of 121·8 given in the German atomic weight tables for 1922. A. R. P.

Tables for Sugar Analysis. G. D. ELSDON (*Analyst*, 1923, 48, 435—443).—Tables are given showing the quantities of dextrose, lævulose, hydrated lactose, anhydrous lactose, maltose, invert-sugar, sucrose, and starch corresponding with weights of cupric oxide (also cuprous oxide and metallic copper) for every mg. from 100 to 460. The tables are based mainly on those published previously by Brown, Morris, and Miller (T., 1897. 100, 281).

W. P. S.

Estimation of Dextrose and Lævulose. F. LUCIUS (*Z. Unters. Nahr. Genussm.*, 1923, 46, 94—95).—In the estimation of dextrose and lævulose by the method based on the inversion of the latter with dilute inorganic acids (A., 1920, ii, 132), the period of heating may be reduced to three hours by doubling the concentration of acid employed. Any further increase in acid concentration above this figure (20 c.c. of 5*N*-hydrochloric acid and 50 c.c. of sugar solution) leads to an appreciable decomposition of dextrose. A series of ten analyses carried out on mixtures of known composition using this method gave results for dextrose 95—96·7%, and for lævulose 96·1—101% of the amounts actually present.

H. C. R.

Biochemical Characterisation of Galactose in a Mixture containing Galactose and Arabinose. MARC BRIDEL and JEAN CHARPENTIER (*Compt. rend.*, 1923, 177, 908—910).—Emulsin acts on a mixture of galactose and arabinose in 70% alcohol, at 37°, to give β -ethylgalactoside, and galactose may therefore readily be identified, as, for example, in the products of hydrolysis of gum arabic (cf. this vol., i, 540). If the enzyme is renewed from time to time, some ethyl arabinoside is also formed, but, without such renewal, only the galactose is converted into a glucoside. E. E. T.

Estimation of Sugars in Mixtures of Sucrose, Invert-sugar, and Lactose. HANS JESSEN-HANSEN (*Comptes rend. Trav. Lab. Carlsberg*, 1923, 15, No. 3, 21 pp.).—Sucrose when heated with an alkaline copper solution causes a deposition of cuprous oxide, although this deposition may be reduced to a minimum by a suitable choice of conditions. The quantity of cuprous oxide deposited by a mixture of sucrose and a reducing sugar, or of two reducing sugars, is not equal to the sum of the quantities which each sugar would deposit if it were the only constituent of the mixture. Series of analyses were therefore carried out to determine the amount of copper deposited under standard conditions (1) by pure invert-sugar, (2) by mixtures of sucrose and invert-sugar in which the total weight of sugar present was always equal to 0·240 g.; (3) by pure lactose; (4) by mixtures of 0·200 g. of sucrose with increasing quantities of lactose, and (5) by mixtures of 0·050 g. of lactose with increasing

quantities of invert-sugar. In each case, a formula was calculated to cover the experimental results obtained. The following are the formulæ for the five different cases: (1) $Cu = 0.20 + 1.97122S - 0.000735S^2$; (2) $Cu = 1.94 + 1.97755S - 0.00079444S^2$; (3) $Cu = 0.58 + 1.25431L - 0.000008784L^2$. (4) $Cu = 1.94 + 1.2597L - 0.00000025L^2$. (5) $Cu = 64.91 + 1.897912I - 0.00050226I^2$. From these formulæ, five sets of tables are calculated giving the number of mg. of the various sugars in question corresponding with quantities of copper of from 0 to 440 mg. The exact procedure used for obtaining the copper is as follows: 8.65 g. of potassium sodium tartrate, 25 c.c. of 3.25*N*-sodium hydroxide, and 25 c.c. of copper sulphate solution containing 69.278 g. of $CuSO_4 \cdot 5H_2O$ (=17.592 g. of copper) per litre were mixed just before use in a 150 c.c. conical flask. The sugar solution was added and the total volume made up to 100 c.c. with water. Hydrogen was passed through the flask until all the air was displaced, and the flask then placed in a large boiling water-bath so that the surfaces of the liquid inside and outside the flask were at the same level. The flask was allowed to remain in the bath for exactly five minutes, after which it was removed and the contents were immediately filtered through an Allihn's asbestos tube, using suction. The cuprous oxide was carefully washed with warm boiled water and alcohol and completely transferred to the asbestos tube, which was finally washed with absolute alcohol and ether, dried by suction, and the oxide reduced to metallic copper by passing a current of hydrogen through the tube, heated in an air oven. When completely reduced, the copper was allowed to cool in a current of hydrogen and weighed. In using the tables for the analysis of a mixture of sucrose and invert-sugar, a 2% solution of the sugar is made up, and 50 c.c. of this are inverted according to Nicol. The acid is neutralised and the volume made up to 100 c.c. The invert-sugar in this is obtained from table (1) (=a). The original solution is then analysed, taking a quantity corresponding with 240 mg. of invert-sugar, and from the amount of copper obtained and table (2) the original amount of invert-sugar (=b) is obtained. The original sucrose present is therefore $0.95(a-b)$. In the case of mixtures of lactose and sucrose, the approximate quantity of lactose is first obtained from the weight of copper, using table (4). A solution containing about 1% of lactose is then prepared, and 50 c.c. of this are inverted by Nicol's method as above, neutralised, made up to 100 c.c. and the amount of copper obtained from 10 c.c. of this is weighed. The approximate quantity of invert-sugar present in this and consequently of sucrose in the original solution, can then be read off table (5). In order to obtain more exact values, a portion of the original solution containing exactly 200 mg. of sucrose is taken and the quantity of lactose present in this obtained from the weight of copper and table (4). A portion of the inverted solution containing, according to the last analysis, 50 mg. of lactose will then, by using table (5), give the true amount of invert-sugar present, and consequently of sucrose in the original mixture. Concrete examples are given which make the method of using the tables clear.

H. C. R.

Estimation of Pentoses and Pentosans. I. Formation and Distillation of Furfuraldehyde. NORVILLE C. PERVIER and ROSS A. GORTNER (*Ind. Eng. Chem.*, 1923, **15**, 1167—1169).—Distillations of materials containing pentoses carried out according to the method of the Association of Official Agricultural Chemists take place from hydrochloric acid of 18—20% concentration instead of from 12% acid, as usually stated. Hydrochloric acid of this concentration has a considerable destructive effect on furfuraldehyde and this is partly responsible for the low yields of furfuraldehyde that are obtained from all pentoses when the official method is used. The passage of a slow current of steam through the distillation mixture is sufficient to carry off the furfuraldehyde as rapidly as it is formed, thereby avoiding its destruction by long contact with strong acid. Details of a method for the distillation of pentoses based on these considerations are given. By means of this method, theoretical yields of furfuraldehyde have been obtained from all the pure pentoses that have been tested. Representative data are given.

H. C. R.

Estimation of Acetyl and on Methylation. KARL FREUDENBERG (*Annalen*, 1923, **433**, 230—237).—[With MAX HARDER.]—Perkin's method (T., 1905, **87**, 107) for the estimation of the acetyl group is improved by the use of aromatic sulphonic acids, particularly of toluenesulphonic acid, instead of sulphuric acid. This procedure offers the following advantages. The hydrolysis requires less time, less charring or formation of by-products occurs, and, in alcoholic solution, the sulphonic acids exert great solvent action. The method is shown to give good results in the analysis of catechin penta-acetate, dextrose penta-acetate, maltose octa-acetate, cellobiose octa-acetate, methylmaltoside hepta-acetate, chloromaltose hepta-acetate, bromoglucose acetate, dichlorocatechin penta-acetate, dimethyl tartrate diacetate, silver acetate, acetanilide, trihydroxypenta-acetatochromic acetate, or dihydroxyhexa-acetatochromic chloride.

[With ERNST COHN.]—Quercetin can be converted into its penta-methyl ether, and phloroglucinol into its trimethyl ether, in yields of, respectively, 75—80% and 80—85% of the theoretical, by conversion into the penta-acetate and triacetate, respectively, and treatment of the latter, in methyl-alcoholic solution, with a large excess of methyl sulphate, followed by the gradual addition of 50% aqueous potassium hydroxide solution (cf. Freudenberg and Purmann, this vol., i, 697).

W. S. N.

Polarimetric Estimation of Malic Acid. F. AUERBACH and D. KRÜGER (*Z. Unters. Nahr. Genussm.*, 1923, **46**, 97—154).—The method depends on the large increase in the optical activity of malic and tartaric acids caused by uranium and molybdenum compounds. A suitable and constant excess of the compound used to increase the optical activity is employed and the hydrogen-ion concentration of the solution is kept constant at its optimum value by the use of mixtures of buffer salts. The relationship between optical activity and concentration for malic and tartaric

acids was determined experimentally using the above conditions and a process was worked out for estimating these acids when present alone in the form of their sodium salts, with satisfactory accuracy. The molecular rotatory powers of uranium-malic and molybdenum-tartaric acids under the conditions chosen were found to be constant up to a concentration of 0.1 mol. per litre and to be equal to -700° and $+1,044^\circ$, respectively. On increasing the concentration, the values obtained gradually fell. The molecular rotatory power of uranium-tartaric acid increased with the concentration up to a maximum of $+650^\circ$, after which it fell slowly with increasing concentration. The molecular rotatory power of molybdenum-malic acid also increased up to a maximum of $+1,020^\circ$, remaining, however, approximately constant at this figure on further increasing the concentration. The fact that the directions of rotation of uranium-malic and uranium-tartaric acids are opposed, whilst the rotations of the corresponding molybdenum acids are of the same sign enabled a purely polarimetric method of estimating malic and tartaric acids in mixtures to be worked out. Willaman's graphical method of obtaining the percentage of malic acid from the polarimeter readings of the uranium and molybdenum solutions (A., 1918, ii, 249) is adapted to the conditions employed by the authors. The influence of other organic acids on the molecular rotatory powers of these uranium and molybdenum acids was investigated. In the case of uranium-malic and molybdenum-tartaric acids, the alkali salts of other organic acids only slightly decreased the figures obtained. In the case of uranium-tartaric acid, a more considerable disturbance is produced. In the case of molybdenum-malic acid the optical activity is considerably increased by the presence of salts of other hydroxy-acids, citrates almost doubling the molecular rotatory power. In the presence of citric acid, therefore, the polarimetric estimation of malic and tartaric acids in the same solution is impossible and when certain other organic acids are present, the estimation becomes untrustworthy. In determining malic acid polarimetrically in fruit juices and similar acid mixtures, it is therefore advisable not to attempt the simultaneous polarimetric estimation of tartaric acid and to carry out the removal of the sugars, pectins, and colouring matter in such a way that the greater part of the tartaric, citric, and other organic acids are separated from the malic acid at the same time. This can be effected by aid of the different solubilities of the respective barium salts in water and alcohol, by which means the malic acid is obtained as barium malate in aqueous solution containing only small quantities of barium tartrate and barium citrate. The malic acid can be estimated polarimetrically in this solution in the same way as in sodium malate solution. The molecular rotatory power of barium malate in the presence of uranium is somewhat lower than that of sodium malate under similar conditions and increases slowly with the concentration. In the presence of molybdenum, the molecular rotatory power is lower in low concentration and higher in high concentration than is the case with sodium malate. In

order to make the estimation independent of the small quantity of tartrates and citrates present in the barium malate solution, the solution was always saturated with these salts. The relationship between the small quantities of tartrate and citrate present and the polarimeter readings was calculated and that between the concentration of malic acid and the polarimeter readings under these conditions obtained both by experiment and by calculation. By these means malic acid can be estimated with sufficient accuracy from two independent polarimetric measurements even in the presence of tartaric and citric acids. H. C. R.

Analysis of Crude Tartar and Argol. CHEMISCHE FABRIK VORM. GOLDENBURG, GEROMONT & CIE (*Z. anal. Chem.*, 1923, **63**, 111—116).—The solution of the substance in hydrochloric acid is boiled with an excess of potassium carbonate and the filtered liquid is evaporated to a small bulk, treated with potassium chloride, and made exactly neutral to phenolphthalein with hydrochloric acid. The liquid is then acidified with diluted acetic acid, digested on the water-bath for a few minutes, and set aside over-night. The precipitate of potassium hydrogen tartrate is collected on a vacuum filter, washed with 20% potassium chloride solution saturated with potassium hydrogen tartrate, and dissolved in 200 c.c. of water. The solution is titrated with sodium hydroxide, using phenolphthalein as indicator.

The above method has been tested in the Chem. Lab. Fresenius (*ibid.*, 116—117) and found to give excellent results. It is cheaper and simpler to carry out than the older method involving precipitation of the potassium hydrogen tartrate by means of alcohol followed by titration as above, but using litmus-paper as indicator. [Cf. *J.S.C.I.*, 1923, Dec.] A. R. P.

The Bromine Number. PAUL BECKER (*Z. angew. Chem.*, 1923, **36**, 539).—A few drops of linseed oil were spread in a thin layer on a sheet of glass (4.5 by 15 cm.) which was then inserted in a horizontal glass tube of 4.6 cm. diameter. A watch-glass containing a few drops of bromine was placed under the glass plate and the tube corked at both ends. After a time, air was passed through the tube, and finally the glass plate was heated in an oven at 50—60° to remove excess of bromine and the increase in weight noted. As an alternative, the glass plate and containing tube may be placed vertically over pieces of glass rod between which a few drops of bromine have been poured. The addition of bromine was complete within half an hour and concordant results were obtained which, when calculated as iodine values, agreed well with those found directly by Wijs's method. W. T. K. B.

New Method of Estimating the Iodine Value of Oils and Fats by using Pyridine Sulphate Dibromide. K. W. ROSENMUND and W. KUHNHEIM (*Z. Unters. Nahr. Genussm.*, 1923, **46**, 154—159).—A solution of pyridine sulphate dibromide in glacial acetic acid can be used for determining the iodine value of oils and fats. The solution is of about the same stability as the Hanus

iodine bromide solution and has the advantages that the results given by it are independent of the amount of excess of the reagent used, that the reaction progresses more rapidly than in the case of the Hanus solution in the case of oils of high iodine values, and that a considerable economy is effected, especially when the excess of reagent is titrated with arsenious acid solution. The reaction is complete in 5 minutes even in the case of linseed oil, and the results obtained agree with those given by Hanus's method within the limits of experimental error. The excess of the reagent can either be treated with potassium iodide and titrated with thio-sulphate, or titrated directly with arsenious acid, the two methods giving identical results. Phenol and arsenic may also be estimated by titration with pyridine sulphate dibromide in glacial acetic acid.

H. C. R.

Estimation of the Acetyl Value (of Fats and Oils). JESSIE R. POWELL (*Ind. Eng. Chem.*, 1923, **15**, 622).—The André-Cook method (A., 1922, ii, 324) is trustworthy, but concordant results cannot be obtained by methods involving the separation of the acetic acid by filtration or distillation.

W. P. S.

Detection of Adulterants in Cacao Butter. MARCEL PICHARD (*Ann. Falsif.*, 1923, **16**, 197—215).—The method proposed depends on the differences observed in the rise of temperature during the solidification of cacao butter and other fats. Fifty g. of the fat are melted at 50°, placed in a vertical tube provided with a thermometer, and surrounded by a jacket through which a current of air at 10° is circulated, and the temperature is noted at definite intervals during the solidification of the fat. The temperature at first falls to a point at which solidification commences, then rises gradually to a maximum, and afterwards falls again. The curve showing the temperature during the solidification of cacao butter is distinctly different from that obtained with other fats.

W. P. S.

Benzidine as a Reagent for Aldehydes. P. N. VAN ECK (*Pharm. Weekblad*, 1923, **60**, 1204—1208).—A large number of aldehydes give good colour reactions in presence of benzidine dissolved in glacial acetic acid. Fatty aldehydes give yellow to orange colorations. Benzaldehyde gives a yellow, crystalline solid, cuminaldehyde an orange solid, anisaldehyde yellow-orange crystals, and phenylacetaldehyde dark, blood-red crystals; microchemical tests detect these readily. Vanillin gives a dark, orange-red colour, which becomes red on adding water; the reaction is extremely sensitive.

S. I. L.

Detection and Characterisation of Small Quantities of Vanillin. H. HÉRISSEY and P. DELAUNEY (*J. Pharm. Chim.*, 1923, [vii], **28**, 257—262).—When aqueous solutions of vanillin are oxidised with ferric chloride, a blue coloration is formed, which, when the mixture is heated for five minutes in the boiling water-bath and then cooled, disappears and is replaced by a precipitate (thin, microscopic, colourless needles, m. p. 302—305°) of dehydrodi-

vanillin, $[\text{C}_6\text{H}_2(\text{CHO})(\text{OMe})\cdot\text{OH}]_2$. This precipitate may be observed, and collected by centrifuging, in solutions containing as little as 0.01% of vanillin. Vanillin is somewhat difficultly volatile in steam, but may be detected and characterised in plant extracts containing as little as 0.05%, as follows. Twenty c.c. of the solution to be tested are heated in a bath containing a solution of calcium chloride at 130–140°, and two fractions of 10 c.c. of distillate are collected. Further quantities of 10 c.c. of water are added to the residue and again distilled off, this being repeated until nine or ten such fractions have been collected. The presence of vanillin in these fractions is then determined as above with ferric chloride.

W. T. K. B.

The Salt Error of Nitramine (Picrylmethyl Nitroamine).

I. M. KOLTHOFF (*Rec. trav. chim.*, 1923, **42**, 964–968; cf. A., 1922, ii, 222).—Using nitramine as an indicator, the salt error of electrolytes with univalent ions is -0.09 (in p_{OH}) in seminormal solution. In normal solution, the error depends on the salt, and is greater for potassium than for sodium salts. The error increases with rising valency of the anion. Thus the correction for $N\text{-KCl}$ is $+0.16$, for $N\text{-K}_2\text{SO}_4$, $+0.30$, and for $N\text{-K}_4\text{Fe}(\text{CN})_6$ it is $+0.34$ in p_{OH} . H. H.

Review of Methods for the Estimation of Acetanilide.

EDWARD S. ROSE (*Amer. J. Pharm.*, 1923, **95**, 743–754).—Both Seidell's tribromoaniline method (A., 1907, ii, 914) and the acetyl radicle method, in which the acetic acid liberated by hydrolysis with dilute sulphuric acid and distilled off is titrated, give good results in estimating acetanilide. When interfering substances have to be removed, the former method is somewhat more rapid. One method may be made a check on the other by distilling off and titrating the acetic acid and titrating the acid residue containing the aniline with bromide-bromate solution as in the tribromoaniline method. With preparations containing such substances as solid and powdered extracts, alkaloids and their salts, antipyrine, or pyramidone, the acetyl radicle method is more advantageous as it can be applied directly to the residue from the chloroform extraction. When phenacetine is present, it should be removed as periodide (Emery, A., 1914, ii, 755).

H. C. R.

The Triketohydrindene Reaction. V. S. SADIKOV and N. D.

ZELINSKI (*Biochem. Z.*, 1923, **141**, 105–108).—In contradistinction to the coloration formed by ninhydrin and hydroxy-compounds, that produced in the presence of amino-acids is resistant to boiling, to decinormal alkali, and to 1% phosphoric acid, and is soluble in amyl alcohol. Methylalanine gives the reaction after prolonged boiling. The ninhydrin pigment is unstable and slowly disappears, even when air is excluded. The esters of monocarboxylic amino-acids and dicarboxylic imino-acids give a carmine-red pigment insoluble in amyl alcohol, and after hydrolysis with acid an amyl alcohol soluble blue pigment. Free methylaspartic acid gives the reaction, but its ester does not. 3-Amino-1-methylcyclopentane-carboxylic acid gives a violet colour extractable by amyl alcohol.

It is concluded that a number of types of reaction between amino-acids and the ninhydrin reagent are possible. J. P.

Estimation of Hydrogen Cyanide in Cyanogenetic Plants. E. KOHN-ABREST and J. RICARDONI (*Compt. rend.*, 1923, **177**, 771—773).—The powdered plant material is digested with water at 37° for four hours, or at the ordinary temperature for twenty hours. Purified air is then blown through the resulting mixture and then through standard potassium hydroxide solution, the hydrogen cyanide absorbed by the latter being estimated in the usual manner. The results of analyses of various specimens of *Phaseolus lunatus* (eleven varieties) show the method to be as satisfactory as the ordinary (distillation) method. E. E. T.

Qualitative Scheme for the Detection of Cyanamide and Related Compounds. G. H. BUCHANAN (*Ind. Eng. Chem.*, 1923, **15**, 637—640).—Systematic directions are given for the detection of ammonia, cyanamide, cyanide, dicyanodiamide, guanidine, guanyl carbamide, nitrate, thiocyanate, thiocarbamide, and carbamide in fertiliser mixtures containing any or all of these compounds. W. P. S.

An Iodometric Method for Estimating Uric Acid in Urine. OTTO FÜRTH, JOSEPHA URBACH, and PAUL WERMER (*Biochem. Z.*, 1923, **141**, 236—247).—The authors have devised a rapid method for estimating uric acid in urine which does not necessitate lengthy and troublesome filtrations and washings. Five c.c. of urine, measured into a 50 c.c. centrifuge tube, are made alkaline by the addition of sodium carbonate and 5 c.c. of 30% ammonium chloride are added. The tube is left for two hours, centrifuged for five minutes, and after separation of the supernatant liquid, the precipitated ammonium urate is stirred with 5 c.c. of 10% ammonium sulphate and again centrifuged for six or seven minutes. The washed precipitate is dissolved in 50 c.c. of 0.1*N*-sodium hydroxide, 20 c.c. of 0.01*N*-iodine solution are added, the solution is at once acidified by the addition of 70 c.c. of 0.1*N*-sulphuric acid, and the excess of free iodine is titrated with 0.01*N*-sodium thiosulphate. Under the conditions employed, 1 mol. of uric acid takes up 3.5 atoms of iodine. The estimation is completed in two and a half hours, including the two hours allowed for separation of the ammonium urate. J. P.

The Relationship between Colour and Constitution in Azo-dyes. MIECZYŚLAW DOMINIKIEWICZ (*Roczniki Chemji*, 1923, **2**, 314—335).—A theoretical paper in which the known facts relating to azo-dyes are reviewed and discussed mainly from the point of view of the quinonoid theory. For the "colour analysis" of various dyes, a method is suggested whereby any given colour is matched by mixing three fundamental colours (blue, red, and yellow) and the quantities of each are noted. The dyes chosen as standard are patent blue V, rhodamine B, and quinoline yellow O; the standard aqueous solutions of these should contain 0.6350, 0.4785, and 0.8658 g. per litre, respectively. G. A. R. K.

A Nephelometric Method for Estimating Small Amounts of Proteins. P. RONA and H. KLEINMANN (*Biochem. Z.*, 1923, **140**, 461—477).—For the nephelometric estimation of proteins, to 5 c.c. of the protein solution are added, in the order given, 5 c.c. of 25% hydrochloric acid, 8 c.c. of a 20% solution of sodium sulphosalicylate, and the whole is diluted to 20 c.c. The resulting turbidity, which is measured against suitable standards in a Kleinmann-Schmidt and Haensch nephelometer, reaches a maximum in three minutes and is permanent for at least an hour. Its intensity is directly proportional to the amount of protein present. A 20% increase in the acidity of the solution, or the addition of ammonium sulphate, magnesium sulphate, or thymol, is without influence on the results, nor does the presence of the soluble products of peptic hydrolysis interfere with the determination. The method may be used for the estimation of quantities of protein as small as 0.06 mg. J. P.

The Estimation of Fibrinogen. WILHELM STARLINGER (*Biochem. Z.*, 1923, **140**, 203—229).—A lengthy critical survey of the various gravimetric, Kjeldahl, and refractometric methods hitherto employed in estimating fibrinogen, which is chiefly based on refractometric measurements on native hirudin, citrate, oxalate, and fluoride plasmas and sera. In place of the "recalcification" method of Leendertz, the author has employed a new process dependent on refractometric determinations on citrated plasma, and on the serum after separation of the precipitate of fibrinogen produced by heating for five minutes to 56°. The determination can be carried out on 0.5 c.c. of plasma. J. P.

Estimation of Fibrinogen by Precipitation with Sodium Sulphate compared with the Precipitation of Fibrin by the Addition of Calcium Chloride. PAUL E. HOWE (*J. Biol. Chem.*, 1923, **57**, 235—240).—Results in good agreement with those given by Cullen and Van Slyke's method (*A.*, 1920, ii, 398) have been obtained for the fibrinogen content of blood by estimating the nitrogen content before and after precipitation with 10.6% sodium sulphate (or certain other salts) at 37°. Similar results were obtained by Gram's (*A.*, 1922, ii, 240), Foster and Whipple's (*Amer. J. Physiol.*, 1921—1922, **58**, 393), and Wu's (*A.*, 1922, ii, 406) methods. E. S.

The Estimation of Fibrinogen in Blood Plasma. STEFAN RUSZNYÁK and I. BARÁT (*Biochem. Z.*, 1923, **141**, 476—478).—A nephelometric method for the estimation of fibrinogen in blood plasma is described. 0.1 C.c. of citrate plasma is treated with 50 c.c. of an acid solution of ammonium sulphate (1 part of 0.2N-hydrochloric acid, 1 part of saturated ammonium sulphate), and the resulting opalescence, which is due to the total plasma proteins, is compared with that produced by fibrinogen alone when 0.4 c.c. of the plasma is treated with 25 c.c. of a 27% saturated ammonium sulphate solution. J. P.

A Micro-method for the Estimation of the Protein Fractions of Plasma. STEFAN RUSZNYÁK (*Biochem. Z.*, 1923, 141, 479—482).—The proteins of separate small volumes of plasma are fractionally precipitated and estimated nephelometrically using the total protein fraction as the standard. The total proteins and fibrinogen are precipitated as already described (cf. preceding abstract) and the other fractions are obtained as follows: globulin + fibrinogen by treating 0.1 c.c. of citrate plasma with 25 c.c. of half-saturated ammonium sulphate, euglobulin + fibrinogen by the addition to 0.4 c.c. of the plasma of 25 c.c. one-third saturated ammonium sulphate, ψ -globulin I and II by treating 0.1 c.c. plasma with 40% saturated ammonium sulphate. J. P.

A New Permanent Standard for Estimation of Hæmoglobin by the Acid Hæmatin Method. EDWIN E. OSGOOD and HOWARD D. HASKINS (*J. Biol. Chem.*, 1923, 57, 107—110).—The standard consists of 32 g. of ferric sulphate + 80 mg. of chromic sulphate in 100 c.c., and when set at 15 mm. in a colorimeter should match a 1% acid hæmatin solution set at 10 mm. The intensity of its colour changes with temperature. E. S.

A New Permanent Standard for Sahli's Hæmoglobinometer. HOWARD D. HASKINS (*J. Biol. Chem.*, 1923, 57, 111—113; cf. preceding abstract).—This consists of a mixture of solutions of ferric and cobalt sulphates. It must be standardised against a 1% acid hæmatin solution. E. S.

A Method for the Estimation of the Bile Acids in Duodenal Juice. ERNST CHRISTOPH MEYER (*Biochem. Z.*, 1923, 140, 356—367).—As a result of the study of the influence of dilution, hydrogen-ion concentration, and the presence of salts, mucin, and other substances on the drop number of pure bile salt solutions and of duodenal juice, a method is given for the estimation of the bile acids in the latter. The slightly alkaline duodenal juice is suitably diluted from ten to one hundred times, made slightly acid to Congo-red by the addition of one or two drops of 15% hydrochloric acid, and from the drop number of the resulting solution, which should lie within the limits 105 to 135, the milligram percentage of sodium glycocholate is obtained directly from a curve which is given. J. P.

Estimation of Ash, Arsenic, Copper, and Zinc in Gelatin. R. M. MEHURIN (*Ind. Eng. Chem.*, 1923, 15, 942—943).—Undesirable features of published methods for estimating small quantities of arsenic, copper, and zinc are pointed out and rapid and accurate methods for estimating these elements and the ash in gelatin are described. The arsenic is estimated by a modification of Gutzeit's method, the ash by incinerating 20—40 g. in an electric muffle at 500—550° for four to five hours, the copper is estimated colorimetrically with potassium ferrocyanide against a standard copper solution, and the zinc by precipitation with hydrogen sulphide in acetic acid solution containing sodium acetate and weighing as oxide. Attention is directed to sources of error against which precautions must be taken. H. C. R.

The Estimation of Pepsin and the Behaviour of Pepsin in the Body. KÄTHE VOIGT (*Biochem. Z.*, 1923, **142**, 101—107).—For the estimation of peptic activity, to 1 c.c. of blood serum are added 8 c.c. of 0.1N-hydrochloric acid and 1 c.c. of the pepsin solution. After twenty-four hours' incubation, 0.3 c.c. of the mixture is treated with 20 c.c. of water and 2.5 c.c. of 10% sulphosalicylic acid and the resulting opalescence, caused by the residual unhydrolysed protein, is measured in a nephelometer. Using this method of detecting the enzyme, it is found that pure pepsin (Witte) injected intravenously into dogs undergoes a very rapid destruction, which also occurs with blood serum-pepsin mixtures in vitro. The destruction of the enzyme is ascribed in the main to the reaction of the blood. J. P.

The Recognition of Trypsin and its Natural Inhibitor in Serum. H. PFEIFFER and F. STANDENATH (*Fermentforsch.*, 1923, **7**, [1], 14—53).—Under carefully chosen conditions the Fuld-Gross method for the detection of trypsin is very sensitive. Using this method, the authors have sought to determine whether trypsin adsorbed by charcoal can be estimated by its digestion of casein, and whether in serum an excess of trypsin or antitrypsin can be recognised by use of charcoal. It is found that charcoal adsorbs trypsin and casein, but not the antitrypsin of serum, but if mixtures of trypsin and antitrypsin be treated with charcoal, the filtrate loses both its tryptic and inhibitory properties. H. K.

Estimation of Diastase in Blood. G. M. FYFE (*Brit. J. Exp. Path.*, 1923, **4**, 127—131).—By an estimation of blood-sugar by Maclean's method (*A.*, 1919, ii, 434), followed by a second estimation after 0.2 c.c. of blood has been incubated for half an hour at 37° with 1 c.c. of 0.1% starch solution, almost concurrent readings of the blood-sugar and blood diastase figures may be obtained using a small amount of blood. CHEMICAL ABSTRACTS.

A Colour Test for Water-soluble [Vitamin]-B. ALADÁR JENDRASSIK (*J. Biol. Chem.*, 1923, **57**, 129—138).—Extracts containing vitamin-B have been found consistently to reduce ferric ferriocyanide with the formation of a blue colour. Similar extracts made from foods which do not contain this vitamin did not give this reaction. E. S.

Microscopic Estimation of Soil Colloids in Soil Separates. WILLIAM H. FRY (*J. Agric. Res.*, 1923, **24**, 879—883).—After removing the clay fraction from soil by the ordinary means of mechanical analysis, an ultra-microscopic examination of the separated fractions revealed much undispersed colloidal matter. By using a squared eye-piece it was found possible to estimate the relative proportion of mineral and colloidal aggregate by direct observation of the field. Inaccuracies due to difference in shape and density of particles, etc., were shown to be small. From 30—60% of the clay fraction of soils was found to remain undispersed among mineral particles after thorough washing and rubbing in weak ammonia solutions. A. G. P.

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ERRATA.

VOL. 82 (ABSTR., 1902).

Page Line

1. 31 13* *for "favour" read "retard."*

VOL. 98 (ABSTR., 1910).

i. 532 6* *for "When X" read "When R."*

3* "magnesium derivative of bromoquinol dimethyl ether" rec
"bromomagnesium derivative of quinol dimethyl ether."

VOL. 124 (ABSTR., 1923).

i. 171 8* for "BLANCH" read "BLANCK."

i. 449 24* "CALVARY" read "CALVERY."

i. 613 19 ,, "MOGGO" read "MOGGI."

i. 660 28 ,, " $\beta\gamma$ -diaminopropionic acid" read " $\alpha\beta$ -diaminopropionic acid."

i. 756 6 „ “HENTIKKA” read “HINTIKKA.”

i. 1124 22 and 23 for "5-chloro-1:3-dihydroxynicotinonitrile" read "6-chloro-2:4-dihydroxynicotinonitrile."

20* „ “1:3:5-” read “2:4:6-” (in each case).

18* ,, "5-chloro-1:3-dihydroxynicotinamide"

2:4-dihydroxynicotinamide."

8* „ “5-chloro-1:3-dimethoxynicotinonitrile” read “6-chloro-2:4-dimethoxynicotinonitrile.”

3* „ “1:3:5-” read “2:4:6-”

ii. 11 16* for "POLITZER" read "POLLITZER."

ii. $\left. \begin{smallmatrix} 32 & 21 \\ & 22 \end{smallmatrix} \right\}$ „ “face centered cube” read “hexagonal close packed.”

ii. 186 11* „ “acetic” read “tartaric.”

ii. 214 15* „ “freed” *read* “free.”

14* *delete* "by passing it through a tube immersed in liquid air."

ii. 440 2* „ „ THALHIMER" read "THALLINNER."

ii. 443 12 ,, "NANUSSO" read "NANUSSI."

ii. 535 10 ,, "VIEHAENER" read "VIEHOEVER."

ii. 717 1 ,, "unable" read "able."

COLLECTIVE INDEX 1913—1922 (AUTHORS).

Page

209 col. i. last two entries should be under "**Dale, Henry Hallett, and Harold Ward Dudley**" in col. ii.

* From bottom.